INVERSTIGATION ON TEMPERTURE DEPENDENTEXCESS THERMODYNAMICAL PROPERTIES OF BINARY MIXTURE

A project report submitted to
DEPARTMENT OF PHYSICS
ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI
Affiliated to
MANONMANIAM SUNDARANAR UNIVERSITY
TIRUNELVELI
In partial fulfillment of the requirements for the award of
MASTER OF SCIENCE IN PHYSICS
Submitted by
J.ANUSHYA
Reg. No: 19SPPH01
Under the supervision and guidance of
Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,

DEPARTMENT OF PHYSICS
ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI
(Re-accredited with 'A+' Grade by NAAC)
2020-2021

CERTIFICATE

This is to certify that this project work entitled **"INVERSTIGATION ON TEMPERTURE DEPENDENT EXCESS THERMODYNAMICAL PROPERTIES OF BINARY MIXTURE"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** in partial fulfillment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the year 2020-2021 by

J. ANUSHYA **Register No: 19SPPH01**

Signature of the Guide

Signature of the SSC Coordinator

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

A. Nirmala Shirley

Signature of the Examiner

ACKNOWLEDGEMENT

"GIVE THANKS TO THE LORD FOR HE IS GOOD"

First of all, I thank the Lord Almighty for his blessing and grace to complete this comprehension work.

I am deeply indebted to our Principal **Rev. Dr. Sr. A. S. J. LUCIA ROSE M. Sc., PGDCA., M. Phil., Ph. D.,** for the encouragement she bestowed upon us.

I wish to express my sincere thanks to our Director of SSC, **Rev.Dr. Sr. F. MARY JOYCE BABY** for her support in my work.

I would like to express my special thanks of gratitude **Dr. S. EUCHRISTM.Sc., M.Phil., Ph.D.** Head of the Department, for her inspirational words and encouragement to complete this project.

I am thankful to **Mrs. P. PADMAVATHI M.Sc.,M.Phil.,SET.,** SSC Coordinator and my guide, for the continuous support, patience, motivation, and immense knowledge. Her guidance had encouraged me to do this project successfully.

I am grateful to my parents and my sister who have provided me through moral and emotional support to complete my work.

An endeavor over a long period can be successful only with the advice and supports of many well-wishers. I take this opportunity to express my gratitude and appreciations to all these people.

CHAPTER I

CHAPTER-1

THE LIQUID STATE

1.1 INTRODUCTION

While it is often said that a liquid is intermediate in its properties between a solid and a gas, this statement should not be understood to mean that every property of a liquid is intermediate in value between those of the other two states. If the actual figures are compared, it is found that in the great majority of cases the value of any property of a liquid is approximately equal either to that of the solid or to that of the gas. The intermediateness, then, is a statistical one-a liquid has some of the properties of a solid, and some of the properties of gas. The most obvious resemblance between liquids and gases is their lack of rigidity neither offers permanent resistance to a shearing stress. The immediate consequence of this is that neither a liquid nor a gas possesses shape of its own, but always offer a resistance to shearing stress.

Between liquids and solids, the most prominent resemblance is that both possess cohesion, which enables each to maintain a free surface, whereas a gas will always completely fill any container. A second, and hardly less fundamental, property common to liquids and solids, is their relative incompressibility compared to gases. While the compressibility of solids are usually of the order or of10^{-6} atm^{-1}, those of liquids are only slightly larger (about10^{-5} atm^{-1}).

The compressibility of a gas, on the other hand, is roughly equal to the reciprocal of the pressure, or, at a pressure of one atmosphere, about 10^5 times as great as that of liquid. Closely allied to the second similarity between liquids and solids is the third: their similarity in density. The density change which takes place when a solid melts is usually of the order of 10 to 50 percent, but on vapourization the density decreases by a factor of 100 or 1,000.

From these simple facts considerable information can be obtained about the nature of the molecular arrangement in liquids. From the density, for example, the mean distance between molecules can be calculated. Taking Argon as a typical example, the molar volumes of the solid, liquid and gas at the boiling point are respectively 24.3 cc, 28.1 cc and 7.050 cc. As a first molecules of the liquid and gas are arranged like those of the solids in a face centered cubic lattice. To obtain the correct densities it is then necessary to assume that the distance between nearest neighbours is 3.84 A° in the solid

4.03 A° in the liquid 25.4 A° in the gas. In the solid, the molecules are in contact. In the liquid, there is a little space (about 5 percent of the molecular diameter) between molecules is about six times the molecular diameter.

Since the forces between molecules are short range forces, and act through a distance of only two or three times the molecular diameter, it is immediately obvious that in the gas these forces are of little importance. Any such regular arrangement of molecules as that we have assumed will therefore be destroyed by the thermal motions of the molecules, and the usual assumption that the molecules of a gas are arranged in space and are randomly distributed.

In the solid, on the other hand, the close-packed arrangement of the molecules prevents any molecule moving from moving far from its original position, which results in turn in the rigidity of the crystal. At the same time the low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must be accomplished by reducing the size of the molecules themselves. If the liquid maintains the arrangement we have assumed, it is difficult to see how to explain its fluidity. The molecules are packed so closely together that no interior molecule can change its position by much more than can the molecule of the solid. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane molecule. Such a motion, however, would require the simultaneous lengthening of a great number of intermolecular distances and hence a large energy of activation for the flow process. To avoid this difficulty it is obviously necessary to assume that a few molecules move at a time, but this in turn implies that it must be relatively easy for molecules to become displaced from the regular lattice.

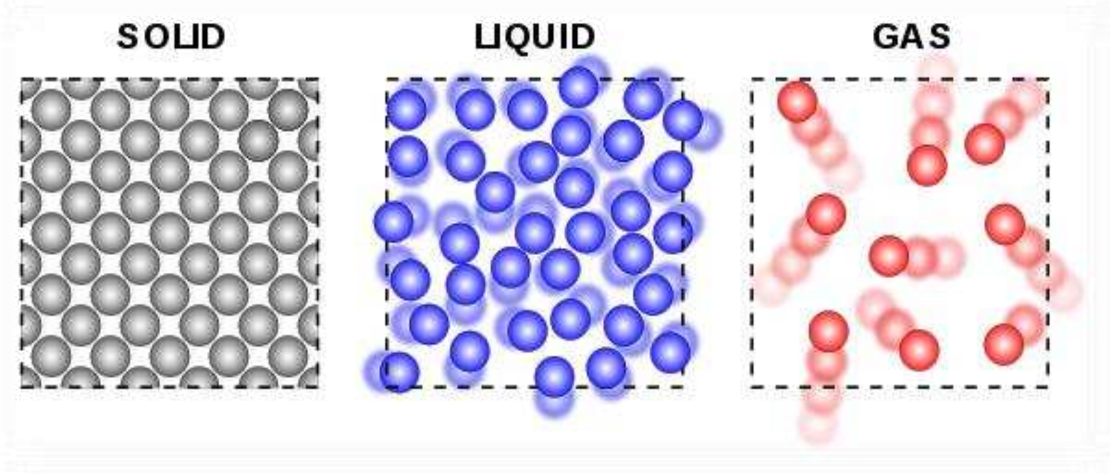


Fig1.1Relative spacing of molecules in solid, liquid and Gaseous Phases

On the other hand, the problem of packing so many spheres into a given volume does not permit any great variation from the regular closed packed structure. In fact the only reasonable modifications which can be made are two in number. First, there may be local irregularities caused by groups of molecules coming closer together, leaving wider spaces elsewhere in the structure. Second, there may be gradual distortion of the structure as we go from molecule to molecule, so that although the pattern in the immediate neighbourhood of a given molecule be quite regular, the pattern is irregular at a distance.

1.2 SHORT AND LONG RANGE ORDER

The tendency of a liquid molecule to surround itself with a more or less definite number of neighbouring molecules at a near a definite distance shows that if we consider a region in the liquid so small that it contain only a few molecules, - say about 20 – these molecules must be arranged very nearly in as regular fashion as in the corresponding crystal. On the other hand, if the size of the region is enlarged, the irregularities mount up, and the positions of the molecule no longer can be related to a lattice of the type occupied by the molecules in the crystal. The regularity exhibited by the crystal is now generally referred to as long range order, since the positions of molecules many diameters away from a central molecule can be predicted from a knowledge of the position of the central molecule and the molecules immediately surrounding it.

In the liquid, on the other hand, this long range order has disappeared. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite, we can say that the liquid still possesses short range order. The crystal, of course, has short range order as well as long range order, but in the gas phase even the short range order has disappeared.

We can, therefore, state as an experimental fact that the melting of a crystal is accompanied by the disappearance of long range order, and the evaporation of a liquid is accompanied by the disappearance of short range order.

1.3 THE LOOSE PACKING OF RIGID SPHERES

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied a minimum, them a regular crystal-like lattice-either hexagonal or cubic is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of the structure will disappear. This has been demonstrated in two dimensions by a number of experimenters[1] who have studied the distribution of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by

Morrell and Hildebrand[2] by suspending hard gelatin spheres in a solution of the same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

It would appear from this experimental evidence that the principal factor in the determination of the radial distribution function in a liquid is the volume occupied by the molecules themselves, that is to say, the repulsive forces between the molecules rather that their attraction.

1.4 THEORIES OF LIQUID STATE

The readiness with which liquids flow and diffuse suggests a random molecular structure analogous to the gas. On the other hand the cohesion and compactness exhibited by liquids indicate a structure resembling that of a solid. The similarities between a liquid and a solid make one to consider the two states of matter collectively as a "condensed matter" while the properties of fluidity shared by liquid and gas connect them collectively as "fluids". Hence liquid state theories are broadly of two types.

1. Considering it as a condensed gas so that the interaction between the neighbouring molecules may be calculated through "pair potential functions" and
2. Considering it as a disordered solid lattice.

1.5 MOLECULAR INTERACTION IN LIQUIDS

There are two kinds of interaction

1. Dispersion interaction and

2. Dipole-dipole interaction in liquids.

In the case of non polar molecules the average dipole moment averaged over all phases of electronic motions is zero while the instantaneous dipole moment is never zero.

If two non-polar molecules are placed near each other, the instantaneous dipole moment will interact and will produce some potential energy, which may be positive (or) negative. Such interaction between the molecules is termed as dispersion interaction and is present in all the aggregates of molecules irrespective of the nature of the atoms and molecules.

The second category of interaction is specific. It requires a Hydrogen atom attached to a fairly high electronegative atom and an atom at an optimum distance with non bonded electrons (ion-pairs). This results in the formation of complexes between molecules while the dispersion interaction leads to positive contributions to excess thermodynamic quantities, the latter category makes negative contribution.

The determination of sound velocity, density, viscosity etc., leads to an understanding of the nature and type of molecular interactions especially in binary mixtures of liquids through the excess thermodynamic quantities. Normal liquids obey certain empirical rules such as Trouton's rule, The heat of vaporization at the boiling point is nearly equal to $85 \pm 10\, JK^{-1} mole^{-1}$, the associated liquids (having hydroxyl group), do not obey these empirical rules. The deviation is due to association of molecules found in the vapor to form larger molecules in liquids. In the case of alcohols and acids, the links between the individuals are provided by hydrogen bonds.

The protic dipolar liquids are ordinarily intermolecular hydrogen bonded. This class of liquids has been extensively studied, the best example being water. Aliphatic and aromatic alcohols and amines, carboxylic acids and amides are typical representatives of this class of liquids. The liquids of this class possess an entropy of vaporization which is 30% higher than for normal non-associated liquids. A notable exception is the carboxylic acids.

The alcohols show regularly changing liquid properties as the aliphatic chain length is increased (or) as the number of hydroxyl groups is increased. For example, the di-electric constant drops as the chain length increases, but increases with the increase in number of hydroxyl groups.

When two liquids are mixed, the solution is said to be ideal if there is no volume change (or) enthalpy change on mixing. But in practice, solutions of liquids are never ideal. The deviation from ideality is much more marked in the case of associated solutions. The thermal energy is less than the interaction energy. The thermal perturbation cannot disturb the association very much. In a binary system of associated liquids, a distortion occurs depending on the concentration. The distortion in the structure of the associated molecules leads to large changes in the physical properties such a dielectric constant, viscosity, free volume etc. Considerable dissociation must occur when alcohols are mixed with diluents, the hydrogen bonds are broken and this explains the positive heats of reactions.

Self associations in alcohols are shown on fig 1.2. The earliest model of self association in alcohols is that of Oster and Kirkwood[5], which assumed long chain association with free rotations of the O.H. around the H-bond in such a situation,

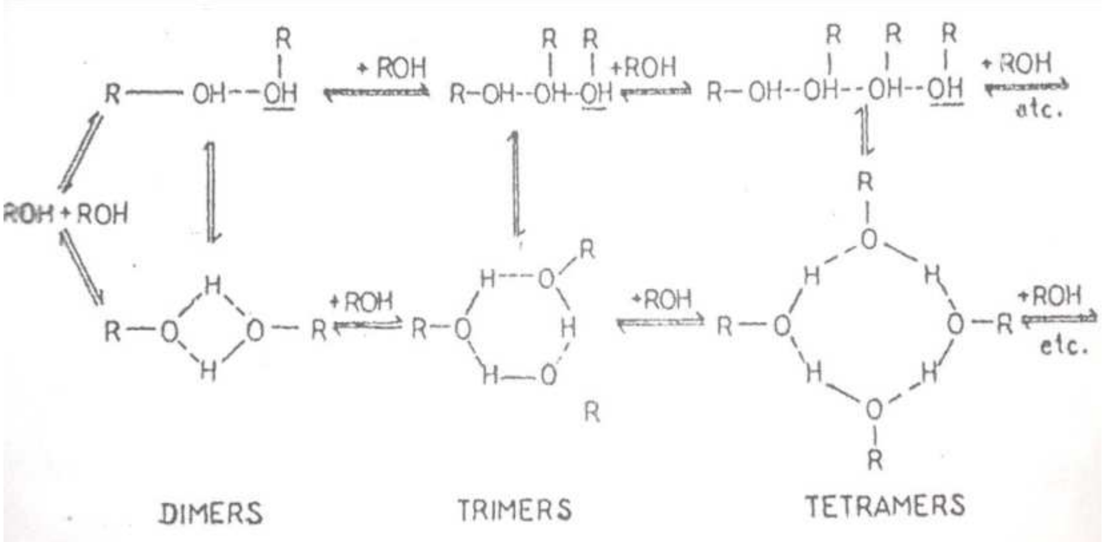


Fig: 1.2 POSSIBLE EQUILIBRIA IN THE SELF-ASSOCIATION OF ALCOHOLS

Dipole moment of the alcohol solution should be greater than that of its monomer unit, which is not the case always[6, 7]. In the most alcohols, dilution with non polar solvents resulted in a dip in dipole moment at a definite concentration[8], which means qualitatively that dilution leads to the formation of cyclic multimers of lesser dipole moment. Bellamy and Pace[9] and Coburn Oxrunwald[10] were of the view that such cyclic structures must be multimers and not dimmers because of unfavourable bonding angles in dimers. Since the cyclic form possesses one additional H-bond compared to the open (or) linear form, the change in enthalpy AH° for cyclic form should be greater than that corresponding to the open structure. Hence it is possible to look for specific information from the experimental studies of enthalpy and entropy. Such studies[11, 12] also do not provide sufficient data to permit a decision in favour of or against a particular model. Bordewijk[13], from his dielectric studies showed in mono alcohols, the large multimers are cyclic, probably tetramers, without of plane Oxygen and Hydrogen atoms.

Though there are plenty of data available on the ultrasonic behavior of mono alcohols[14-19] and in mixtures with inert solvents, they do not provide enough information on the model of mono alcohols.

Since the ultrasonic velocity is very sensitive to change in the free volume, it is desirable to look at the data on ultrasonic compressibility's of liquids from the thermo-dynamic point of view. The change in free volume results in a large change in the internal pressure of the liquids and hence the enthalpy of the system. The ease with which one can distort the fluid structure is determined by the energy holding the lattice together. In H-bonded liquids, it is reasonable to assume that this internal energy is related directly to the number of H-bonds per unit volume. The ultrasonic wave propagation in such liquids should result on the distortion of the fluids structures. Based on this concept, Sabesan et.al[20] studied the internal pressure and excess of mixing (H^E) for several alcohols including cyclo hexanol, amyl alcohol, Isoamyl alcohol, Isopropanol, n-butonol, 2-butonol, Isobutanol and tert-butanol in dioxin at different concentrations at 303, 308 and 313K. The positive values of H^E for the systems reported was explained as arising due to the stronger, self associations that was broken, rather strongly by dioxin compared to n-heptane (or) n-hexane. Among that the isomer alcohols, the n-compounds were found to have less H^Eat a given concentration and temperature, than the corresponding isomer. The role of free volume in systems involving propylene, glycol in several interacting systems was analyzed by Varadarajan and Bharathi[21]. The length of the side chain of hexanols was found to have a definite influence on the excess enthalpy values, on mixing with the interacting solvents [22].

1.6 VELOCITIES OF ULTRASONIC WAVES IN LIQUIDS

The first extensive measurements of ultrasonic velocity in organic liquids were done by Parthasarathy. He arrived at the assumptions that the aromatic compounds usually have higher velocities than the corresponding aliphatic compounds, although their densities are higher velocity in liquids of high density is low, but not in proportion, the increase in density being to some extent set off by an accompanying decrease in compressibility, polar molecules favour high velocities, long molecules give rise to higher velocity, a double bond of unsaturation tends to lower velocity and in similar derivatives changes from a light to a heavy atom lowers velocity. The results in many organic liquids indicate that as a rule an increase in density is to some extent balanced by an accompanying increase in β_0[23]. Nevertheless, since a number of inconsistencies developed from some of these rules, no quantitative derivations were possible[24]. However, Schaaffs had contradicted Parthasarathy's rule arguing that the aromatic substances have generally higher velocities than aliphatics. Increasing density through a homologous series ought to decrease u, but, in fact does not. In halogen compounds the abnormal in molecular weight accounts for the observed fall in U through a series. Increase in molecular volume and the density go hand in hand. These are the factors, which cause the increase of U when heavier atoms are substituted and not increased in molecular weight per sec. There is real evidence that dipole moment is of important in this connection[25].

The velocity of ultrasonic waves in liquids varies from about 900 to $2000 ms^{-1}$. The value of U also depends on the temperature and pressure.

For most pure liquids at temperatures far from the critical values the value of U decreases as the temperature increases. Water is an exception to this general rule and in this case U increases by about 2 ms^{-1} for each Kelvin rise in temperature and reaches a maximum at 346 mK, above this temperature, U decreases as the temperature rises further. As far as pressure changes are concerned, the velocity U increases in an approximately linear way with pressure for all liquids. This is simply as consequence of the fact that the bulk modulus increases as the molecules are squeezed closer together. For water U increases by about 0.2 ms^{-1} for every increases of one atmosphere[26].

In ultrasonic work, it is convenient to work with plane waves of small amplitude. When an ultrasonic waves passes through a liquid, the pressure and density of an element of liquid vary periodically with time. The variations in P and ρ may be assumed reversible and adiabatic. An ultrasonic wave is propagated as a longitudinal wave in a liquid because the particles of the liquid oscillate in the same direction in which the wave is moving. This is because the liquid possesses only one elastic modulus, the bulk modulus K. The propagation velocity, U, of the wave depends on this modulus and on the density ρ_0 of the liquid according to the equation,

$$U = \sqrt{\frac{Ks}{\rho_0}} \tag{1.1}$$

where K_s is the adiabatic bulk modulus. The above equation holds for small excess pressure amplitudes for which ρ_0 can be considered to remain a constant. This excess or acoustic pressure P is equal to the difference between the instantaneous pressure P and the ambient hydrostatic pressure ρ_0 i.e.,

$$P = P - \rho_0 \tag{1.2}$$

Let us consider a plane wave traveling in a liquid in the x-direction. Its propagation is given by the well known equation,

$$\frac{\partial^2 p}{\partial t^2} = U^2 \frac{\partial^2 p}{\partial X^2} \tag{1.3}$$

As the wave proceeds, each particle of the liquids sutlers a certain displacement from its mean position, we denote this particle displacement we denote this particle displacement by 'ξ'. The corresponding particle velocity v in the medium is given by v $=\frac{\partial \xi}{\partial t}$ and the particle acceleration by

$$a = \frac{\partial v}{\partial t} = \frac{\partial^2 \xi}{\partial t^2} \tag{1.4}$$

In equation (1.3), the propagation of sound wave has been described in terms of the acoustic pressure, p. This equation is also satisfied by other quantities such as velocity potential cp, particle displacement ~ and particle acceleration

$$\frac{\partial^2 \xi}{\partial t^2} = U^2 \frac{\partial^2 \xi}{\partial X^2} \tag{1.5}$$

We consider the typical solution

$$\xi = \xi_0 . \exp j\ (\omega t - kx) \tag{1.6}$$

In this equation ξ_0 represents the peak value of the particle displacement, $\omega = 2\pi f$ f is the angular frequency and k $=\frac{\omega}{U} = 2\frac{\pi}{\lambda}$ is the wave number[27, 28].

CHAPTER II

CHAPTER-2

LITERATURE SURVEY

2.1 REVIEW

Dash Ashok Kumar et al.,(2014)[29] proposed that the ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of binary mixture of dimethyl acetamide (DAMC) and diethyl ether at temperature 308K have been measured at different frequencies (2MHZ, 4MHz 6MHZ and 8MHZ). Adiabatic compressibility (K_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and their respective excess values have been computed for entire range of concentration and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time (τ), excess enthalpy (H^E) and absorption coefficient (α/f2) have been calculated and discussed. On the basis of the experimental values of density, ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixture, it is concluded that there exists dipole-dipole, dipole-induced dipole and dispersion interactions
in the binary liquid mixture of DMAC diethyl ether.

D. Ubagaramary et al.,(2018)[30] discovered that the functions of ultrasonic velocity, density and viscosity for ternary liquid mixtures of 1-proponol, 1- butanol and 1-pentanol with tetra hydro furan are determined by

303.15 K-313.15 K. This data is used to calculate various parameters like the excess free volume, excess internal pressure and Gibb's free energy, which is used to discuss molecular interactions in the ternary liquid mixtures.

Nabaparna Chakraborty et al.,[31] revealed that the Velocity of sound and density of binary liquid mixture of Dichloromethane with Ethanolamine have been calculated at different range of temperatures for various concentrations. Liquid-liquid interaction is confirmed by obtaining experimental values of fundamental parameters; ultrasonic velocity and density. Then these parameters are used to determine various other dependent parameters such as acoustic impedance (Z), intermolecular free length (Lf), adiabatic compressibility (β), Rao's constant (R), Wada's constant (W), Vander Waal's constant (b), effective molecular weight and Relative strength. Graphs are plotted for all parameters versus mole fraction. The linear variation of most of the acoustical parameters shows the absence of complex formation in the mixture. The decrease in ultrasonic velocity indicates that there is weak interaction between the molecules of the mixture. The solution tested, consisting of Dichloromethane and Ethanolamine, was selected in order to obtain data on the molecular interaction between their constituent particles.

R. K. Kolhe et al.,(2020)[32] proposed that the viscosity (η**)**, density (ρ) and ultrasonic velocity (U) of dimethylsulphoxide with 1-Octanol have been measured at different concentrations and temperatures from 303.15K to 318.15K. Above measured data is used to calculate the parameters like adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), free volume (V_f), and available molar volume ($V\alpha$). These calculated parameters are helpful to explain the strength of interaction among the molecules of liquid binary mixture under investigation. From observed values of ultrasonic speed, viscosity and density of mixture, other parameters such as adiabatic compressibility, acoustic impedance, free length, free volume and available volume for binary mixtures of dimethylsulphoxide with 1-Octanol at various temperatures, it is found that, molecular association is present among the molecules of liquid combinations.

Nabil M. Abdel Jabbar et al.,(2017)[33] proposed that the ultrasonic velocities have been measured for different binary mixtures of common choline chloride-based deep eutectic solvents (DESs), namely, reline, glyceline and ethaline with water, in the range of temperature: 303.15–353.15 K. The experimental data measurements with different mole fractions of DES–water solutions were utilised in fitting four different models for speed of sound. These models correlate the speed of sound with some physical properties such as molar volumes, molar components sound velocity, densities, molecular weights, collision factors etc. A close match was obtained with these models with an average relative error of less than 4% for all data points used. It was observed that the ultrasonic velocity increases with the concentration of DES solvent and decreases with temperature. Moreover, this study roughly indicated that the intermolecular interactions in reline and ethaline aqueous mixtures exist in the form of disruption of dipole–dipole interactions (that varies considerably as a function of DES mixture composition and solution temperature). On the other hand, the interactions on the molecular level in glyceline aqueous solution are mainly due to dipole–dipole intermolecular forces. The speed of sound and density data of different aqueous solutions of three common choline chloride-based DESs were measured as a function of temperature within the range 323.15–353.15 K.

K. P. Singh et al.,[34] the work presented in this paper deals with the study of thermodynamic properties of new working fluids for absorption machines, mainly for characterization of absorbent–refrigerant pairs that could improve the cycle performance. The study of atomic motion in liquids plays an important role in understanding the solid-like behaviour of liquids. The accurate measurement of the energy changes due to scattering can be used to study the dynamical behaviour of liquids. Measurements of the ultrasonic velocity (u), density (ρ) and viscosity (η) for binary mixtures of polyethylene glycol 250 dimethyl ether with 1-propanol and 1-butanol have been made at three temperatures (T = 293, 303 and 313 K) over the entire composition range in order to investigate the nature of intermolecular interactions between the components of these liquid mixtures. Non-linear variation of derived quantities

with the mole fraction supports the molecular interaction occurring between component molecules. From above studies, it is concluded that presence of strong interaction through hydrogen bonding between unlike molecules is characterised by non-linear behaviour of excess values of Gibbs's free energy of activation for viscous flow (ΔG^{*E}) and internal pressure (π_i^E).

N. P. Mohabansi et al.,(2020)[35] discovered that the Density(ρ), Viscosity(η), Ultrasonic Velocity(U) and Surface Tension(γ) of an aqueous-consolute, Na2SO4 solution of [2-(dimethylamino)-1-(4-methoxyphenyl) ethyl] cyclohexan-1-ol (Venlafaxine) 0.0201,0.0402,0.0804,0.1608 mol/kg were measured at 293.15, 303.15 and 313.15K. The resulting data were used to calculate various acoustical parameters, acoustic impedance (Z), adiabatic compressibility (β), Intermolecular free length (L_f), Wada's Constant (W), Rao's Constant (R), free volume (V_f), Relative Association (RA) were calculated which provides valuable information regarding drug-electrolyte (Na2SO4) interaction. The excess parameters viz. partial molar volume and excess adiabatic compressibility (β^E), excess inter molecular free length (L_f^E), excess free volume (V_f^E) were also calculated. These calculations help in predicting the intermolecular interactions. In an aqueous 2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]cyclohexan-1-ol and co-solute Na2SO4 solution, ultra-sonic velocity, density, viscosity and surface tension are measured at 293.15, 303.15 and 313.15K.

S. R. Dandwate et al.,(2018)[36] in the present studyattempt has been made to determine acoustic and thermodynamic parameters for binary liquid mixture of DMSO with methanol at 295.15 K, 300.15 K, 305.15 K, 310.15 K and 315.15 K temperatures. The excess values of isentropic compressibility, acoustic impedance, and internal pressure have been calculated using experimental data of ultrasonic velocity, density and viscosity. Molecular interactions in mixture form have been discussed depending upon deviations in excess values. Experimental data have been validated using Redlich-Kister polynomial equation. The values of excess isentropic compressibility have been found negative over entire concentration range at all temperatures.

P. S. Syed Ibrahim et al.,[37] deal the values of ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary liquid mixtures containing meta methoxy phenol and 1-propanol in n-hexane at different temperature 303 K,308 K and 313 K at a fixed frequency of 2MHz., experimentally. Using the experimental data of velocity, density and viscosity, various acoustical and thermodynamical parameters like Gibb's free energy, entropy, molecular interaction parameter, stability constant and excess property like solvation number are either calculated or computed. All these parameters have been discussed to throw light on intermolecular interactions between the component of ternary mixtures. The dependence of excess property in particular solvation number of the ternary mixture is compared and discussed in the context of intermolecular interaction and other factors. The result is interpreted in terms of molecular interactions under the influence of ultrasonic sound. From this present study it is concluded that the values of solvation number support the molecular reactions rather than the ionic reactions and henceforth interaction will be allowed due to dipole-dipole interactions and dipole – induced dipole interactions and nature of the hydrogen bonding and some extent due to steric effect of the substituent present in the benzene ring between MMP and 1- propanol in n hexane and these facts are substantiated by the values of thermodynamic properties such as ΔG^0 & ΔS.

V. Vanathi et al.,(2019)[38] proposed that the ultrasonic velocity (U), density (ρ), viscosity (η) for the ternary mixture of benzene þ chloroform þ cyclohexane in the whole range of composition has been carried out at various temperatures 303.15, 308.15 and 313.15K. From the measured parameters U, ρ and η, some derived parameters β, Lf, Vf, πi, Z, R,W with molar enthalpy (Hm) and apparent molar volume (ϕv) are also estimated. The decreasing trend of η, R,W, Hm, and ϕv with concentrations and other parameters are in increasing trend were observed. The trend of acoustical and physico-chemical parameters confirm the dynamics of molecules at higher temperature and the magnitude of intermolecular interactions among the constituents of the mixtures always reflects the nature of substance. The role of enthalpy and apparent molar volume has been used to determine their thermal response. The sign and magnitude of these properties are evident for the nature of interactions between component molecules. In summary, the ultrasonic velocity, density and viscosity measurements on ternary organic mixtures at various temperatures are carried out.

Sudhir P. Dange et al.,(2020)[39] reported that the Ultrasonic velocity (u), density (ρ) and viscosity (η) at 2 MHz in the binary mixtures of Riboflavin with methanol in the concentration range (0 to 0.1 M) and at temperature of 298K using ultrasonic interferometer technique. The experimental parameters, ultrasonic velocity, density and viscosity were used to calculate various acoustic and thermodynamic parameters. The obtained results support the nature and strength of molecular interaction, Physico-chemical behaviour in the binary liquid mixture of Riboflavin and Methanol. The Non-linear variation of thermo-acoustical parameters with molar concentration reveals that, there exist intermolecular forces in the binary liquid mixture of Riboflavin and methanol.

Pallavi B. Nalle et al.,(2019)[40] discovered that the ultrasonic velocity, density and viscosity of drug *Piperine* with MgCl2 have been measured as a function of number of moles n = (0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) at 323.15 K, 328.15 K and 333.15 K. The experimentally collected data have been used to calculate various acoustical, thermodynamic and excess parameters such as excess values of adiabatic compressibility, excess intermolecular free length, excess specific acoustic impedance, excess relaxation amplitude and excess relaxation time have been calculated. Above excess

parameters are fitted to the Redlich-Kister equation. The results of acoustical, thermodynamic and excess properties reveal the existence of strong molecular interaction in the mixtures. The drug works as a structure breaker (it breaks the structure of $MgCl2$) and there is ion formation in the system. Acoustic, thermodynamic and excess parameter of mixture reflects the structural deformation in terms of intermolecular interaction. As the isentropic compressibility goes on increasing in a negative manner, the prepared solvent mixture maleic acid and methanol (60/40) can be used for the bleaching purpose of coconut coir fibres.

T Karunakar et al.,[41] revealed that the ultrasonic velocity and density measurements for binary mixtures of aniline + 1-butanol at T= (303.15 – 318.15) K, are conducted at atmospheric pressure. Some thermo acoustical parameters like adiabatic compressibility (β), molar volume (V_m), inter molecular free length (L_f) and acoustic impedance (Z) have been calculated from experimental measurements. The results have been used qualitatively to explain the molecular interaction between the components of these mixtures. Further, the results are further supported by FT-IR spectra. From the data of ultrasonic velocity and density various acoustical parameters of the mixtures of aniline with 1-butanol at 303.15, 308.15, 313.15 and 318.15 K were calculated.

R. C. Verma et al.,(2014)[42] proposed that Density, Ultrasound velocity and viscosities of Ethyl propionate with butanol-1 and pentanol-1 have been measured over entire range of composition at 308 K and atmospheric pressure. The computed acoustic and thermodynamic properties of Ethyl propionate in higher alcohols will give the excess values of issentropic compressibility, molar volume and viscosity. The excess value will decided the nature and extent of molecular interaction of Ethyl propionate in butanol-1 and pentanol-1.

L. Palaniappan et al.,(2019)[43] proposed that the ultrasonic velocity, density and viscosity measurements carried out for the binary mixtures of toluene, m-xylene with some butanols at 303 K. Various theoretical models have been applied to these binary systems; evaluate the sound velocity values and compared with the experimental values. The validity of Nomoto theory (NT), Van Deal-Vangeal (IMR) and Free length theory (FLT) is checked and a comparative study of the above models is made. The non-ideal behaviour of the system is explained in terms of molecular interactions of the constituents of the mixture. The interactions further, evident with percentage deviation, molecular interaction parameter and goodness fit test. Among the three theories taken up for the prediction of sound velocity, Namoto Relation is found to yield excellent comparison with the experimental value for the systems investigated.

Sk. Md Nayeem et al.,(2015)[44] that the ultrasonic velocities, u, and densities, q, of binary liquid mixtures of dimethyl sulphoxide (DMSO) with ketones such as acetophenone (AP), cyclohexanone (CH), and 3-pentanone (3P), including pure liquids, over the entire composition range have been measured at 308.15 K. Using the experimental data, deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess molar volume, V_m^E, excess intermolecular free length, L_f^E and excess acoustic impedance, Z^E, partial molar volumes, $V_{m,1}$, $V_{m,2}$, and excess partial molar volumes, $V^E_{m,1}$, $V^E_{m,2}$, have been calculated. Molecular interactions in the systems have been studied in the light of variation of excess/deviation values of calculated properties and these properties have been fitted to Redlich–Kister type polynomial equation. The observed positive values of V_m^E, Δk_s, L_f^E and negative values of Δu, Z^E for all the binary liquid mixtures studied clearly indicate the presence of the dominance of weak physical interactions between the components of molecules. Further, FTIR spectra support the conclusions drawn from deviation/excess properties. Moreover, theoretical values of ultrasonic velocity in the mixtures have been evaluated using various theories and such values were compared with experimental velocities to verify the applicability of such theories to the systems investigated.

Johnson.S et al.,(2017)[45] proposed that the densities and viscosities of ternary liquid mixtures of isopropanol +1,2-propanediol + cyclohexanone, were measured at 308.15 K and 318.15 K over entire range of composition. From the density and viscosity data, the excess thermodynamic properties, viz., the excess volume (VE), molar volume (V), deviation in viscosity, interaction parameter (d) and excess Gibbs free energy of activation of viscous flow were calculated. The values of excess parameters namely VE, and were fitted to Redlich Kister type polynomial equation. Further heat of mixing and IR spectra were studied at equimolar concentration. From these results, the nature of interaction have been discussed interms of intermolecular interaction between the mixing components.

N.A.Kalambe et al.,(2017)[46] proposed that the density (d) and ultrasonic velocity (v) values have been measured in the solvent ethanol containing 2-hydroxy substituted quinoxaline using different concentration at 305.85 K. The experimental data of density (d), ultrasonic velocity (v), adiabatic compressibility, intermolecular free length (Lf), specific acoustic impedance (Z) and relative association (RA) were calculated. The results obtained in this study have been interpreted in terms of different interactions among solute-solute and solute-solvent.

CHAPTER III

Chapter III

Materials and Methods

3.1 Introduction:

Ultrasonic, thermo-physical and thermodynamic properties of liquid mixtures are of great significance in obtaining an in depth knowledge of inter and intra-molecular interactions, structural and physiochemical behavior and also in verifying various liquid state theories which attempt in estimating the properties of liquid mixtures. Systematic study of thermodynamic properties of solutions with a new type of multi-frequency ultrasonic interferometer is done for precise measurement of the velocity of sound in liquids. The path length in the cell is varied by motion of a reflector, at the electrical reaction of the cell upon the oscillator is used to fix standing wave position at a standard frequency, and their locations are determined with a suitable cathetometer.

An investigation in the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been found to be an excellent quantitative way to elicit information about molecular structure and intermolecular forces in liquid mixtures. This has given impetus to the theoretical and experimental investigation of excess thermodynamic properties of liquid mixtures. Measurement of physiochemical properties such as density and ultrasonic velocity of pure components and their binary mixtures are being increasable used as tools for investigations of the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures. The significance reasons for the study of thermo-physical and thermodynamic properties of multi-component liquid mixtures are as follows:

- They provide way for studying the physical forces acting between molecules of different species.
- The study of liquid mixtures provides appearance of new phenomena, which are absent in pure liquids. The most interesting of these are the new types of phase equilibria, which are introduced by the variation in the promotion of the pure components.
- Liquid mixtures are the most direct source for studying the various parameters. The study of thermo-physical and thermodynamic properties of liquid mixtures helps in obtaining in depth knowledge about molecular interactions.

3.2. Theory:

Ultrasonic interferometer is a simple and direct device which yields accurate and consistent data, from which one can determine the velocity of ultrasonic sound in a liquid medium with a high degree of accuracy. A crystal-controlled interferometer (model M-83S) supplied by Mittal Enterprises, New Delhi, operating frequency 2 MHz has been used to measure the ultrasonic velocity.

3.3. Ultrasonic:

Ultrasonic sound refers to sound pressure with a frequency greater than the human available range (20 Hz to 20 KHz). When an ultrasonic wave propagates through a medium, the molecules in that medium vibrate over short distance in a direction parallel to the longitudinal wave. During this vibration, momentum is transferred among molecule. This causes the wave to pass through the medium.

3.4. Ultrasonic Interferometer:

An Ultrasonic Interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy.

Fig 1: Experimental setup for ultrasonic interferometer.

The salient features of ultrasonic interferometer are given below:

- It is a simple in design, rugged and gives very accurate and reproducible results.
- Experiments may be performed over a wide range of temperature from -30 ^{0} C to +80 ^{0} C on all liquids except those which reacts with the plating of cell and crystal.
- Nearly 10 ml of experimental liquid is required.
- There is no danger of any change such as depolymerisation, due to ultrasonic effect since a very small ultrasonic energy is required.

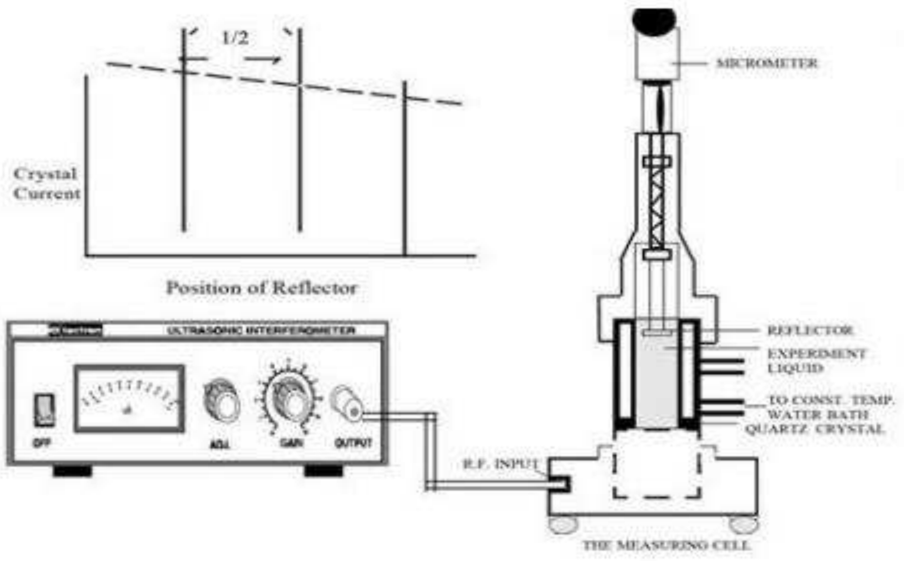


Fig 2: Cross section of the liquid cell and graph plotted position of reflector versus crystal current.

In an ultrasonic interferometer, the ultrasonic waves are produced by the piezoelectric methods. At a fixed frequency variable path interferometer, the wavelength of the sound in an experimental liquid medium is measured, and from this one can calculate its velocity through that medium. The ultrasonic cell consists of a double walled brass cell with chromium plated surfaces having a capacity of 10 ml. The double wall allows water circulation around the experimental liquid to maintain it at a known constant temperature. The micrometer scale is marked in units of 0.01 mm and has an overall length of 25 mm. Ultrasonic waves of known frequency are produced by a quartz crystal which is fixed at the bottom of the cell. There is a movable metallic plate parallel to the quartz plate, which reflects the waves. The waves interfere with their reflections, and if the separation between the plates is exactly an integer multiple of half wave length of sound, standing waves are produced in the liquid medium. Under these circumstances, acoustic resonance occurs.

The resonant waves are a maximum in amplitude, causing a corresponding maximum in the anode current of the piezoelectric generator. The ultrasonic interferometer consists of the following mainly two parts:

3.4.1. The high frequency generator.

3.4.2. The measuring cell.

3.4.1. The high frequency generator

The high frequency generator is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the “measuring cell”. A micrometer to observe the changes in current two controls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the high frequency generator.

3.4.2. The measuring cell

The measuring cell is specially designed for maintaining the temperature of the liquid constant during the experiment. A fine digital micrometer screw (LC 0.001 mm) has been provided at the top, which can lower or raise the reflector plate in the liquid within the cell through a known distance. It has a quartz crystal fixed at its bottom.

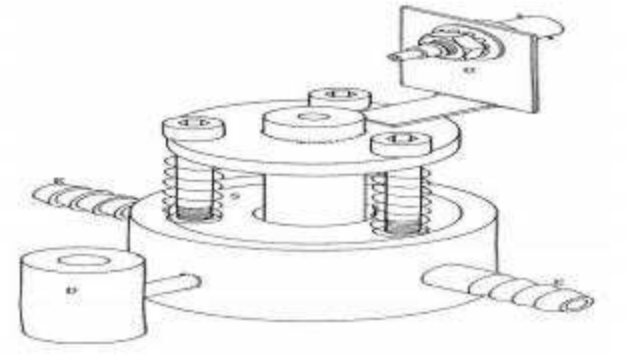


Fig 3: Ultrasonic interferometer cell liquid mixtures.

3.5: Working principle

The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ)in the medium. Ultrasonic waves of known frequency (f) are produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator become a maximum. If the distance is now increased or decreased and the variation is exactly one-halfwavelengths($\lambda/2$) or multiple of it, anode current become maximum from the knowledge of wavelength (λ) the velocity (U) can be obtained by the relation:

Velocity = Wavelength × Frequency $U = \lambda \times f$ (1)

3.6: Adjustment of ultrasonic interferometer

For initial adjustment two knobs are provided on high frequency generator, one is marked with “ADJ” to adjust the position of the needle on the ammeter and the knob marked “GAIN” is used to increase the sensitivity of the instrument for greater deflection, if desired. The ammeter is used to notice the number of maximum deflection while micrometer is moved up or down in liquid.

3.7. Procedure

7.1 Unscrew the knurled cap of cell and lift it away from double walled construction of the cell. In the middle position of it pour experimental liquid and screw the knurled cap. Wipe out excess liquid overflowing from the cell.

7.2 Insert the cell in the heavy base socket and clamp it with the help of a screw provided on its side. 7.3 Connect the high frequency generator with cell by coaxial cable provided with the instrument. In ultrasonic interferometer frequency selector knob should be positioned at desired frequency (same frequency as that of liquid cell chosen).

7.4 Move the micrometer slowly in either clockwise or anticlockwise direction till the anode current on the ammeter on the high frequency generator shows a maximum or minimum.

7.5 Note the reading of micrometer corresponding to the maximum or minimum (which is sharper) in microammeter. Take about 50 reading of consecutive maximum or minimum and tabulate them. 7.6 Take average of all differences (λ/2).

7.7 Once the wavelength (λ) is known the velocity (U) in the liquid can be calculated with the help of the relation.

3.8. Sample calculations Sample:

water Average (λ/2): 0.375mm.

Ultrasonic velocity in sample: U = λ ×f = 1480 m/sec.

Density of the liquid = 996.458 Kg/m3

Adiabatic compressibility (ŧad) = 1/ρv2 = 1/996.458 ×(1480)2 ad = 4.58 × 10-10 N/m2 .

3.9. Measurement of the density:

The density measurements were made by dilatometer. It was placed in a high precision water bath for temperature control. The dilatometer was calibrated initially using distilled water. The reliability of the dilatometer was checked for liquid like benzene and carbon tetrachloride at known temperatures. The densities measured for A.R. grade benzene and carbon tetrachloride were found to be 0.8735 and 1.5845 g/cc respectively at 298.15K. The literature values of densities for benzene and carbon tetrachloride were found to be 0.8737 and 1.5844 g/cc respectively. Thus, the measured values were good agreement with their literature values.

10. Measurement of viscosity

The viscosity measurements were done through Ostwald's viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. The water in the viscometer is allowed for some time to attain the experimental temperature. Using a suitable arrangement, the water is sucked above the marked level and then it is allowed to flow freely. The time taken for the flow of water is noted. The water is replaced with a mixture, whose viscosity is to be determined. Using the same procedure, the time taken for flow of liquid mixture at the experimental temperature was determined. Using the time taken for the distilled water and mixture, the viscosity of unknown liquid mixture is determined:

ꝗs / ηw = ρs/ ρw × ts/ tw (2)

Where ηw, ρw and tw are the viscosity, density and time flow of water respectively and ꝗs, ρs and ts are the viscosity, density and time flow of unknown liquid mixture respectively. Viscosity is an important transport property for process design in petroleum, petrochemical, chemical and other chemical industries involving fluid transportation, mixing agitation, heat exchange and concentration. The estimation of the viscosity of a mixture is more difficult than of the pure compound. The prediction of the viscosity of liquid mixtures is a goal of long standing with both experimental and theoretical importance. Many industrial, chemical processes or laboratory works need experimental data of viscosity at any given temperature and composition for the liquid mixtures.

Theoretical methods for the estimation of acousticalthermodynamic parameters of liquid and liquid mixtures

Adiabatic compressibility (βad)

The adiabatic compressibility is the fractional decrease ofvolume per unit increase of pressure, when no heat flows inor out. These changes are related to the compressibility of themedium by thermodynamic relation; [18]

□ad= □

□[□□/□p] (21)

It can also be calculated from the speed of sound (U) and thedensity of the medium (ρ) using the equation of NewtonLaplace as;

□ad =□/□ρ2Kg-1ms2 (22)

Intermolecular free length (Lf)

The intermolecular free length is the distance covered bysound wave between the surfaces of the neighboringmolecules. It is measure of intermolecular attractionsbetween the components in binary mixture. The increase or decrease in free length indicates weakling and strengthen ofintermolecular attraction. As the ultrasonic velocity increasedue to the increases in concentration, the interaction freelength has to decrease and vice-versa. It is related toultrasonic velocity and density as; [14]

Lf= K/□□U) 1/2m (27)

The adiabatic compressibility of a liquid can be expressed interms of the intermolecular free length which is the distancebetween the surfaces of the neighboring molecules and isgiven by the relation, [19]

Lf = KT β1/2 (28)

Where, KT= (93.875+0.345T) ×10-8

12.7. Free volume (Vf)

Free volume is one of the significant factors in explaining thevariations in the physio-chemical properties of liquids andliquid mixtures. The free space and its dependent propertieshave close connection with molecular structure and it may show interesting features about interactions, which mayoccur when two or more liquids are mixed together. Thismolecular interactions between like and unlike molecules areinfluenced by structural arrangements along with shape andsize of the molecules.

A liquid may be treated as if it were composed of individualmolecules each moving in a volume Vf in an averagepotential due to its neighbors. That is, the molecules of aliquid are not quite closely packed and there are some free spaces between the molecules for movement and the volumeVf is called the free volume. Eyring and Kincaid defined thefree volume as the effective volume in which particularmolecule of the liquid can move and obey perfect gas laws.

Free volume in terms of Ultrasonic velocity (U) and the
Viscosity of the liquid (η) as; [15]

Vf = [MeffU/Kη]1/□ (29)

Where

Meffis the effective molecular weight.

Meff = □□□□ in which Mi and Xi are the molecular weight andthe mole fraction of the individual constituents respectively).

K is a temperature independent, constant which is equal to4.28x109 for all liquids.

12.8. Relaxation time (□)

Relaxation time is the time taken for the excitation energy toappear as translational energy and it depends on temperatureand on impurities. The dispersion of the ultrasonic velocityin binary mixture reveals information about theCharacteristic time of the relaxation process that causesdispersion. The relaxation time (τ) can be calculated from therelation; [8]

β = □

□β η (30)

Acoustic impedance (Z)

Sound travels through materials under the influence of soundpressure. Because molecules or atoms of a solid are boundelastically to one another, the excess pressure results in wavepropagation through the solid.

The acoustic impedance (Z) of a materials is defined as theproducts of its density (□) and ultrasonic velocity (u) givenas; [8]

Z □ Uβ □31□

12.10. Internal Pressure (πi)

The measurement of internal pressure is important in thestudy of the thermodynamic properties of liquids. Theinternal pressure is the cohesive force, which is a resultant offorce of attraction and force of repulsion between the molecules. Cohesion creates a pressure within the liquid ofvalue between 103 and 104 atmospheres. Internal pressurealso gives an idea of the solubility characteristics. Dissolvedsolutes exist under the internal pressure of the medium andtheir interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic (or) Vander Waal'sinteraction. The term a/v2 in Vander Waal's equation beingthe measure of attractive force of the molecule is called thecohesive (or) internal pressure.

The internal pressure is the single factor which varies due toall type of solvent-solute, solute-solute and solvent-solventinteractions. The internal pressure, (πi) can be calculated byusing equation; [15]

$\Pi i = bRT [K\eta/U]1/2[\rho 2/3/M7/6]$ (32)

Where K is a constant. T is the absolute temperature.$\eta$is theviscosity in NSm-2. U is the ultrasonic velocity in ms-1andρ isthe density in kgm-3of the liquid.

Gibb's free energy (ΔG)

The relaxation time (□) is related to the activation freeenergyfor a given transition. The variation of □ withtemperature can be expressed in the form of Eyring saltprocess theory and the rearranged equation is given as; [2]

$\Delta G = -KT$

$\log [h/KT \square]$ (37)

Where K is the Boltzmann constant and h is the plank's constant.

Excess parameters

The excess values are calculated using the formula; [2]

AEXCESS = AEXP - AIDEAL (45)

Where, Aid = Σ □iXi, where Ai is any acoustical parameter and Xi is the mole fraction of liquid component.

CHAPTER IV

CHAPTER-4

RESULT AND DISCUSSION

s

THERMODYNAMIC PROPERTIES OF BINARY MIXTURES OF ETHYL PROPIONATE WITH ETHANOL AT DIFFERENT TEMPERATURES

A project report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI.

In partial fulfillment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

L. JEFERLIN

Reg. No: 19SPPH02

Under the supervision and guidance of

Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this project work entitled **"THERMODYNAMIC PROPERTIES OF BINARY MIXTURES OF ETHYL PROPIONATE WITH ETHANOL AT DIFFERENT TEMPERATURES"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** in partial fulfillment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the year 2020-2021 by

L. JEFERLIN **Register No: 19SPPH02**

Padmavathi S.P
Signature of the Guide

Padmavathi S.P
Signature of the SSC Coordinator

Joyce
Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rosa
Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

A. Nirmala Shirley
Signature of the Examiner

ACKNOWLEDGEMENT

"GIVE THANKS TO THE LORD FOR HE IS GOOD"

First of all, I thank the Lord Almighty for his blessing and grace to complete this comprehension work.

I am deeply indebted to our Principal **Rev. Dr. Sr. A. S. J. LUCIA ROSE M. Sc., PGDCA., M. Phil., Ph. D.,** for the encouragement she bestowed upon us.

I wish to express my sincere thanks to our Director of SSC, **Rev. Dr. F. MARY JOYCE BABY M.A., M.Phil., Ph. D.,** for her support in my work.

I would like to express my special thanks of gratitude to **Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D.,** Head of the Department, for her inspirational words and encouragement to complete this project.

I am thankful to **Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,** SSC Coordinator and my guide, for the continuous support, patience, motivation, and immense knowledge. Her guidance had encouraged me to do this project successfully.

I am grateful to my parents and my sister who have provided me through moral and emotional support to complete my work.

Abstract:

The ultrasonic velocity(U),density(ρ), viscosity (η) have been measured in binary liquid mixtures of Ethyl Propionate with Ethanol at 308K, 318K and 328K. From these data some of acoustical parameters such as Adiabatic compressability (β_{ad}), Acoustic impedance(z), Free length (L_f) and Relaxation time (τ) have been computed using standard relations. The variations in ultrasonic velocity and other parameters play a significant role in understanding the solute-solvent, intra and intermolecular interactions between the constituent molecules.

LIST OF CONTENTS

List of tables

List of figures

Symbols, Abbreviations & Nomenclature	**Meanings**
H^E	Excess of mixing for several alcohols
U	Velocity
K	Wave number
K_s	Adiabatic bulk modulus
ρ	Density
ρ_0	Ambient hydrostatic pressure
ρ_{mix}	Density of binary mixtures
P	Acoustic pressure
α	Cubical expansion coefficient
β_α	Adiabatic compressability
γ	Ration of specific heats
ω	Angular frequency
ξ	Particle displacement
ξ_0	Peak value of the particle displacement
m	Molecular weight
U_T	Isothermal sound velocity
R	Gas constant

Symbols, Abbreviations & Nomenclature	**Meanings**
T	Temperature
N_A	Avogadro number
R_m	Molar refraction
Z_i	No. of atoms in the i^{th} molecules
A_i	Additive volume
W	Sound velocity
T_c	Critical Temperature
T_0	Melting point
V_0	Volume per mole
V_f	Free volume
V_a	Available volume
V_{OA},V_{OB} A, B	Molar volume of the components
L_f	Free length
L_{mix}	Free length in binary mixtures

CHAPTER I

CHAPTER-1

THE LIQUID STATE

1.1 INTRODUCTION

While it is often said that a liquid is intermediate in its properties between a solid and a gas, this statement should not be understood to mean that every property of a liquid is intermediate in value between those of the other two states. If the actual figures are compared, it is found that in the great majority of cases the value of any property of a liquid is approximately equal either to that of the solid or to that of the gas. The intermediateness, then, is a statistical one-a liquid has some of the properties of a solid, and some of the properties of gas. The most obvious resemblance between liquids and gases is their lack of rigidity neither offers permanent resistance to a shearing stress. The immediate consequence of this is that neither a liquid nor a gas possesses shape of its own, but always offer a resistance to shearing stress.

Between liquids and solids, the most prominent resemblance is that both possess cohesion, which enables each to maintain a free surface, whereas a gas will always completely fill any container. A second, and hardly less fundamental, property common to liquids and solids, is their relative incompressibility compared to gases. While the compressibility of solids are usually of the order or of10^{-6} atm^{-1}, those of liquids are only slightly larger (about10^{-5} atm^{-1}).

The compressibility of a gas, on the other hand, is roughly equal to the reciprocal of the pressure, or, at a pressure of one atmosphere, about 10^5 times as great as that of liquid. Closely allied to the second similarity between liquids and solids is the third: their similarity in density. The density change which takes place when a solid melts is usually of the order of 10 to 50 percent, but on vapourization the density decreases by a factor of 100 or 1,000.

From these simple facts considerable information can be obtained about the nature of the molecular arrangement in liquids. From the density, for example, the mean distance between molecules can be calculated. Taking Argon as a typical example, the molar volumes of the solid, liquid and gas at the boiling point are respectively 24.3 cc, 28.1 cc and 7.050 cc. As a first molecules of the liquid and gas are arranged like those of the solids in a face centered cubic lattice. To obtain the correct densities it is then necessary to assume that the distance between nearest neighbours is 3.84 A° in the solid 4.03 A° in the liquid 25.4 A° in the gas. In the solid, the molecules are in contact. In the liquid, there is a little space (about 5 percent of the molecular diameter) between molecules is about six times the molecular diameter.

Since the forces between molecules are short range forces, and act through a distance of only two or three times the molecular diameter, it is immediately obvious that in the gas these forces are of little importance. Any such regular arrangement of molecules as that we have assumed will therefore be destroyed by the thermal motions of the molecules, and the usual assumption that the molecules of a gas are arranged in space and are randomly distributed.

In the solid, on the other hand, the close-packed arrangement of the molecules prevents any molecule moving from moving far from its original position, which results in turn in the rigidity of the crystal. At the same time the low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must be accomplished by reducing the size of the molecules themselves. If the liquid maintains the arrangement we have assumed, it is difficult to see how to explain its fluidity. The molecules are packed so closely together that no interior molecule can change its position by much more than can the molecule of the solid. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane molecule. Such a motion, however, would require the simultaneous lengthening of a great number of intermolecular distances and hence a large energy of activation for the flow process. To avoid this difficulty it is obviously necessary to assume that a few molecules move at a time, but this in turn implies that it must be relatively easy for molecules to become displaced from the regular

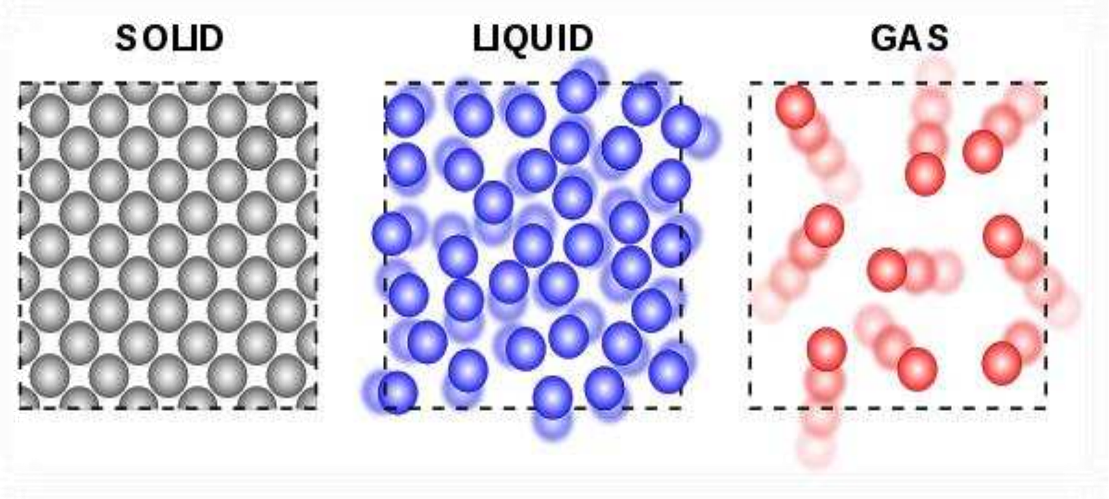


Fig1.1Relative spacing of molecules in solid, liquid and Gaseous Phases

On the other hand, the problem of packing so many spheres into a given volume does not permit any great variation from the regular closed packed structure. In fact the only reasonable modifications which can be made are two in number. First, there may be local irregularities caused by groups of molecules coming closer together, leaving wider spaces elsewhere in the structure. Second, there may be gradual distortion of the structure as we go from molecule to molecule, so that although the pattern in the immediate neighbourhood of a given molecule be quite regular, the pattern is irregular at a distance.

1.2 SHORT AND LONG RANGE ORDER

The tendency of a liquid molecule to surround itself with a more or less definite number of neighbouring molecules at a near a definite distance shows that if we consider a region in the liquid so small that it contain only a few molecules, - say about 20 – these molecules must be arranged very nearly in as regular fashion as in the corresponding crystal. On the other hand, if the size of the region is enlarged, the irregularities mount up, and the positions of the molecule no longer can be related to a lattice of the type occupied by the molecules in the crystal. The regularity exhibited by the crystal is now generally referred to as long range order, since the positions of molecules many diameters away from a central molecule can be predicted from a knowledge of the position of the central molecule and the molecules immediately surrounding it.

In the liquid, on the other hand, this long range order has disappeared. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite, we can say that the liquid still possesses short range order. The crystal, of course, has short range order as well as long range order, but in the gas phase even the short range order has disappeared.

We can, therefore, state as an experimental fact that the melting of a crystal is accompanied by the disappearance of long range order, and the evaporation of a liquid is accompanied by the disappearance of short range order.

1.3 THE LOOSE PACKING OF RIGID SPHERES

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied a minimum, them a regular crystal-like lattice-either hexagonal or cubic is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of the structure will disappear. This has been demonstrated in two dimensions by a number of experimenters[1] who have studied the distribution of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by Morrell and Hildebrand[2] by suspending hard gelatin spheres in a solution of the same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

It would appear from this experimental evidence that the principal factor in the determination of the radial distribution function in a liquid is the volume occupied by the molecules themselves, that is to say, the repulsive forces between the molecules rather that their attraction.

1.4 THEORIES OF LIQUID STATE

The readiness with which liquids flow and diffuse suggests a random molecular structure analogous to the gas. On the other hand the cohesion and compactness exhibited by liquids indicate a structure resembling that of a solid. The similarities between a liquid and a solid make one to consider the two states of matter collectively as a “condensed matter” while the properties of fluidity shared by liquid and gas connect them collectively as “fluids”. Hence liquid state theories are broadly of two types.

1. Considering it as a condensed gas so that the interaction between the neighbouring molecules may be calculated through “pair potential functions” and

2. Considering it as a disordered solid lattice.

1.5 MOLECULAR INTERACTION IN LIQUIDS

There are two kinds of interaction

1. Dispersion interaction and
2. Dipole-dipole interaction in liquids.

In the case of non polar molecules the average dipole moment averaged over all phases of electronic motions is zero while the instantaneous dipole moment is never zero.

If two non-polar molecules are placed near each other, the instantaneous dipole moment will interact and will produce some potential energy, which may be positive (or) negative. Such interaction between the molecules is termed as dispersion interaction and is present in all the aggregates of molecules irrespective of the nature of the atoms and molecules.

The second category of interaction is specific. It requires a Hydrogen atom attached to a fairly high electronegative atom and an atom at an optimum distance with non bonded electrons (ion-pairs). This results in the formation of complexes between molecules while the dispersion interaction leads to positive contributions to excess thermodynamic quantities, the latter category makes negative contribution.

The determination of sound velocity, density, viscosity etc., leads to an understanding of the nature and type of molecular interactions especially in binary mixtures of liquids through the excess thermodynamic quantities. Normal liquids obey certain empirical rules such as Trouton's rule, The heat of vaporization at the boiling point is nearly equal to $85 \pm 10\, JK^{-1} mole^{-1}$, the associated liquids (having hydroxyl group), do not obey these empirical rules.

The deviation is due to association of molecules found in the vapor to form larger molecules in liquids. In the case of alcohols and acids, the links between the individuals are provided by hydrogen bonds.

The protic dipolar liquids are ordinarily intermolecular hydrogen bonded. This class of liquids has been extensively studied, the best example being water. Aliphatic and aromatic alcohols and amines, carboxylic acids and amides are typical representatives of this class of liquids. The liquids of this class possess an entropy of vaporization which is 30% higher than for normal non-associated liquids. A notable exception is the carboxylic acids.

The alcohols show regularly changing liquid properties as the aliphatic chain length is increased (or) as the number of hydroxyl groups is increased. For example, the di-electric constant drops as the chain length increases, but increases with the increase in number of hydroxyl groups.

When two liquids are mixed, the solution is said to be ideal if there is no volume change (or) enthalpy change on mixing. But in practice, solutions of liquids are never ideal. The deviation from ideality is much more marked in the case of associated solutions. The thermal energy is less than the interaction energy. The thermal perturbation cannot disturb the association very much. In a binary system of associated liquids, a distortion occurs depending on the concentration. The distortion in the structure of the associated molecules leads to large changes in the physical properties such a dielectric constant, viscosity, free volume etc. Considerable dissociation must occur when alcohols are mixed with diluents, the hydrogen bonds are broken and this explains the positive heats of reactions.

Self associations in alcohols are shown on fig 1.2. The earliest model of self association in alcohols is that of Oster and Kirkwood[5], which assumed long chain association with free rotations of the O.H. around the H-bond in such a situation,

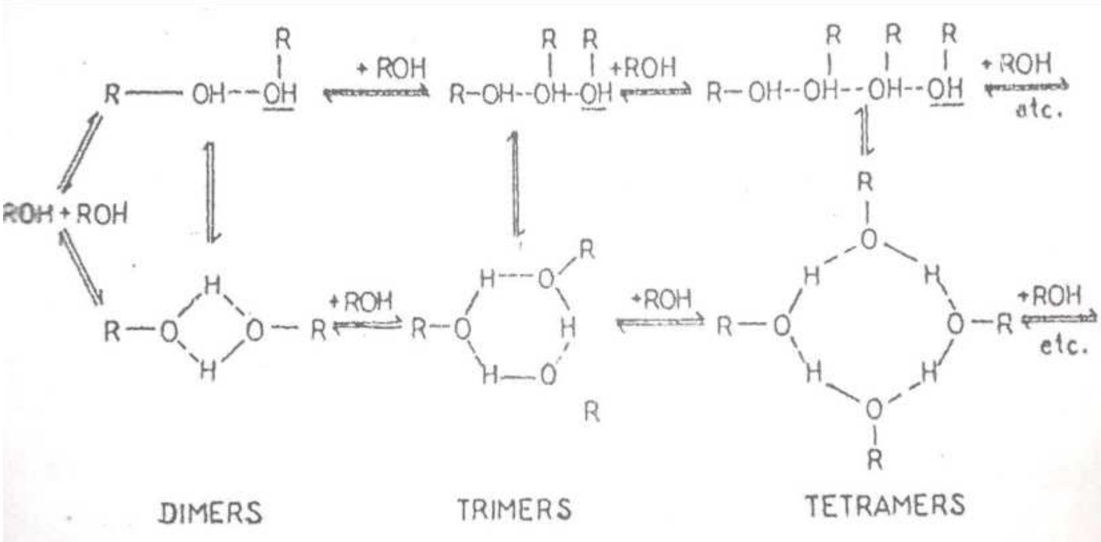


Fig: 1.2 POSSIBLE EQUILIBRIA IN THE SELF-ASSOCIATION OF ALCOHOLS

Dipole moment of the alcohol solution should be greater than that of its monomer unit, which is not the case always[6, 7]. In the most alcohols, dilution with non polar solvents resulted in a dip in dipole moment at a definite concentration[8], which means qualitatively that dilution leads to the formation of cyclic multimers of lesser dipole moment. Bellamy and Pace[9] and Cobur Oxrunwald[10] were of the view that such cyclic structures must be multimers and not dimmers because of unfavourable bonding angles in dimers. Since the cyclic form possesses one additional H-bond compared to the open (or) linear form, the change in enthalpy AH^o for cyclic form should be greater than that corresponding to the open structure. Hence it is possible to look for specific information from the experimental studies of enthalpy and entropy. Such studies[11, 12] also do not provide sufficient data to permit a decision in favour of or against a particular model. Bordewijk[13], from his dielectric studies showed in mono alcohols, the large multimers are cyclic, probably tetramers, without of plane Oxygen and Hydrogen atoms.

Though there are plenty of data available on the ultrasonic behavior of mono alcohols[14-19] and in mixtures with inert solvents, they do not provide enough information on the model of mono alcohols.

Since the ultrasonic velocity is very sensitive to change in the free volume, it is desirable to look at the data on ultrasonic compressibility's of liquids from the thermo-dynamic point of view. The change in free volume results in a large change in the internal pressure of the liquids and hence the enthalpy of the system. The ease with which one can distort the fluid structure is determined by the energy holding the lattice together. In H-bonded liquids, it is reasonable to assume that this internal energy is related directly to the number of H-bonds per unit volume. The ultrasonic wave propagation in such liquids should result on the distortion of the fluids structures. Based on this concept, Sabesan et.al[20] studied the internal pressure and excess of mixing (H^E) for several alcohols including cyclo hexanol, amyl alcohol Isoamyl alcohol, Isopropanol, n-butonol, 2-butonol, Isobutanol and tert-butanol in dioxin at different concentrations at 303, 308 and 313K. The positive values of H^E for the systems reported was explained as arising due to the stronger, self associations that was broken, rather strongly by dioxin compared to n-heptane (or) n-hexane. Among that the isomer alcohols, the n-compounds were found to have less H^E at a given concentration and temperature, than the corresponding isomer. The role of free volume in systems involving propylene, glycol in several interacting systems was analyzed by Varadarajan and Bharathi[21]. The length of the side chain of hexanols was found to have a definite influence on the excess enthalpy values, on mixing with the interacting solvents [22].

1.6 VELOCITIES OF ULTRASONIC WAVES IN LIQUIDS

The first extensive measurements of ultrasonic velocity in organic liquids were done by Parthasarathy. He arrived at the assumptions that the aromatic compounds usually have higher velocities than the corresponding aliphatic compounds, although their densities are higher velocity in liquids of high density is low, but not in proportion, the increase in density being to some extent set off by an accompanying decrease in compressibility, polar molecules favour high velocities, long molecules give rise to higher velocity, a double bond of unsaturation tends to lower velocity and in similar derivatives changes from a light to a heavy atom lowers velocity. The results in many organic liquids indicate that as a rule an increase in density is to some extent balanced by an accompanying increase in β_0 [23]. Nevertheless, since a number of inconsistencies developed from some of these rules, no quantitative derivations were possible[24]. However, Schaaffs had contradicted Parthasarathy's rule arguing that the aromatic substances have generally higher velocities than aliphatics. Increasing density through a homologous series ought to decrease u, but, in fact does not. In halogen compounds the abnormal in molecular weight accounts for the observed fall in U through a series. Increase in molecular volume and the density go hand in hand. These are the factors, which cause the increase of U when heavier atoms are substituted and not increased in molecular weight per sec. There is real evidence that dipole moment is of important in this connection[25].

The velocity of ultrasonic waves in liquids varies from about 900 to $2000ms^{-1}$. The value of U also depends on the temperature and pressure. For most pure liquids at temperatures far from the critical values the value of U decreases as the temperature increases. Water is an exception to this general rule and in this case U increases by about 2 ms^{-1} for each Kelvin rise in temperature and reaches a maximum at 346 mK, above this temperature, U decreases as the temperature rises further. As far as pressure changes are concerned, the velocity U increases in an approximately linear way with pressure for all liquids. This is simply as consequence of the fact that the bulk modulus increases as the molecules are squeezed closer together. For water U increases by about 0.2 ms^{-1} for every increases of one atmosphere[26].

In ultrasonic work, it is convenient to work with plane waves of small amplitude. When an ultrasonic waves passes through a liquid, the pressure and density of an element of liquid vary periodically with time. The variations in P and ρ may be assumed reversible and adiabatic. An ultrasonic wave is propagated as a longitudinal wave in a liquid because the particles of the liquid oscillate in the same direction in which the wave is moving. This is because the liquid possesses only one elastic modulus, the bulk modulus K. The propagation velocity, U, of the wave depends on this modulus and on the density ρ_0 of the liquid according to the equation,

$$U = \sqrt{\frac{Ks}{\rho_0}} \tag{1.1}$$

where K_s is the adiabatic bulk modulus. The above equation holds for small excess pressure amplitudes for which ρ_0 can be considered to remain a constant. This excess or acoustic pressure P is equal to the difference between the instantaneous pressure P and the ambient hydrostatic pressure ρ_0 i.e.,

$$P = P - \rho_0 \tag{1.2}$$

Let us consider a plane wave traveling in a liquid in the x-direction. Its propagation is given by the well known equation,

$$\frac{\partial^2 p}{\partial t^2} = U^2 \frac{\partial^2 p}{\partial X^2} \qquad (1.3)$$

As the wave proceeds, each particle of the liquids sutlers a certain displacement from its mean position, we denote this particle displacement we denote this particle displacement by 'ξ'. The corresponding particle velocity v in the medium is given by v =$\frac{\partial \xi}{\partial t}$ and the particle acceleration by

$$a = \frac{\partial v}{\partial t} = \frac{\partial^2 \xi}{\partial t^2} \qquad (1.4)$$

In equation (1.3), the propagation of sound wave has been described in terms of the acoustic pressure, p. This equation is also satisfied by other quantities such as velocity potential cp, particle displacement ~ and particle acceleration

$$\frac{\partial^2 \xi}{\partial t^2} = U^2 \frac{\partial^2 \xi}{\partial X^2} \qquad (1.5)$$

We consider the typical solution

$$\xi = \xi_0 . \exp j\ (\omega t - kx) \qquad (1.6)$$

In this equation ξ_0 represents the peak value of the particle displacement, $\omega = 2\pi f$ f is the angular frequency and k =$\frac{\omega}{U} = 2\frac{\pi}{\lambda}$ is the wave number[27, 28].

CHAPTER II

CHAPTER-2

LITERATURE SURVEY

2.1 REVIEW

Dash Ashok Kumar et al.,(2014)[29] proposed that the ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of binary mixture of dimethyl acetamide (DAMC) and diethyl ether at temperature 308K have been measured at different frequencies (2MHZ, 4MHz 6MHZ and 8MHZ). Adiabatic compressibility (K_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and their respective excess values have been computed for entire range of concentration and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time (τ), excess enthalpy (H^E) and absorption coefficient (α/f2) have been calculated and discussed. On the basis of the experimental values of density, ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixture, it is concluded that there exists dipole-dipole, dipole-induced dipole and dispersion interactions in the binary liquid mixture of DMAC diethyl ether.

D. Ubagaramary et al.,(2018)[30] discovered that the functions of ultrasonic velocity, density and viscosity for ternary liquid mixtures of 1-proponol, 1- butanol and 1-pentanol with tetra hydro furan are determined by 303.15 K-313.15 K. This data is used to calculate various parameters like the excess free volume, excess internal pressure and Gibb's free energy, which is used to discuss molecular interactions in the ternary liquid mixtures.

Nabaparna Chakraborty et al.,(2020)[31] revealed that the Velocity of sound and density of binary liquid mixture of Dichloromethane with Ethanolamine have been calculated at different range of temperatures for various concentrations. Liquid-liquid interaction is confirmed by obtaining experimental values of fundamental parameters; ultrasonic velocity and density.

Then these parameters are used to determine various other dependent parameters such as acoustic impedance (Z), intermolecular free length (Lf), adiabatic compressibility (β), Rao's constant (R), Wada's constant (W), Vander Waal's constant (b), effective molecular weight and Relative strength. Graphs are plotted for all parameters versus mole fraction. The linear variation of most of the acoustical parameters shows the absence of complex formation in the mixture. The decrease in ultrasonic velocity indicates that there is weak interaction between the molecules of the mixture. The solution tested, consisting of Dichloromethane and Ethanolamine, was selected in order to obtain data on the molecular interaction between their constituent particles.

R. K. Kolhe et al.,(2020)[32] proposed that the viscosity (η**),** density (ρ) and ultrasonic velocity (U) of dimethylsulphoxide with 1-Octanol have been measured at different concentrations and temperatures from 303.15K to 318.15K. Above measured data is used to calculate the parameters like adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), free volume (V_f), and available molar volume (Vα). These calculated parameters are helpful to explain the strength of interaction among the molecules of liquid binary mixture under investigation. From observed values of ultrasonic speed, viscosity and density of mixture, other parameters such as adiabatic compressibility, acoustic impedance, free length, free volume and available volume for binary mixtures of dimethylsulphoxide with 1-Octanol at various temperatures, it is found that, molecular association is present among the molecules of liquid combinations.

Nabil M. Abdel Jabbar et al.,(2017)[33] proposed that the ultrasonic velocities have been measured for different binary mixtures of common choline chloride-based deep eutectic solvents (DESs), namely, reline, glyceline and ethaline with water, in the range of temperature: 303.15–353.15 K. The experimental data measurements with different mole fractions of DES–water solutions were utilised in fitting four different models for speed of sound. These

models correlate the speed of sound with some physical properties such as molar volumes, molar components sound velocity, densities, molecular weights, collision factors etc. A close match was obtained with these models with an average relative error of less than 4% for all data points used. It was observed that the ultrasonic velocity increases with the concentration of DES solvent and decreases with temperature. Moreover, this study roughly indicated that the intermolecular interactions in reline and ethaline aqueous mixtures exist in the form of disruption of dipole–dipole interactions (that varies considerably as a function of DES mixture composition and solution temperature). On the other hand, the interactions on the molecular level in glyceline aqueous solution are mainly due to
dipole–dipole intermolecular forces. The speed of sound and density data of different aqueous solutions of three common choline chloride-based DESs were measured as a function of temperature within the range 323.15–353.15 K.

K. P. Singh et al.,(2018)[34] the work presented in this paper deals with the study of thermodynamic properties of new working fluids for absorption machines, mainly for characterization of absorbent–refrigerant pairs that could improve the cycle performance. The study of atomic motion in
liquids plays an important role in understanding the solid-like behaviour of
liquids. The accurate measurement of the energy changes due to scattering can be used to study the dynamical behaviour of liquids. Measurements of the ultrasonic velocity (u), density (ρ) and viscosity (η) for binary mixtures of polyethylene glycol 250 dimethyl ether with 1-propanol and 1-butanol have been made at three temperatures (T = 293, 303 and 313 K) over the entire composition range in order to investigate the nature of intermolecular interactions between the components of these liquid mixtures. Non-linear variation of derived quantities with the mole fraction supports the molecular interaction occurring between component molecules. From above studies, it is

concluded that presence of strong interaction through hydrogen bonding between unlike molecules is characterized by non-linear behavior of excess values of Gibbs's free energy of activation for viscous flow (ΔG^{*E}) and internal pressure (π_i^E).

N. P. Mohabansi et al.,(2020)[35] discovered that the Density(ρ), Viscosity(η), Ultrasonic Velocity(U) and Surface Tension(γ) of an aqueous-consolute, Na2SO4 solution of [2-(dimethylamino)-1-(4-methoxyphenyl) ethyl] cyclohexan-1-ol (Venlafaxine) 0.0201,0.0402,0.0804,0.1608 mol/kg were measured at 293.15, 303.15 and 313.15K. The resulting data were used to calculate various acoustical parameters, acoustic impedance (Z), adiabatic compressibility (β), Intermolecular free length (L_f), Wada's Constant (W), Rao's Constant (R), free volume (V_f), Relative Association (RA) were calculated which provides valuable information regarding drug-electrolyte (Na2SO4) interaction. The excess parameters viz. partial molar volume and excess adiabatic compressibility (β^E), excess inter molecular free length (L_f^E), excess free volume (V_f^E) were also calculated. These calculations help in predicting the intermolecular interactions. In an aqueous 2-(dimethylamino)-1-(4-methoxyphenyl)ethyl cyclohexan-1-ol and co-solute Na2SO4 solution, ultra-sonic velocity, density, viscosity and surface tension are measured at 293.15, 303.15 and 313.15K.

S. R. Dandwate et al.,(2018)[36] in the present study attempt has been made to determine acoustic and thermodynamic parameters for binary liquid mixture of DMSO with methanol at 295.15 K, 300.15 K, 305.15 K, 310.15 K and 315.15 K temperatures. The excess values of isentropic compressibility, acoustic impedance, and internal pressure have been calculated using experimental data of ultrasonic velocity, density and viscosity. Molecular interactions in mixture form have been discussed depending upon deviations in excess values. Experimental data have been validated using Redlich-Kister polynomial equation. The values of excess isentropic compressibility have been found negative over entire concentration range at all temperatures.

P. S. Syed Ibrahim et al.,(2019)[37] deal the values of ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary liquid mixtures containing meta methoxy phenol and 1-propanol in n-hexane at different temperature 303 K,308 K and 313 K at a fixed frequency of 2MHz., experimentally. Using the experimental data of velocity, density and viscosity, various acoustical and thermodynamical parameters like Gibb's free energy, entropy, molecular interaction parameter, stability constant and excess property like solvation number are either calculated or computed. All these parameters have been discussed to throw light on intermolecular interactions between the component of ternary mixtures. The dependence of excess property in particular solvation number of the ternary mixture is compared and discussed in the context of intermolecular interaction and other factors. The result is interpreted in terms of molecular interactions under the influence of ultrasonic sound. From this present study it is concluded that the values of solvation number support the molecular reactions rather than the ionic reactions and henceforth interaction will be allowed due to dipole-dipole interactions and dipole – induced dipole interactions and nature of the hydrogen bonding and some extent due to steric effect of the substituent present in the benzene ring between MMP and 1-propanol in n hexane and these facts are substantiated by the values of thermodynamic properties such as ΔG^0 & ΔS.

V. Vanathi et al.,(2019)[38] proposed that the ultrasonic velocity (U), density (ρ), viscosity (η) for the ternary mixture of benzene þ chloroform þ cyclohexane in the whole range of composition has been carried out at various temperatures 303.15, 308.15 and 313.15K. From the measured parameters U, ρ and η, some derived parameters β, Lf, Vf, πi, Z, R,W with molar enthalpy (Hm) and apparent molar volume (ϕv) are also estimated. The decreasing trend of η, R,W, Hm, and ϕv with concentrations and other parameters are in increasing trend were observed. The trend of acoustical and physico-chemical parameters confirm the dynamics of molecules at higher temperature and the magnitude of intermolecular interactions among the constituents of the mixtures always reflects the nature of substance. The role of enthalpy and apparent molar volume has been used to determine their thermal response. The sign and magnitude of these properties are evident for the nature of interactions between component molecules. In summary, the ultrasonic velocity, density and viscosity measurements on ternary organic mixtures at various temperatures are carried out.

Sudhir P. Dange et al.,(2020)[39] reported that the Ultrasonic velocity (u), density (ρ) and viscosity (η) at 2 MHz in the binary mixtures of Riboflavin with methanol in the concentration range (0 to 0.1 M) and at temperature of 298K using ultrasonic interferometer technique. The experimental parameters, ultrasonic velocity, density and viscosity were used to calculate various acoustic and thermodynamic parameters. The obtained results support the nature and strength of molecular interaction, Physico-chemical behaviour in the binary liquid mixture of Riboflavin and Methanol. The Non-linear variation of thermo-acoustical parameters with molar concentration reveals that, there exist intermolecular forces in the binary liquid mixture of Riboflavin and methanol.

Pallavi B. Nalle et al.,(2019)[40] discovered that the ultrasonic velocity, density and viscosity of drug *Piperine* with MgCl2 have been measured as a function of number of moles n = (0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) at 323.15 K, 328.15 K and 333.15 K. The experimentally collected data have been used to calculate various acoustical, thermodynamic and excess

parameters such as excess values of adiabatic compressibility, excess intermolecular free length, excess specific acoustic impedance, excess relaxation amplitude and excess relaxation time have been calculated. Above excess parameters are fitted to the Redlich-Kister equation. The results of acoustical, thermodynamic and excess properties reveal the existence of strong molecular interaction in the mixtures. The drug works as a structure breaker (it breaks the structure of MgCl2) and there is ion formation in the system. Acoustic, thermodynamic and excess parameter of mixture reflects the structural deformation in terms of intermolecular interaction. As the isentropic compressibility goes on increasing in a negative manner, the prepared solvent mixture maleic acid and methanol (60/40) can be used for the bleaching purpose of coconut coir fibres.

T Karunakar et al.,(2013)[41] revealed that the ultrasonic velocity and density measurements for binary mixtures of aniline + 1-butanol at T= (303.15 – 318.15) K, are conducted at atmospheric pressure. Some thermo acoustical parameters like adiabatic compressibility (β), molar volume (V_m), inter molecular free length (L_f) and acoustic impedance (Z) have been calculated from experimental measurements. The results have been used qualitatively to explain the molecular interaction between the components of these mixtures. Further, the results are further supported by FT-IR spectra. From the data of ultrasonic velocity and density various acoustical parameters of the mixtures of aniline with 1-butanol at 303.15, 308.15, 313.15 and 318.15 K were calculated.

R. C. Verma et al.,(2014)[42] proposed that Density, Ultrasound velocity and viscosities of Ethyl propionate with butanol-1 and pentanol-1 have been measured over entire range of composition at 308 K and atmospheric pressure. The computed acoustic and thermodynamic properties of Ethyl propionate in higher alcohols will give the excess values of issentropic compressibility, molar volume and viscosity. The excess value will decided the nature and extent of molecular interaction of Ethyl propionate in butanol-1 and pentanol-1.

L. Palaniappan et al.,(2020)[43] proposed that the ultrasonic velocity, density and viscosity measurements carried out for the binary mixtures of toluene, m-xylene with some butanols at 303 K. Various theoretical models have been applied to these binary systems; evaluate the sound velocity values and compared with the experimental values. The validity of Nomoto theory (NT), Van Deal-Vangeal (IMR) and Free length theory (FLT) is checked and a comparative study of the above models is made. The non-ideal behaviour of the system is explained in terms of molecular interactions of the constituents of the mixture. The interactions further, evident with percentage deviation, molecular interaction parameter and goodness fit test. Among the three theories taken up for the prediction of sound velocity, Namoto Relation is found to yield excellent comparison with the experimental value for the systems investigated.

Sk. Md Nayeem et al.,(2015)[44] proposed that the ultrasonic velocities, u, and densities, q, of binary liquid mixtures of dimethyl sulphoxide (DMSO) with ketones such as acetophenone (AP), cyclohexanone (CH), and 3-pentanone (3P), including pure liquids, over the entire composition range have been measured at 308.15 K. Using the experimental data, deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess molar volume, V_m^E, excess intermolecular free length, L_f^E and excess acoustic impedance, Z^E, partial molar volumes, $V_{m,1}$, $V_{m,2}$, and excess partial molar volumes, $V^E_{m,1}$, $V^E_{m,2}$, have been calculated. Molecular interactions in the systems have been studied in the light of variation of excess/deviation values of calculated properties and these properties have been fitted to Redlich–Kister type polynomial equation. The observed positive values of V_m^E, Δk_s, L_f^E and negative values of Δu, Z^E for all the binary liquid mixtures studied clearly indicate the presence of the dominance of weak physical interactions between the components of molecules. Further, FTIR spectra support the conclusions drawn from deviation/excess properties. Moreover, theoretical values of ultrasonic velocity in the mixtures have been evaluated using various theories and such values were compared with experimental velocities to verify the applicability of such theories to the systems investigated.

Subhraraj Panda.,(2020)[45] proposed that the measurement of ultrasonic velocity is helpful to interpret solute-solute, solute-solvent interaction in aqueous medium. The ultrasonic speed (U), density (ρ) and viscosity (η) at 313 K have been determined using ultrasonic interferometer at four different frequencies *i.e.* 1MHz, 5MHz, 9MHz and 12 MHz, pycnometer and Ostwald's viscometer of dextran in aqueous medium respectively. All the three measurements were carried out in a water bath of constant temperature with an uncertainty of ±0.1 0C. The derived acoustical parameters such as free volume (Vf,), internal pressure (πi), absorption coefficient (α), molar sound velocity (R) and molar sound compressibility (W) have been determined from experimental data. The outcomes are described in terms of molecular interaction between the solution components. Ultrasonic speed, density and viscosity have been measured for aqueous dextran solution at different frequencies in constant temperature.

R. Chithra Devi et al.,(2019)[46] proposed that the density (ρ), viscosity and ultrasonic velocity (u) in ternary liquid mixture of acrylonitrile (AN) with benzene in N-N-di methyl aniline have been measured at (303,308 and 313)K respectively, over the entire composition range by using an ultrasonic interferometer for measuring velocity at 2MHz frequency. From the experimental data various acoustical and thermodynamical parameters such as; adiabatic compressibility(β), Intermolecular free length (Lf), Specific acoustic Impedance (Z), relative association(RA) and molar sound velocity have been computed using the standard relations. The results have been analysed on the basis of variation in thermodynamic parameters. These parameters are found to be very sensitive in exploring the interaction between the component molecules, which enable to have better understanding of the liquid mixtures. Since the system show similar trends for evaluated parameter so the constituent ternary mixture at different temperatures. The results have been interpreted in terms of dipole induced dipole interaction. The results obtained for the present study indicates that the molecular interaction is present in the liquid mixtures.

CHAPTER III

Chapter III

Materials and Methods

3.1 Introduction:

Ultrasonic, thermo-physical and thermodynamic properties of liquid mixtures are of great significance in obtaining an in depth knowledge of inter and intra-molecular interactions, structural and physiochemical behavior and also in verifying various liquid state theories which attempt in estimating the properties of liquid mixtures. Systematic study of thermodynamic properties of solutions with a new type of multi-frequency ultrasonic interferometer is done for precise measurement of the velocity of sound in liquids. The path length in the cell is varied by motion of a reflector, at the electrical reaction of the cell upon the oscillator is used to fix standing wave position at a standard frequency, and their locations are determined with a suitable cathetometer.

An investigation in the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been found to be an excellent quantitative way to elicit information about molecular structure and intermolecular forces in liquid mixtures. This has given impetus to the theoretical and experimental investigation of excess thermodynamic properties of liquid mixtures. Measurement of physiochemical properties such as density and ultrasonic velocity of pure components and their binary mixtures are being increasable used as tools for investigations of the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures. The significance reasons for the study of thermo-physical and thermodynamic properties of multi-component liquid mixtures are as follows:

- They provide way for studying the physical forces acting between molecules of different species.

- The study of liquid mixtures provides appearance of new phenomena, which are absent in pure liquids. The most interesting of these are the new types of phase equilibria, which are introduced by the variation in the promotion of the pure components.
- Liquid mixtures are the most direct source for studying the various parameters. The study of thermo-physical and thermodynamic properties of liquid mixtures helps in obtaining in depth knowledge about molecular interactions.

3.2. Theory:

Ultrasonic interferometer is a simple and direct device which yields accurate and consistent data, from which one can determine the velocity of ultrasonic sound in a liquid medium with a high degree of accuracy. A crystal-controlled interferometer (model M-83S) supplied by Mittal Enterprises, New Delhi, operating frequency 2 MHz has been used to measure the ultrasonic velocity.

3.3. Ultrasonic:

Ultrasonic sound refers to sound pressure with a frequency greater than the human available range (20 Hz to 20 KHz). When an ultrasonic wave propagates through a medium, the molecules in that medium vibrate over short distance in a direction parallel to the longitudinal wave. During this vibration, momentum is transferred among molecule. This causes the wave to pass through the medium.

3.4. Ultrasonic Interferometer:

An Ultrasonic Interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy.

Fig3.1: Experimental setup for ultrasonic interferometer.

The salient features of ultrasonic interferometer are given below:

- It is a simple in design, rugged and gives very accurate and reproducible results.
- Experiments may be performed over a wide range of temperature from -30 ^{0}C to +80 ^{0}C on all liquids except those which reacts with the plating of cell and crystal.
- Nearly 10 ml of experimental liquid is required.
- There is no danger of any change such as depolymerisation, due to ultrasonic effect since a very small ultrasonic energy is required.

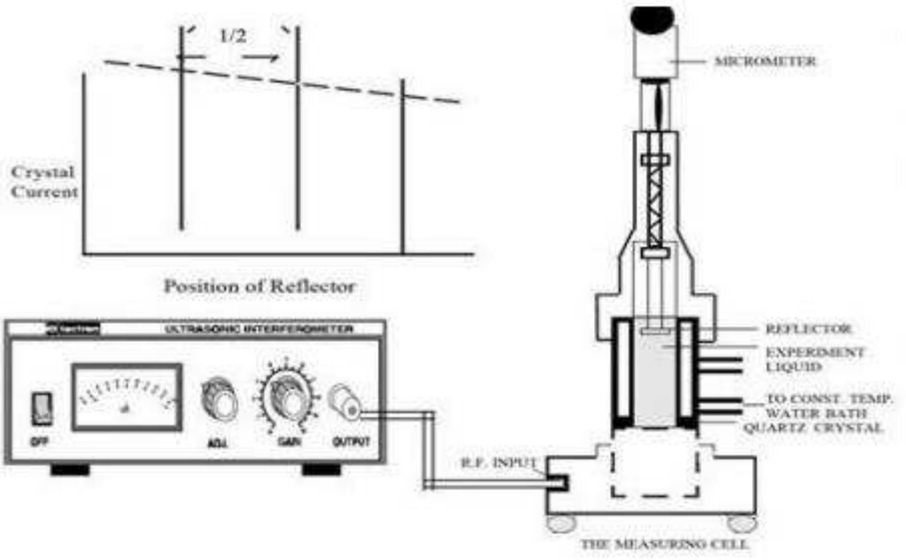


Fig 3.2: Cross section of the liquid cell and graph plotted position of reflector versus crystal current.

In an ultrasonic interferometer, the ultrasonic waves are produced by the piezoelectric methods. At a fixed frequency variable path interferometer, the wavelength of the sound in an experimental liquid medium is measured, and from this one can calculate its velocity through that medium. The ultrasonic cell consists of a double walled brass cell with chromium plated surfaces having a capacity of 10 ml. The double wall allows water circulation around the experimental liquid to maintain it at a known constant temperature. The micrometer scale is marked in units of 0.01 mm and has an overall length of 25 mm. Ultrasonic waves of known frequency are produced by a quartz crystal which is fixed at the bottom of the cell. There is a movable metallic plate parallel to the quartz plate, which reflects the waves. The waves interfere with their reflections, and if the separation between the plates is exactly an integer multiple of half wave length of sound, standing waves are produced in the liquid medium. Under these circumstances, acoustic resonance occurs. The resonant waves are a maximum in amplitude, causing a corresponding maximum in the anode current of the piezoelectric generator. The ultrasonic interferometer consists of the following mainly two parts:

3.4.1. The high frequency generator.

3.4.2. The measuring cell.

3.4.1. The high frequency generator

The high frequency generator is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the “measuring cell”. A micrometer to observe the changes in current two controls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the high frequency generator.

3.4.2. The measuring cell

The measuring cell is specially designed for maintaining the temperature of the liquid constant during the experiment. A fine digital micrometer screw (LC 0.001 mm) has been provided at the top, which can lower or raise the reflector plate in the liquid within the cell through a known distance. It has a quartz crystal fixed at its bottom.

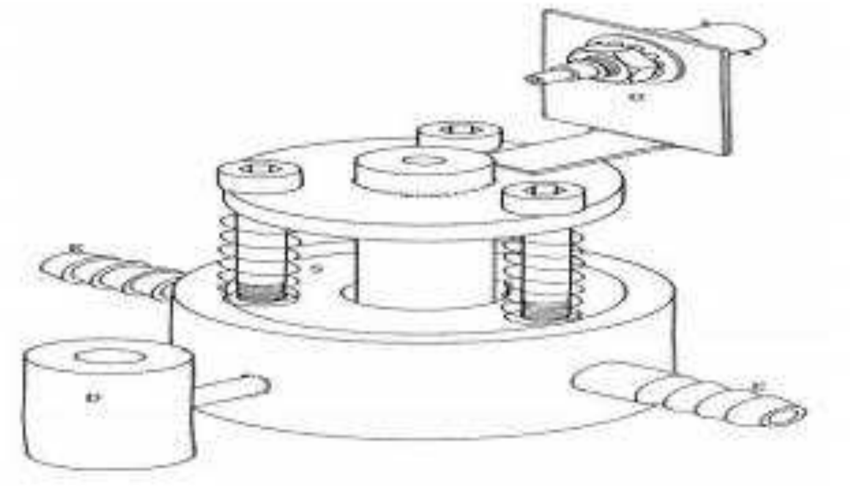


Fig 3.3: Ultrasonic interferometer cell liquid mixtures.

3.5: Working principle

The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ)in the medium. Ultrasonic waves of known frequency (f) are produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator become a maximum. If the distance is now increased or decreased and the variation is exactly one-half wavelengths $(\lambda/2)$ or multiple of it, anode current become maximum from the knowledge of wavelength (λ) the velocity (U) can be obtained by the relation:

Velocity = Wavelength × Frequency

$$U=\lambda\times f \qquad (3.1)$$

3.6: Adjustment of ultrasonic interferometer

For initial adjustment two knobs are provided on high frequency generator, one is marked with “ADJ” to adjust the position of the needle on the ammeter and the knob marked “GAIN” is used to increase the sensitivity of the instrument for greater deflection, if desired. The ammeter is used to notice the number of maximum deflection while micrometer is moved up or down in liquid.

3.7. Procedure

- Unscrew the knurled cap of cell and lift it away from double walled construction of the cell. In the middle position of it pour experimental liquid and screw the knurled cap. Wipe out excess liquid overflowing from the cell.
- Insert the cell in the heavy base socket and clamp it with the help of a screw provided on its side. 7.3 Connect the high frequency generator with cell by coaxial cable provided with the instrument. In ultrasonic interferometer frequency selector knob should be positioned at desired frequency (same frequency as that of liquid cell chosen).
- Move the micrometer slowly in either clockwise or anticlockwise direction till the anode current on the ammeter on the high frequency generator shows a maximum or minimum.
- Note the reading of micrometer corresponding to the maximum or minimum (which is sharper) in microammeter. Take about 50 reading of consecutive maximum or minimum and tabulate them. 7.6 Take average of all differences ($\lambda/2$).
- Once the wavelength (λ) is known the velocity (U) in the liquid can be calculated with the help of the relation.

3.8. Sample calculations:

water Average ($\lambda/2$): 0.375mm.

Ultrasonic velocity in sample: $U = \lambda \times f = 1480$ m/sec.

Density of the liquid = 996.458 Kg/m^3

Adiabatic compressibility (β_{ad}) = $1/\rho v2 = 1/996.458 \times(1480)^2$

$\beta_{ad} = 4.58 \times 10\text{-}10\ N/m^2$.

3.8.1 Measurement of the density:

The density (ρ) of the liquid mixture was determined by a specific gravity bottle of 25 ml capacity. The specific gravity bottle with the liquid mixture was immersed in a temperature controlled water bath. The density was determined using the relation:

$\rho_2=(W_2/W_1)\rho_1$

where W_1, W_2, ρ_1 and ρ_2 are masses of distilled water, mass of liquid mixture, density of distilled water, and density of liquid mixture, respectively.

3.8.2. Measurement of viscosity

The viscosity measurements were done through Ostwald's viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. The water in the viscometer is allowed for some time to attain the experimental temperature. Using a suitable arrangement, the water is sucked above the marked level and then it is allowed to flow freely. The time taken for the flow of water is noted. The water is replaced with a mixture, whose viscosity is to be determined. Using the same procedure, the time taken for flow of liquid mixture at the experimental temperature was determined. Using the time taken for the distilled water and mixture, the viscosity of unknown liquid mixture is determined:

$$\frac{\eta_s}{\eta_w} = \rho s/\rho w \times ts/tw \qquad (3.2)$$

Where ηw, ρw and tw are the viscosity, density and time flow of water respectively ηs, ρs and ts are the viscosity, density and time flow of unknown liquid mixture respectively. Viscosity is an important transport property for process design in petroleum, petrochemical, chemical and other chemical industries involving fluid transportation, mixing agitation, heat exchange and concentration. The estimation of the viscosity of a mixture is more difficult than of the pure compound. The prediction of the viscosity of liquid mixtures is a goal of long standing with both experimental and theoretical importance. Many industrial, chemical processes or laboratory works need experimental data of viscosity at any given temperature and composition for the liquid mixtures.

3.9 THEOTERTICAL METHOD FOR THE ESTIMATION OF ACOUSTICAL THERMODYNAMIC PARAMETERS OF LIQUID AND LIQUID MIXTURES

3.9.1. Ultrasonic velocity

Ultrasonic study of liquid and liquid mixtures has gained much importance in characterizing of thermodynamic and physio-chemical aspects of ternary liquid mixtures. A variety of empirical, semi – empirical and statistical theories in liquids are available in the literature for evaluating ultrasonic velocity in liquids and liquid mixtures.

3.9.2. Adiabatic compressibility (βad)

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation; [47]

$\beta_{ad} = 1/v\ [\partial v/\partial p]$ (3.3)

It can also be calculated from the speed of sound (U) and thedensity of the medium (ρ) using the equation of Newton Laplace as;

$\beta_{ad} = 1/u\rho^2\ Kg^{-1}\ ms^2$

(3.4)

3.9.3.Acoustic impedance (Z)

Sound travels through materials under the influence of sound pressure. Because molecules or atoms of a solid are bound elastically to one another, the excess pressure results in wave propagation through the solid. The acoustic impedance (Z) of a materials is defined as the products of its density (ρ) and ultrasonic velocity (u) given as; [48]

$Z = U\beta$ (3.5)

3.9.4. Relaxation time (τ)

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of the ultrasonic velocity in binary mixture reveals information about the Characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation; [48,49]

$$\beta = 4/3\ \beta\ \eta \qquad (3.6)$$

3.9.5. Intermolecular free length (Lf)

The intermolecular free length is the distance covered by sound wave between the surfaces of the neighboring molecules. It is measure of intermolecular attractions between the components in binary mixture. The increase or decrease in free length indicates weakling and strengthen of intermolecular attraction. As the ultrasonic velocity increase due to the increases in concentration, the interaction free length has to decrease and vice-versa. It is related to ultrasonic velocity and density as; [50]

$L_f = K/\rho U)^{1/}2m$

(3.7)

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighboring molecules and is given by the relation, [51]

$$L_f = KT\ \beta^{1/2} \qquad (3.8)$$

Where, $KT = (93.875+0.345T) \times 10\text{-}8$

CHAPTER IV

CHAPTER-4

RESULT AND DISCUSSION

Experimental values of density viscosity and ultrasonic velocity for the binary mixtures at different temperatures at 308K, 318K, 328K are represented in table 4.1, 4.3, 4.5. The calculated values of different parameters are represented in tables 4.2, 4.4, 4.6.

When the temperature increases, ultrasonic velocity (U) decreases as shown in Figure 4.1 indicating more spacing between the molecules. The nature of change in velocity is also confirmed by observing the change in β_a & L_f.

Further Adiabatic compressability β_a and Free length L_f show an inverse behaviour as compared to the Ultrasonic Velocity U in the mixtures. It is primarily the compressibility that changes with the structure and this leads to the change in Ultrasonic velocity U. The addition of interacting molecules breaks up the molecular clustering of the other, releasing several dipoles for the interactions. Thus structural arrangement of molecule result in increasing β_a thereby showing intermolecular interactions. Similar results in some liquid mixtures were also reported by Researches[52-55]

Acoustic impedance decreases with increase in temperature as shown in figure 4.3 indicating weakening of molecular interaction.[56]

τ increases with increase in mole fraction which is the order of 10^{-12}sec, is due to structural relaxation process[57] and in such a situation, it is suggested that, the molecule gets rearranged due to co-operative process[58].

Table 4.1: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) for Ethyl Propionate + Ethanol at 308K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) 10^{-4} Nsm^{-2}
X_1	X_2			
1.000	0.000	1118.8	869.8	4.61
0.817	0.183	1131.2	856.4	5.43
0.603	0.397	1129.2	910.2	6.61
0.427	0.573	1128.8	828	5.92
0.139	0.861	1117.8	869.8	7.36
0.000	1.000	1118.4	771.8	6.58

Table 4.2: Values of Adiabatic Compressability (β_{ad}), Acoustic impedance (z), Relaxation time (τ), Free Length (L_f) for Ethyl propionate + ethanol at 308K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Acoustic Impedance(z) x10^5 $Kgm^{-2}s^{-1}$	Relaxation time (τ) x10^{-13} s	Free Length L_f x10^{-11} m
X_1	X_2				
1.000	0.000	9.18	9.73	5.64	6.34
0.817	0.183	9.13	9.69	6.61	6.32
0.603	0.397	8.62	10.3	7.59	6.15
0.427	0.573	9.48	9.35	7.48	6.45
0.139	0.861	9.20	9.72	9.03	6.35
0.000	1.000	1.03	8.63	9.09	6.73

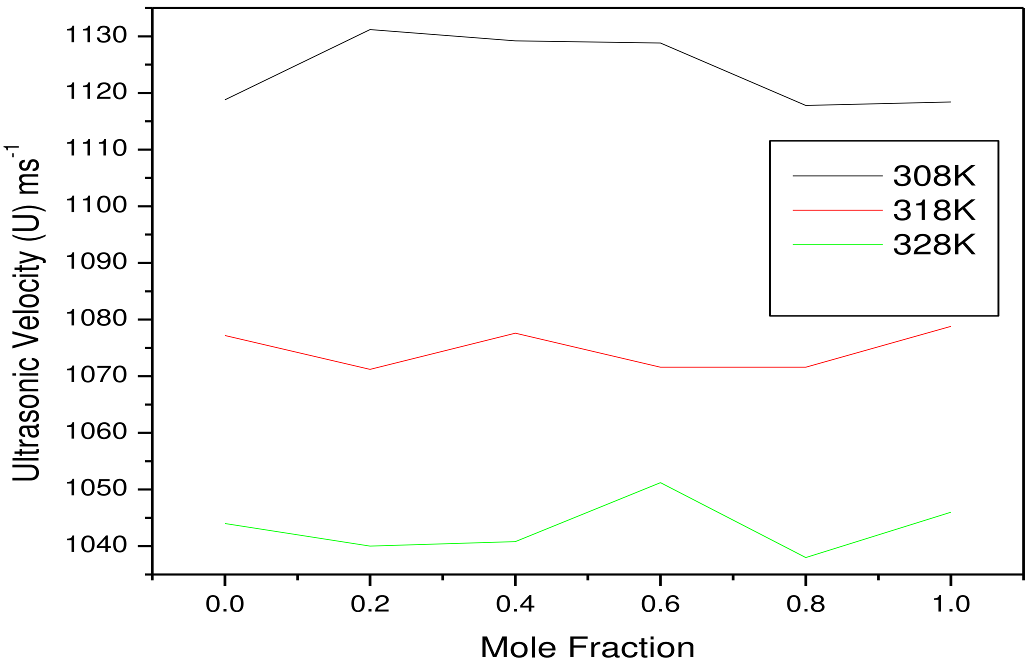


Fig4.1 Mole fraction Vs Ultrasonic Velocity

Table 4.3: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) for Ethyl propionate + Ethanol at 318K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) 10^{-4} Nsm^{-2}
X_1	X_2			
1.000	0.000	1077.2	867.4	4.43
0.817	0.183	1071.2	846.8	5.16
0.603	0.397	1077.6	909.8	6.11
0.427	0.573	1071.6	824.8	5.64
0.139	0.861	1071.6	862.6	6.77
0.000	1.000	1078.8	767.8	6.02

Table 4.4: Values of Adiabatic Compressibility (β_{ad}), Acoustic impedance (z), Relaxation Time (τ), Free Length (L_f) for Ethyl propionate + Ethanol at 318K

Mole fraction		Adiabatic compressibility ($\beta_{ad}\times 10^{-10}$) ms^{-1}	Acoustic Impedance(Z) x10^5 $Kgm^{-2}s^{-1}$	Relaxation time (τ) x10^{-13} s	Free Length L_f x10^{-11} m
X_1	X_2				
1.000	0.000	9.93	9.34	5.87	6.71
0.817	0.183	1.03	9.07	7.08	6.84
0.603	0.397	9.47	9.80	7.71	6.56
0.427	0.573	1.06	8.84	7.94	6.93
0.139	0.861	1.01	9.24	9.11	6.77
0.000	1.000	1.11	8.28	8.99	7.12

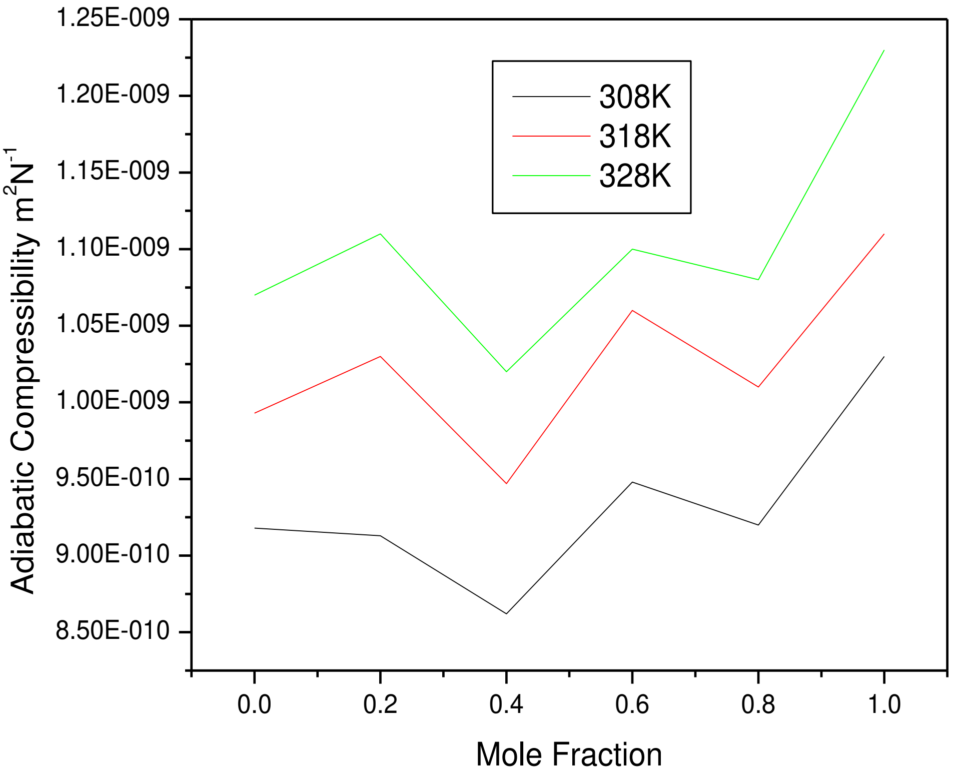


Fig4.2 Molefraction Vs Adiabatic Compressibility

Table 4.5: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) for Ethyl propionate + Ethanol at 328K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) 10^{-4} Nsm^{-2}
X_1	X_2			
1.000	0.000	1044	853.8	4.29
0.817	0.183	1040	836.6	5.05
0.603	0.397	1040.8	909.4	5.91
0.427	0.573	1051.2	819	5.31
0.139	0.861	1038	856.4	6.44
0.000	1.000	1046	765.2	5.76

Table 4.6: Values of Adiabatic Compressability (β_{ad}), Acoustic impedance(z), Relaxation time (τ), Free Length(L_f) for Ethyl propionate + Ethanol at 328K

Mole fraction		Adiabatic compressibility ($\beta_{ad}\times 10^{-10}$) ms^{-1}	Acoustic Impedance(Z) x10^5 $Kgm^{-2}s^{-1}$	Relaxation time (τ) x10^{-13} s	Free Length L_f x10^{-11} m
X_1	X_2				
1.000	0.000	1.07	8.91	6.15	7.10
0.817	0.183	1.11	8.70	7.44	7.21
0.603	0.397	1.02	9.47	7.99	6.91
0.427	0.573	1.10	8.61	7.82	7.21
0.139	0.861	1.08	8.89	9.30	7.14
0.000	1.000	1.23	8.00	9.17	7.49

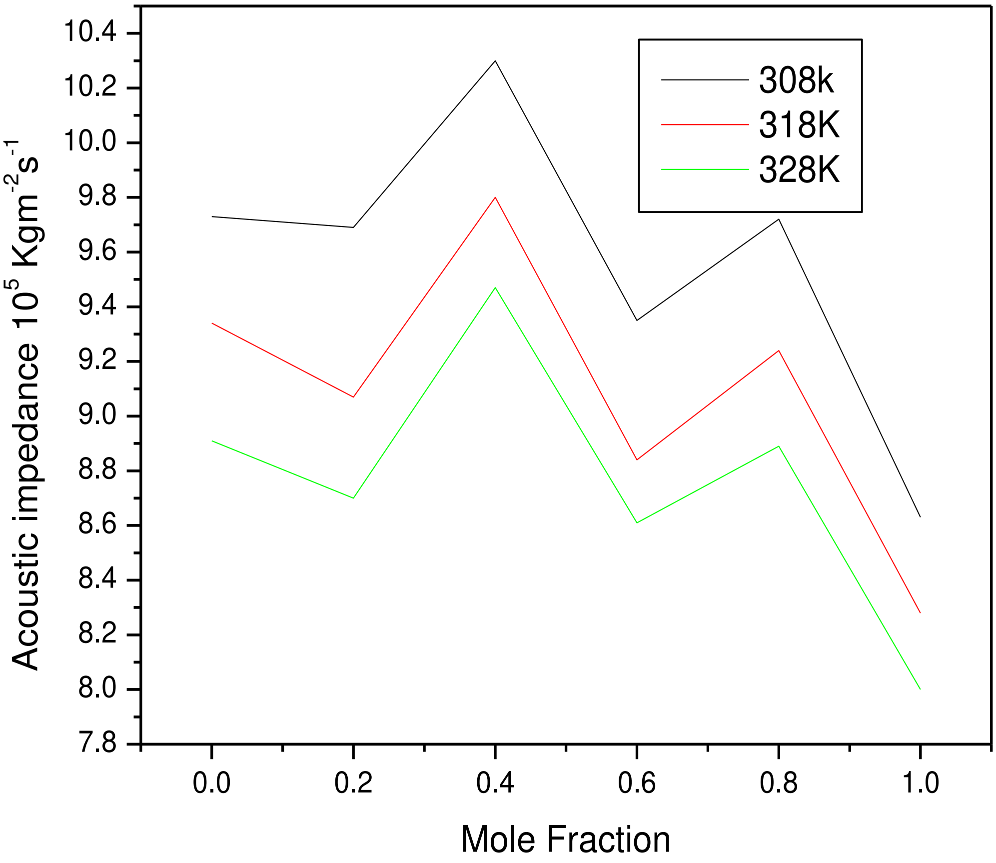


Fig 4.3 Mole fraction Vs Acoustic impedance

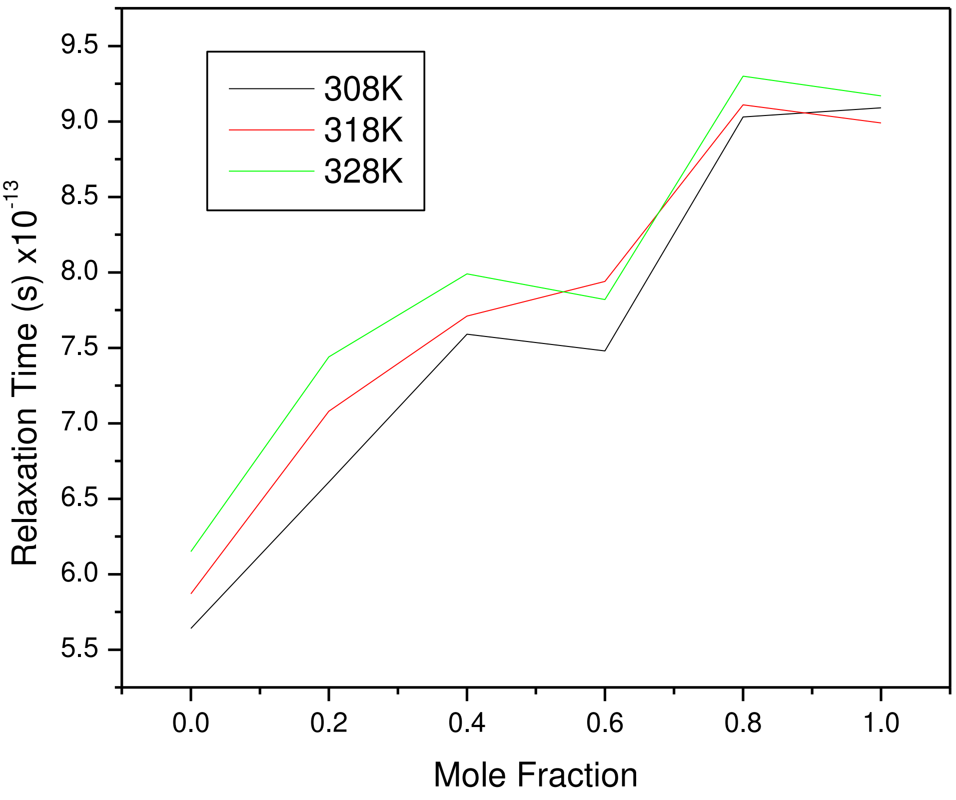


Fig 4.4 Mole fraction Vs Relaxation Time

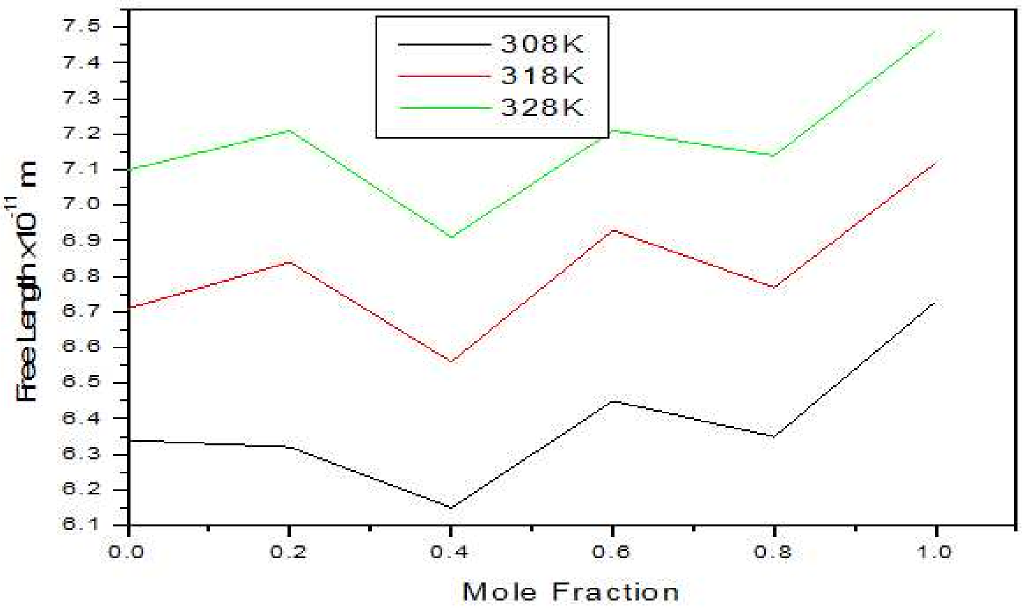


Fig. 4.5 Mole Fraction Vs Free Length

Conclusion

Acoustic properties of Adiabatic Compressibility (β_a), Acoustic impedance(z), Relaxation Time(τ), Free Length (L_f) are determined which explain how these interactions occur & responsible for breaking and making of the structure in the solution. The trends in the variation of parameters derived from Ultrasonic Velocity(U), Density (ρ), Viscosity (η) at different temperatures 308K,318K,328K over entire composition range suggestion existence of molecular interaction in the chosen binary mixture.

REFERENCE:

1. Warren, B. E. (1937), J. Applied Physics, 8,645.

2. Compton, A. H. And Allison, S. K. ‘X-rays in Theory and Experiment’ (Newyork: D. Van Nostrand Co., Inc., 1935), pp. 781-782.

3. G. W. Stewart, Phys. Rev., 37, 9(1931); E. Amaladi, Phuysik. Z., 32, 914(1931); H. H. Meyer, Ann. Physek, 5,701(1930); S. Katzoff, J. Chem. Phys; 2, 841(1934); J. D. Bernal and R. H. Fowler, ibid, 1,515(1933); J. Morgan and B. E. Warren, ibid; 6,666(1938).

4. A. Joffe, Ann. Physik, 72, 461 (1923); J. Frenkel, Z. Physik, 35,652 (1926).

5. Oster, G., and Kirkwood, J. G., J. Chem., Phys., II (1943), 175.

6. Smyth, C. P., and Stoops, W. N., J. Am. Chem. Soc., 51(1929), 3330.

7. Philippe, R., and Piette, A. M., Bull Soc. Chem., Belg., 64(1995), 600.

8. Malecli, J., J. Chem., Phys., 43(1965), 1351.

9. Bellamy, L. J., and Pace, R. J., Specitrochim Acta, 22(1966), 525

10. Copurn, W. C., and Grunwald, E. J., Am. Chem. Soc., 81(1959),6145.

11. Brown, I. Fock, W., and Smit, F., Aust. J. Chem., 17(1964), 1106.

12.Haskell, R. W., Hollinger, H. B and Van Ness, H. C., J. Phys., Chem., 72(1968), 4534.

13. Bordewijk, P., “Fluid Structure and Dielectric behaviour of the mono alcohols”, Ph.D., thesis, University of Leiden, 1968.

14. Reddy, K. S., and Naidu, P. R., J. Chem. Thermodynamics(1976), 1208.

15. Prakash, S., Srivastau, S. B., and Prakash, O., Ind. J. Pure and Apopld. Phys., 13(1975), 19.

16. Ravindraa Prasad, K., Ravimahar, E. L., and Reddy, K. G. Acoust, Lett., 4(1981), 170.

17. Subba Rao, S., and Gobala Krishnan, R. Acoust, Lett., 2(1978), 69.

18. Gopal K. And Prabhakara Rao, N. Acoust Lett., 4(1981), 164.

19.Ramanjappa, T., and Raja Gopal, K., Proc. Latl. Sympoium on Acoustis(1986), 57.

20. Sabesan, R., Ramadurai, R and Rangan, R., J. Acoust. Soc. (India), 11(1983), 5.

21. Vradarajan, R., and Bharathi, G., J. Pure and Appl. Ultrasonics, 9(1987), 15.

22. Sabesan, R., Vradarajan, R., and Natarajan, M., Proc. Natl. Symposium on Acoustic, Tiruchy, 1987, 282.

23. P. Vigoureux, Ultrasonics, Chapman and Hall Ltd, London (1952).

24. T. Robert Beyer, V. Stephen Letcher, Physical ultrasonics Academic Press, New York (1969).

25. E. G. Richardoss, Ultrasonic Physics, Elseveir, London (1952).

26. N. V. Temperley and D. H. Trevena, Ellis Horwood Ltd, Liquids and other properties, John wiley and sons, England (1978).

27. A. B. Bhattia, Ultrasonic Absorption , Oxford (1967).

28. Chandra Bhan Singh, Avanesh Kumar and Soran Singh (2012).

29. Dash Ashok Kumar and Paikaray Rita (2014) ‘Study of Molecular Interaction in Binary mixture of Dimethyl Acetamide with Diethyl Ether using Ultrasonic and Viscosity probes’, Research Journal of Chemical Science vol. 4, No. 3, pp. 45-53.

30. Ubagaramary .D, Muthu Vijayan Enich, Mullainathan .S and Kesavaswamy (2018) ‘Acoustical properties of molecular interactions in 1-propanol, 1-butanol and 1-pentanol with tetrahydrofuran in cyclohexaone at various temperatures’, vol. 29, No. 17, pp. 3276-3281.

31. Nabaparna Chakraborty, Monika Rani and Juglan .K.C (2020) ‘Ultrasonic Investigation of Dichloromethane with Ethanolamine at various temperatures’, vol. 20, pp. 2825-2829.

32. Kolhe .R.K and Bhosale .B.B (2020) ‘Molecular Interaction study in Binary mixtures of DMSO and 1-octanol using ultrasonic method at various concentrations and temperatures’ vol. 11, No. 5, pp. 750-757.

33. Nabil M. Abdel Jabbar and Farouq S. Mjalli (2017) ‘Ultrasonic study of binary aqueous mixtures of three common eutectic solvents’, An International Journal of Physics and Chemistry of Liquids, pp. 1-18.

34. Singh K.P and Singh .S (2018) ‘Thermodynamic and acoustic properties of binary mixtures of PEGDME 250 with 1-propanol and 1-butanol at 293, 303 and 313 °K’, An International Journal of Physics and Chemistry of Liquids, pp. 1-21.

35. Mohabansi N.P, Satone A.K, Gulafsha A.I. Sheikh and Komal Vairagade (2020) ‘Excess Thermodynamic Parameters of 1-[2-(Dimethylamino)-1-(4-Methoxyphenyl)Ethyl] Cyclohexan-1-ol in aqueous Na_2SO_4’, International Journal of Researches in Biosciences, Agriculture and Technology, vol. 3, No. 8, pp. 26-34.

36. Dandwate S.R and Deshmukh S.B (2018) ‘Excess Thermodynamic properties of Binary liquid mixtures of DMSO with Methanol at different temperatures’, International Journal of Universal Print, vol. 4, No. 4, pp. 196-201.

37. Syed Ibrahim P.S, S. Chidambaravinayagam, J. Senthil Murugan and J. Edward Jeyakumar (2019) ‘Studies on some Acoustical and Thermodynamic properties of Ternary liquid mixtures of Meta Methoxy Phenol (MMP), 1-propanol and n-Hexane at different temperatures using

ultrasonic techniques', Journal of Information and Computational Science, vol. 9, No. 7, pp. 391-399

38. V. Vanathi, S. Mullainathan, S. Nithiyanatham, V. Ramasamy and L. Palaniappan (2019) 'Ultrasonic velocity, density, viscosity for the ternary mixture of (benzene+Chloroform+Cyclohexane) at different temperatures', pp. 1-6.

39. Sudhir P. Dange and Omprakash P. Chimankar (2020) 'Molecular Interaction study in Binary mixture of Riboflavin with Methanol at 298K', vol. 7, No. 2, pp. 555-557.

40. Pallavi B. Nalle, R.G. Dorik and K.M. Jadhav (2019) 'Acoustical and excess parameter studies of piperine with $MgCl_2$', Journal of Pure and Applied Ultrasonics, vol. 41, No. 2, pp. 27-35.

41. T Karunakar, CH Srinivasu and K Narendra (2013) 'Thermo Acoustic and Infrared study of Molecular Interactions in Binary mixture Aniline+1-butanol', Journal of Pure and Applied Physics, vol. 1, No. 1, pp. 5-10.

42. R.C. Verma and Vinod Kumar Yadav (2014) 'The study of Excess molar volume and deviation in viscosity of binary mixtures of Ethyl Propionate in Butanol-1 and pentanol-1 at 308K ultrasonically', Journal of Chemical, Biological and Physical Sciences, vol. 4, No. 3, pp. 1988-1991.

43. L. Palaniappan and S. Nithiyanantham (2020) 'Molecular Interactions

from the Experimental and Validation with Estimated Theoretical sound velocity', pp. 277-285.

44. SK. Md Nayeem, M. Kondaiah, K. Sreekanth and D. Krishna Rao (2015) 'Acoustic and volumetric investigatuins in aromatic, cyclic and aliphatic ketones with dimethyl sulphoxide at 308.15K', Arabian Journal of Chemistry, pp. 1-12.

45. Subhraraj Panda (2020) 'Ultrasonic study on dextran in aqueous media at 313K at different frequencies', Adalya Journal, vol. 9, No. 3, pp. 456-462.

46. R. Chithra Devi and R. Mathammal (2019) 'Thermodynamic Behaviour of Ternary mixtures of Acrylonitrile in Benzene with N-N-dimethyl aniline at 303K, 308K and 313K', vol. 8, No. 12, pp. 158-165.

47. Nikam PS and Hasan Mehdi 'Ultrasonic velocity and adiabatic compressability of Monochloric acetic acid in aqueous ethanol at various temperatures. Journal of Chemical and engineering Data. 1988; 88:165-169.

48. Kumar Naidu Vijaya B, Rao sadasiva A, Rao Chowdoji K. Ultrasonic Velocity study in some glycols and polyglycols in formamide solutions. Journal of Acoustical Society of India. 2000; 28(1-4):297-300.

49. Kumar Naidu Vijaya B, Rao sadasiva A, Rao Chowdoji K. Ultrasonic Velocity study in some glycols and polyglycols in formamide solutions.

50. Nikkam PS, Hasan Mehdi. Ultrasonic velocity and apparent molar Compressibility of trichloroacetic acid in aqueos ethanol. Asian Journal of chemistry. 1993; 5(02):319-321.

51. Venkateswarlu P, Raman GK. Sound velocities and isentropic Compressibilities of 1, 2-dibromoethane + ketone at 303.15K. Journal of pure and applied ultrasonics. 1985, 7(02):31-34.

52. Sridevi U, Samatha K & Viswanatha Sarma A, J Pure Appl Ultrason, 26(2004) 1.

53. Kannappan V & Jaya Shanthi R, Indian J Pure & Appl Physics 43(2005) 750.

54. Wahiba Kerboub & Zadjia Atik A, J Chem Thermodynamics, 42(2010)1330.

55. Aravinthraj M, Venkatesan S & Kamaraj M, Indian J Chem Envr & Pharm Res, 2(2011)5.

56. Manoj Kumar Praharaj, molecular interaction in fernary liquid mixtures at different temperature.

57. Kinsler LE & Rray A R, Fundamental of Acoustic Wiley eastern, New Delhi, 1989.

58. Hyder A and Nair A K, Indian journal of pure and applied Physics, 2000, 63,7413.

SYNTHESIS AND CHARACTERIZATION OF STARCH POLYMERIC MATERIAL USING *SOLANUM TUBEROSUM* AND *MANIHOT ESCULENTA*

A project report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS) , THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI .

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

C.KONSHA

Reg No : 19SPPH03

Under the guidance of

Mrs. L. SMILA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARYS'S COLLEGE (AUTONOMOUS),THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020 - 2021

CERTIFICATE

This is to verify that this project work entitled " **SYNTHESIS AND CHARACTERIZATION OF STARCH POLYMERIC MATERIAL USING *SOLANUM TUBEROSUM* AND *MANIHOT ESCULENTA*** " is submitted to **ST. MARYS'S COLLEGE (AUTONOMOUS) , THOOTHUKUDI** , in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year 2020 -2021 by

C.KONSHA Register No : 19SPPH03

Signature of the Guide

Signature of the SSC Co-ordinator

Signature of the Director
Director
Self Supporting Courses
St. Mary's College (Autonomous,
Thoothukudi - 628 001.

Lucia Rose
Signature of the Principal
Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21
Signature of the Examiner

ACKNOWLEDGEMENT

First of all ,I thank the Lord Almighty for his blessing and grace to complete this Project.

I am deeply indebted to our Principal **Rev. Dr . Sr. A. S. J . LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D.,** for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, **Rev. Sr. F.MARY JOYCE BABY M.A., M.Phil.,** for her support in my work.

I would like to express my special gratitude to **Rev . Dr . Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D.,** Head of Department , for her inspirational words to complete this project.

I would convey my heartfelt thanks to **Mrs. P. PADMAVADHI M.Sc., M.Phil., SET.,** SSC Co-ordinator , Department of Physics for her efficient and encouragement in successful completion of this project .

I wish to record my sincere thanks to **Mrs. L.SMILA M.Sc., M.Phil.,** Assistant Professor, Department of Physics for her enthusiastic guidance and support for completion of this Project successfully.

It is my pleasure to extend my thanks to **Dr . J. ANTONY RAJAM M.Sc., M.Phil., SET ., Ph.D.,** Department of Chemistry for her continuous support to complete this project.

ABSTRACT

This study aim to investigate the effect of solanum tuberosum - glycerol and Manihot esculenta - glycerol at different concentration , which has inadequate thermal and mechanical properties . Biopolymer films are prepared by mixing starch – glycerol at various w/w (1 gm - 0.5 gm , 5 gm – 3 gm ,10gm – 6 gm). Bioplastic are obtained by casting method. When plasticizer are added to the starch sample , bio-degradable films are formed .These films were characterized using different techniques such as UV -Visible , SEM , XRD and TGA , FT-IR . The UV – Visible shows peak at 290 nm . Microstructure and chemical interactions in bioplastics were evaluated by SEM and FTIR . The XRD result concludes the average size of solanum tuberosum with glycerol film is 3.4909 nm and Manihot esculenta with glycerol film is 3.5512 nm . Thermo-gravimetric analysis are done for Solanum tuberosum and Manihot esculenta samples .

Keywords : Biopolymers , Starch ,Glycerol , Plasticizer.

CONTENT

List of Tables :

List of Figures :

16	32
17	35
18.1	36
18.2	37
19.1	38
19.2	38
20.1	39
20.2	39
20.3	40
20.4	41
21.1	42
21.2	44
22	47
23.1	48
23.2	49

Symbols , Abbreviations & Nomenclature	Meaning
psi	pounds per square inch
PET	Polyethylene terephthalate
DMSO	Dimethyl Sulfoxide
ANOVA	Analysis of Variance

CHAPTER – I

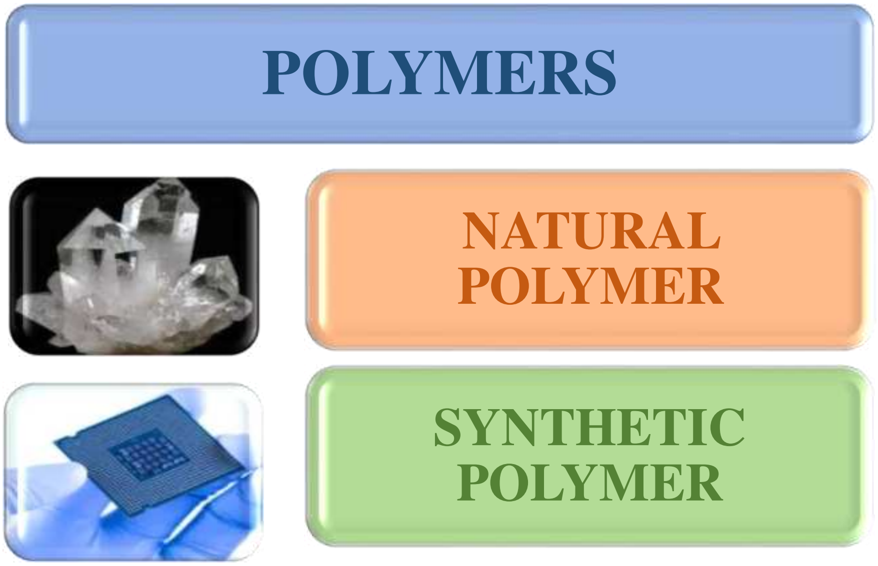
INTRODUCTION

Plastics are a vital asset for humanity, often providing functionality that cannot be easily or economically replaced by other materials. Most plastics are robust and last for hundreds of years. They have replaced metals in the components of most manufactured goods, including products like computers, car parts and refrigerators, and thus made the products cheaper, lighter, safer, stronger and easier to recycle. Plastics have taken over from paper, glass and cardboard in packaging, usually reducing cost and carbon emissions while also providing better care of the items that they protect. A bioplastic is a plastic that is made partly or wholly from polymers derived from biological sources such as sugar cane, potato starch or the cellulose from trees, straw and cotton. Some bioplastics degrade in the open air, others are made so that they compost in an industrial composting plant, aided by fungi, bacteria and enzymes. Others have the robustness and durability of conventional plastics such as polyethylene or PET. Bioplastics can generally be directly substituted for their oil-based equivalent. Indeed, they can generally be made to be chemically identical to the standard industrial plastics.[1]

There has been increased interest in the development of biodegradable films because the environmental damage from conventional plastic packaging is increasingly evident. Bioplastics are produced from 100% renewable raw material which, when discarded in conditions favorable to its decomposition, is rapidly integrated into nature as carbon dioxide, water and biomass. Biodegradable plastics are produced from biopolymers extracted directly from biomass, with or without modification, such as starch, cellulose and proteins. Among these, starch has presented potential for the production of biodegradable materials because is a low-cost raw material, easily available and renewable.[2]

1.1 POLYMERS :

"Poly" comes from the Greek word for many and " mer" comes from the Greek word for parts . A Polymer is a large molecule that comprises repeating structural units joined by the covalent bonds . The building block of the polymer is called as monomer. Polymers which have comparatively low degree of polymerization are called Oligomers . Polymers with high degree of polymerization are called High Polymers.



1.1.2 TYPES OF POLYMERS :

Polymers are divided into three classes contains Plastic , Rubber and Fibres . Plastics are much stronger than rubbers. Some plastic are hard, stiff and dimensionally stable and some are soft and flexible .They are organic materials that can be shaped or moulded by mechanical or chemical action with or without the application of heat . Obviously , a plastic is a permanently deformable and mouldable material. Polymers belonging to this class of materials may have any degree of crystallinity and all molecular structure are possible. Plastic material are classified as Thermoplastic or Thermosetting . Thermoplastic resins are referred as plastics and have the property of increasing plasticity. It has ability to deform plastically with rise in temperature. Thermoplastic on heating make material becomes soft and hardened again upon cooling. Thermosetting plastic materials cannot be resoftened after polymerization. Plastics exhibit tensile strength range between 4000-13,000 psi.

Fig :1

Rubbers are dimensionally unstable . These polymers have long range elasticity. The rubber polymers are characterized by low molecular cohesion. Their mechanical properties are very poor. They exhibit tensile strength ranges between 300 – 1000 psi. They are not produced merely as substitutes for natural rubber. Rubber must withstand a 200 % elongation and rapidly return to its original dimension. This property of a material to recover from the elastic deformation is called as Resilience. Rubbers are elastomers have properties similar to polymers.

Fig : 2

Fibres consists of long molecular chains and all chains are aligned in the direction of length of the fibre. Fibre polymer are quite capable of being drawn into long filaments having at least a 100 : 1 length to diameter ratio. Some polymers used as fibres are nylon and cellulose acetate . Fibres are subjected to varieties of deformation . Fibres materials should have relatively high molecular weight . The structure and configuration of the chain should allow the production of a highly crystalline polymer as a tensile strength increases with degree of crystallinity. They are the strongest of the three different types of polymers. They exhibit tensile strength ranges between 20,000 – 1,50,000 psi .[3]

Fig : 3

1.1.3 BASIS OF MORPHOLOGY :

Based on Morphology Polymers are classified into two classes .

- Crystalline Polymers are invariably do not form perfect crystalline materials but instead are semicrystalline with both crystalline and amorphous regions. The crystalline phase of such polymers are characterised by their melting temperature .
- Amorphous Polymers are characterised by their glass transition temperature , The temperature at which they transform abruptly from the glass state to rubbery state . This transition corresponds to the onset of chain motion. [4]

1.1.4 FORMS OF POLYMERS :

Polymer materials can exist in at least three general form.

- First basic arrangement is the straight line where the monomer molecules are joined together in a linear arrangement.
- The second is the branched chain . These branches may arise as a result of the secondary process or the presence of three reactive groups in a monomer molecule . A special category in branched chain polymer , graft polymer is obtained when the branch consists of a chain composed of variety of monomer species.
- Third arrangement is that cross-links are produced between linear chains.[5]

1.2 BIOPOLYMERS :

Biopolymers are natural polymers produced by the cells in living organisms. Biopolymers consist of monomeric units that are covalently bonded to form larger molecules. Polymer which are found in nature or the synthetic polymers which are biodegradable or biocompatible are grouped in this class. Biopolymer can be used for a vast range of applications include adhesives , coatings , high performance fibres ,cosmetics, pharmaceuticals and for medical and surgical devices . Natural biopolymers are carbohydrate , proteins and nuclei acid etc. Most common synthetic biopolymers include polylactic acid , polyacrylamide , polyethylene glycol etc.

1.3 POTATO :

The potato is a root vegetable native to the Americans, a starchy tuber of the plant Solanum tuberosum . Potatoes are rich in compounds like flavonoids, carotenoids and phenolic acids .

Fig : 4

1.3.1 USES:

- There is a possibilities of using waste potatoes to obtain polylactic acid for use in plastic products , other research projects seek ways to use the starch as a base for biodegradable packaging.
- Potato starch is used in the textile industry as an adhesive, and for the manufacturing of papers and boards.
- Wound-response studies are done using Potato skin. [6]

1.4 CASSAVA :

Manihot esculenta is commonly called as Cassava , is a woody shrub native to South America of the spurge family Euphorbiaceae .Cassava is extensively cultivated for its edible starchy tuberous root, a major source of carbohydrates. Substantial quantities of Cassava are used to extract cassava starch, called tapioca, which is used for food, and industrial purposes. Raw cassava is 60% water, 38% carbohydrates, 1% protein, and has negligible fat .

Fig : 5

1.4.1 USES :

- Cassava has high content starch which is used for production of Bioplastic.
- In many countries, significant research has begun to evaluate the use of cassava as an Ethanol biofuel feedstock. [7]

1.5 STARCH :

Starch is the reverse carbohydrate materials of plants . The main source of starch are the grain and potato. Starch contains two kinds of polymers which differ in their structure and molecular weight . One component is amylose , a linear poly anhydroglucose in which the glucose units are joined by α – 1:4 linkages . The amylose fraction can have molecular weights ranging from 10,000 to 4,00,000 . Amylose starch is easily digested than amylopectin. The other fraction is Amylopectin differs from the amylose in the branching that occurs, with an α – 1:6 linkage every 24 – 30 glucose monomer units . The overall structure of amylopectin is not that of a linear polysaccharide chain , since two glucose units frequently form a branch point , so the result is the molecule most suitable for storage in starch grains. Both amylopectin and amylose are polymers of glucose , and a typical starch polymer chain consists of around 2500 glucose molecules in their varied forms of polymerisation .

Starch is insoluble in water . It can be digested by hydrolysis , catalysed by the enzymes called amylases , which can break the glycosidic bonds between the ‘alpha–glucose’ components of the starch polysaccharide. Humans and other animals have amylases, so they can digest starch. The primary function of starch in plants , is to act as an energy storage molecule for the organism . Structurally , The starch forms clusters of linked linear polymers , where the alpha – 1,4 linked chains from columns of glucose units which branch regularly at the alpha – 1,6 links.

1.6 GYLCEROL :

Glycerol is a colorless, odorless liquid with a sweet taste. It is viscous at room temperature and non-toxic in low concentrations. It is also called glycyl- alcohol, glycerin . The three hydroxyl groups of glycerol allow reactions with many organic acids to form esters. When all three reactive groups are esterified with long chain organic fatty acids, a triglyceride is formed. Triglycerides are among the most common lipids in the human body. Glycerol is a trihydroxy sugar alcohol with three carbon atoms and three hydroxyl groups. The presence of multiple hydroxyl groups and carbon atoms makes it an organic polyol compound with the IUPAC name of 1, 2, 3 – Propanetriol.

1.6.1 PROPERTIES OF GYLCEROL:

Glycerol is seen in biological systems as an intermediate in carbohydrate and lipid metabolism because surplus carbohydrate can be converted into long chain fatty acids and esterified with the three hydroxyl groups. Pure glycerol has a melting point of 17.8°C. Its boiling point is 290°C but it also decomposes at that temperature. The presence of three hydroxyl groups makes the compound hygroscopic, with a tendency to absorb moisture from the air.

Glycerol is easily soluble in water, due to the ability of the polyol groups to form hydrogen bonds with water molecules. Glycerol is slightly denser than water with a specific gravity of 1.26. This means that when glycerol is poured into a container of water, it will sink to the bottom. However, due to its solubility, over time and with mild agitation, glycerol will form an aqueous solution .

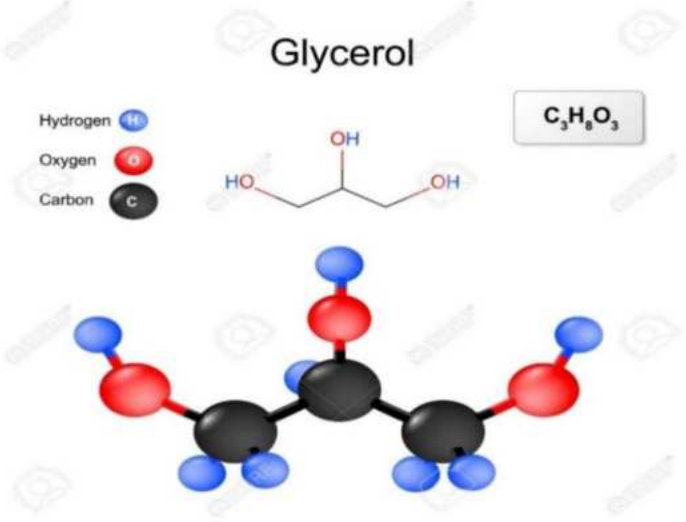


Fig : 6

1.6.2 USES OF GYLCEROL :

- Glycerol is used in a number of industrial applications, in the pharmaceutical industry, in cosmetics and personal care products, in the production of resins, detergents, plastics.
- Crude glycerin is a byproduct of the production of biofuels from soya bean oil and other vegetable oils. It contains over 60% impurities in the form of methanol , soaps and salts, making it difficult to extract pure glycerin.
- They are also commonly used as insulators.

- Pure glycerol is a crucial part of the industrial production of antifreeze, textiles and waxes.[8]

1.7 Scope of work objective :

The main objectives of the present study are ,

- To prepare the starch film using Solanum tuberosum and Manihot esculenta.
- To analyze the functional groups of synthesized starch material by FT-IR Spectroscopy.
- To study the optical properties of starch film.
- To study the surface morphology of starch film using Scanning Electron Microscopy.
- To study the elemental presence by EDX analysis.
- To study the thermal stability of the sample by TGA (Thermogravimetric analysis).
- To find the shape of the molecule and the intensities by XRD analysis .

CHAPTER – II

LITERATURE REVIEW

Fatma Masmoudi et al., reported that , The plastic materials used for packaging are increasing leading to a considerable amount of undegradable solid wastes. This work deals with the reduction of conventional plastics waste and the natural resources preservation by using cellulosic polymers from renewable resources (alfa and luffa). Plasticized starch films syntheses were achieved at a laboratory scale. These natural films showed some very attractive mechanical properties at relatively low plasticizers levels (12 to 17 % by weight). Furthermore, mixtures including polylactic acid polymer (PLA) and cellulose fibers extracted from alfa and luffa were investigated by melt extrusion technique. When used at a rate of 10 %, these fibers improved the mixture mechanical properties. Both developed materials were biodegradable, but the plasticized starch exhibited a faster biodegradation kinetic compared to the PLA/cellulose fibers. These new materials would contribute to a sustainable development and a waste reduction.[9]

A.C. Souza et al., reported that , Glycerol content and its incorporation method on tensile and barrier properties of biodegradable films (BF) based on cassava starch were analyzed. ANOVA showed that the glycerol incorporation method did not influence the results ($P > 0.05$), however the glycerol content influenced significantly the tensile and barrier properties of the films ($P < 0.05$). Films prepared with lower glycerol content presented better tensile and barrier properties than films with higher content. Films were then prepared with addition of clay nanoparticles and their tensile and barrier properties and glass transition temperature were measured. ANOVA indicated that both glycerol and clay nanoparticles influenced significantly the tensile and barrier properties ($P < 0.05$), diminishing film permeability when clay nanoparticles were present, while the glass transition temperature was not influenced ($P > 0.05$).[10]

M.F. Shukur et al., reported that , the effect of glycerol and 1-butyl-3 methylimidazolium chloride (BmImCl) on the conductivity and dielectric properties of potato starch doped with magnesium acetate, $Mg(C_2H_3O_2)_2$ -based electrolytes is studied. The electrolytes are prepared via solution cast technique. The interaction between the materials is proven by Fourier transform infrared (FTIR) analysis. Electrolyte with 20 wt.% $Mg(C_2H_3O_2)_2$ exhibits a room temperature conductivity of $(2.44 \pm 0.37) \times 10^{-8}$ S cm^{-1}. The addition of 30 wt.% glycerol to the best polymer-salt composition has further enhanced the conductivity to 2.60 ± 0.42 $x10^{-6}$ S cm^{-1}. A conductivity of $(1.12 \pm 0.08) \times 10^{-5}$ S cm^{-1} has been achieved when 18 wt.% BmImCl is added to the best polymer-salt-plasticizer composition. From the loss tangent ($\tan \delta$) plot, the relaxation time for selected electrolytes is determined. From transference number measurements, ions are found to be the dominant charge carriers.[11]

S.Ramesh et al., reported that , Biodegradable polymer electrolyte systems of Rice Starch-Lithium Iodide (RS-LiI) films were prepared using solution casting method. At room temperature, RS:LiI film with ratio of 65 wt.% : 35 wt.% demonstrates the highest ionic conductivity of 4.68×10^{-5} S cm^{-1}. Temperature-dependence ionic conductivity study follows Arrhenius model and using related plot, activation energy for highest conducting composition is 0.41 eV. The ac conductivity of each film is increased with increase in LiI content. Dielectric properties of mobility, diffusion coefficient, number density of mobile ions (Li^+) and number of transitions per unit time were determined using Rice and Roth model. At higher conductivity, dielectric parameters were increased due to more mobile ions. The structure of polymer electrolytes was characterized by FTIR spectroscopy.

Infrared spectra of compositions exhibited band shifts at different salt ratios. These shifts confirm complexation between host and salt. [12]

A.S Ahmad Khiar et al., reported that , A proton-conducting polymer electrolyte based on starch and ammonium nitrate (NH_4NO_3) has been prepared through solution casting method. Ionic conductivity for the system was conducted over a wide range of frequency between 50 Hz and 1 MHz and at temperatures between 303 K and 373 K. Impedance analysis shows that sample with 25 wt.% NH_4NO_3 has a smaller bulk resistance (Rb) compared to that of the pure sample. The amount of NH_4NO_3 was found to influence the proton conduction; the highest obtainable room temperature conductivity was 2.83×10^{-5} S cm^{-1}, while at 100 °C, the conductivity in found to be 2.09×10^{-4} S cm^{-1}. The dielectric analysis demonstrates a non-Debye behavior. Transport parameters of the samples were calculated using the Rice and Roth model and thus shows that the increase in conductivity is due to the increase in the number of mobile ions.[13]

Neelam Srivastava et al., reported that , A new bio-polymer electrolyte system is prepared by mixing NH_4I with potato starch. Prepared material is an ionic conductor having ionic transference number ~ 0.95 and ambient electrical conductivity ~2.4×10^{-4} S/cm. Relation between the conductivity trend, mobile ion concentration factor (K) and mobility factor with respect to salt concentration and temperature, is established. The optical micrograph of starch + NH_4I system indicated typical starch–iodine relationship in acidic medium. In conductivity formulism three different regions for power law exponent (n) having values between $0 < n<2$ is found. The regions are associated with dc conductivity, NCL and super linear like behavior. In starch electrolyte, NCL region is obtained at room temperature and low frequency region. Material is humidity immune up to 77%

relative humidity and a very small variation with temperature has been found hence results are encouraging for possible use of starch based electrolytes in humidity immune devices.[17]

Y.M Yusof et al ., reported that ,This work focuses on the characteristics of polymer blend electrolytes based on corn starch and chitosan doped with ammonium iodide NH_4I. The electrolytes were prepared using the solution cast method. A polymer blend comprising 80 wt % starch and 20 wt % chitosan was found to be the most amorphous blend and suitable to serve as the polymer host. Fourier transform infrared spectroscopy analysis proved the interaction between starch, chitosan and NH_4I. The highest room temperature conductivity of $(3.04 \pm 0.32)\times 10^{-4}$ S cm^{-1} was obtained when the polymer host was doped with 40 wt % NH_4I. This result was further proven by field emission scanning electron microscopy study. All electrolytes were found to obey the Arrhenius rule. Dielectric studies confirm that the electrolytes obeyed non-Debye behavior. The temperature dependence of the power law exponent s for the highest conducting sample follows the quantum mechanical tunneling model [15]

M.A Hanna et al., reported that , Chitosan film has potential applications in agriculture, food, and pharmacy. However, films made only from chitosan lack water resistance and have poor mechanical properties. Forming miscible, biodegradable composite film from chitosan with other hydrophilic biopolymers is an alternative. The objective of this study was to prepare chitosan/starch composite films by combining chitosan (deacetylated degree, 90%) solution and two thermally gelatinized corn starches (waxy starch and regular starch with 25% amylose). The film's tensile strength (TS), elongation-at-break (*E*), and water vapor transmission rate (WVTR) were investigated. The possible interactions between the two major components were evaluated by X-ray diffraction and Fourier-transform infrared spectroscopy (FTIR). Regardless of starch type, both the TS and *E* of the composite films first increased and then decreased with starch addition. Composite film made with regular starch showed higher TS and *E* than those with waxy starch. The addition of starch decreased WVTRs of the composite films. The introduction of gelatinized starch suppressed the crystalline peaks of chitosan film. The amino group band of chitosan molecule in the FTIR spectrum shifted from 1578 cm $^{-1}$ in the chitosan film to 1584 cm^{-1} in composite films. These results indicated that there was a molecular miscibility between these two components. [14]

N.G Olaiya et al., reported that, This paper presents a comparison on the effects of blending chitin and/or starch with poly(lactic acid) (PLA). Three sets of composites (PLA–chitin, PLA–starch and PLA–chitin–starch) with 92%, 94%, 96% and 98% PLA by weight were prepared. The percentage weight (wt.%) amount of the chitin and starch incorporated ranges from 2% to 8%. The mechanical, dynamic mechanical, thermal and microstructural properties were analyzed. The results from the tensile strength, yield strength, Young's modulus, and impact showed that the PLA–chitin–starch blend has the best mechanical properties compared to PLA–chitin and PLA–starch blends. The dynamic mechanical analysis result shows a better damping property for PLA–chitin than PLA–chitin–starch and PLA–starch. On the other hand, the thermal property analysis from thermogravimetry analysis (TGA) shows no significant improvement in a specific order, but the glass transition temperature of the composite increased compared to that of neat PLA. However, the degradation process was found to start with PLA–chitin for all composites, which suggests an improvement in PLA degradation. Significantly, the morphological analysis revealed a uniform mix with an obvious blend network in the three composites. Interestingly, the network was more significant in the PLA–chitin–

starch blend, which may be responsible for its significantly enhanced mechanical properties compared with PLA–chitin and PLA–starch samples.[16]

Renata Ferreira Santana et al., reported that , Biodegradable films based on starches from different botanical sources exhibited physicochemical and functional properties which were related with the starch characteristics. However, had inadequate mechanical properties and were hard and brittle. In this research, jackfruit seed starch plasticized with glycerol were developed and characterized. The starch and glycerol concentrations ranged from 2 to 6% w/w and 20 to 60 g/100 g starch, respectively. Bioplastics were obtained by the casting method and characterized in terms of color, mechanical properties, solubility, water vapor permeability (WVP), morphology and free energy of the hydrophobic interaction. Electronic micrographics showed the presence of some intact starch granules. The bioplastics were hydrophilic and those of 6% starch and 40% glycerol were the most hydrophilic ($DG_{tot\ sas} = 41.35$ m J m^{-1}). The solubility of the films presented a direct relationship with the starch concentration ranging from 16.42 to 23.26%. Increased opacity and color difference were observed with increasing starch concentration. The WVP ranged from 1.3749 10^{-3} to 3.07 9 10 $^{-4}$ g m/day m_2 which was positively related with the concentration of starch and glycerol. Tensile strength, percent elongation and Young's Modulus indicated that the jackfruit starch and glycerol provided a film with good mechanical properties. The results replaced that jackfruit starch can be used to develop films, with low opacity, moderate WVP and relatively high mechanical stability, by using glycerol in the gelatinized starch dispersions . [18]

Farayde Matta Fakhoury et al., reported that ,The interest in the development of edible and biodegradable films has increased because it is every day more evident that non-degradable materials are doing much damage to the environment. In this research, bioplastics were based on blends of manioc starch (native and modified) and gelatin in different proportions, added of glycerol or sorbitol, which were used as plasticizers. The objective was to study the effect of two different plasticizers, glycerol and sorbitol, and different concentrations of starch and gelatin on the barrier (water vapor permeability e WVP), mechanical (tensile strength and elongation at break), physicochemical (solubility in water and in acid) and physical properties (opacity and thickness) of the obtained bioplastics samples. As a result, all of them showed transparency and resistance to tensile strength, as well as increasing in thickness values and in the WVP, as the gelatin content increased in the formulations. Finally, all results for tensile strength and elongation at break obtained for those samples plasticized with sorbitol were better than those plasticized with glycerol.[19]

Natta Laohakunjit et al., reported that **,**The effect of plasticizers, glycerol, sorbitol and poly(ethylene glycol) 400 (PEG 400), on mechanical and barrier properties of rice starch film has been investigated. Sorbitol and glycerol-plasticized starch films appeared homogeneous, clear, smooth, and contained less insoluble particles compared to unplasticized rice starch films. PEG 400 did not form plasticized films of suitable characteristics. The softness and stickiness of films improved with increasing concentrations of glycerol and sorbitol. In general, films plasticized with glycerol and sorbitol displayed a better solubility in water than unplasticized films, i.e. 35% (w/w) glycerol and 45% w/w (sorbitol) (optimum solubility). The tensile strength of films decreased especially in the high concentration regime of plasticizers, between 20–45% (w/w) of plasticizer/rice starch film. Through the entire concentration regime, the tensile strength of glycerol-plasticized films was significantly lower than that of sorbitol-plasticized films, but their elongation was larger. The water vapor transmission rate (WVTR) through plasticized films and the oxygen transmission rate (OTR) increased with glycerol and sorbitol concentrations, however, glycerol was revealed to be significantly more effective in reducing the tensile strength as well as increasing the WVTR and the OTR compared to sorbitol. With the higher tensile strength and the smaller OTR and WVTR, the 30% sorbitol-plasticized film reveals an improved coating performance in terms of a reduction of coating failures.[20]

J.A. Mbey et al., reported that, The influence of kaolinite content within a plasticized starch matrix on the glass transition and decomposition temperatures, water uptake, transparency and UV–vis blocking is reported. Exfoliation of the kaolinite clay within the composite is enhanced when previously intercalated with DMSO. The DMSO intercalated kaolinite brings in advantages for the clay dispersion within the polymer matrix, the transparency and the water uptake. The transparency of the films is better preserved when DMSO intercalated kaolinite is used and a clay load between 2% and 6%, leads to a significant reduction of the UV light transmission.[21]

Narpinder Singh et al., reported that , In the present study the effect of iodine on the structural characteristics (by infrared spectroscopy and X-ray) of films made from kidney bean starch was evaluated. The pasting properties as affected by iodine and glycerol were also evaluated. Kidney bean starch showed C-type (mixture of A- and B-type) crystalline structure, the conversion of starch into films resulted into reduction in intensity of diffractograms. The starch powder FTIR spectra had peaks centered at 1020 and 995cm^{-1} with a higher intensity at 1020cm^{-1}, which is consistent with a partially crystalline material since fully crystalline material show similar intensity peaks centered around 1020 and 1006cm^{-1}. Films without iodine showed one main peak centered around 1000cm^{-1} consistent with a disordered state similar to that in gelatinized starch. Iodine addition gradually increased the intensity of the bands around 1020cm^{-1} consistent with the formation of more ordered conformation similar to that in the crystalline material. Iodine encourages the formation of helical structures, however, the formation of crystalline material cannot be inferred. The increasing amounts of iodine up to 0.33% level progressively increased the peak-, through- and breakdown-viscosity. Iodine beyond 0.33% level gradually decreased peak, trough, breakdown and setback-viscosity. Pasting temperature gradually increased with the increase in iodine.[22]

Angelica Aimoto Shimazu et al., reported that , In this work were studied the plasticizing – anti-plasticizing effects of glycerol and sorbitol on moisture sorption and mechanical properties of cassava starch films. Films were produced by casting with cassava starch (3g starch/100g filmogenic solution) and different concentrations of glycerol or sorbitol (0, 5, 10, 15, 30 and 40 g/100 g starch). Glycerol and sorbitol acted as anti-plasticizers when used at a low concentration (≤ 15 g/100 g starch) and low values of water activity (≤ 0,58). The anti-plasticizing effect could be demonstrated by the decrease in hydrophilicity and in flexibility of the films at these conditions. At higher concentrations and higher water activity values, the employed plasticizers exerted its plasticizing effect.[23]

CHAPTER – III

EXTRACTION METHODS

3.1 EXTRACTION OF STARCH :

- Take 500 gm of Potato and 750 gm of Cassava .
- After removing adhering dirt and soil by washing , outer skin of Potato and Cassava were peeled off and grinded with a grater.
- The grinded pieces are rinsed several times using distilled water , for this we have taken 200 ml of water for each wash.
- Let the two beakers containing grinded pieces of Potato and Cassava immersed in distilled water were left aside for few hours such that the starch settles at the bottom.
- After few hours , pure starch of Potato and Cassava were obtained .
- Starch is dried at room temperature for a week .

CASSAVA

POTATO

Fig : 7

3.2 Preparation of Starch based Bioplastic :

- Bioplastic were prepared using the casting technique .
- Potato starch powder of about 1gm , 5 gm and 10 gm and Glycerol as a plasticizer at concentration of 0.5 gm , 3 gm and 6 gm were dissolved in 50ml of distilled water .
- The suspension was heated to 70˚C under a stirring on a magnetic hot plate for about 30 mins .
- After the heat treatment , film forming solution is transferred to the petri dish and dried in an oven at 105 ˚C for 3 hrs.
- After few hours, Biopolymer film is formed in a petri dish .
- Same procedure is followed for making Bioplastic film for Cassava

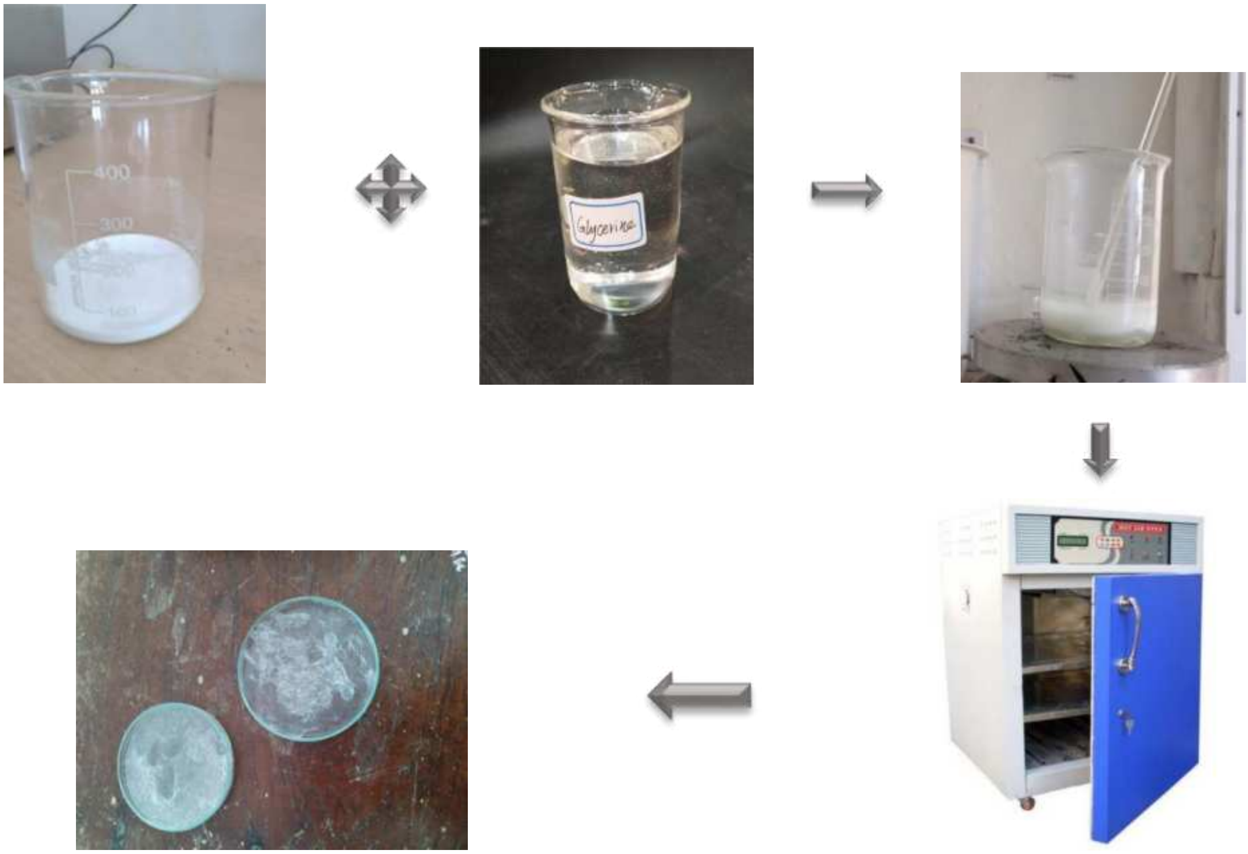


Fig : 8

EXPERIMENTAL METHODOLOGY

4.1 FT-IR :

Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

Fig : 9

4.1.1 SAMPLE ANALYSIS PROCESS :

- The Source :

Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample .

- The Interferometer :

The beam enters the interferometer where the "spectral encoding" takes place. The resulting interferogram signal then exists the interferometer.

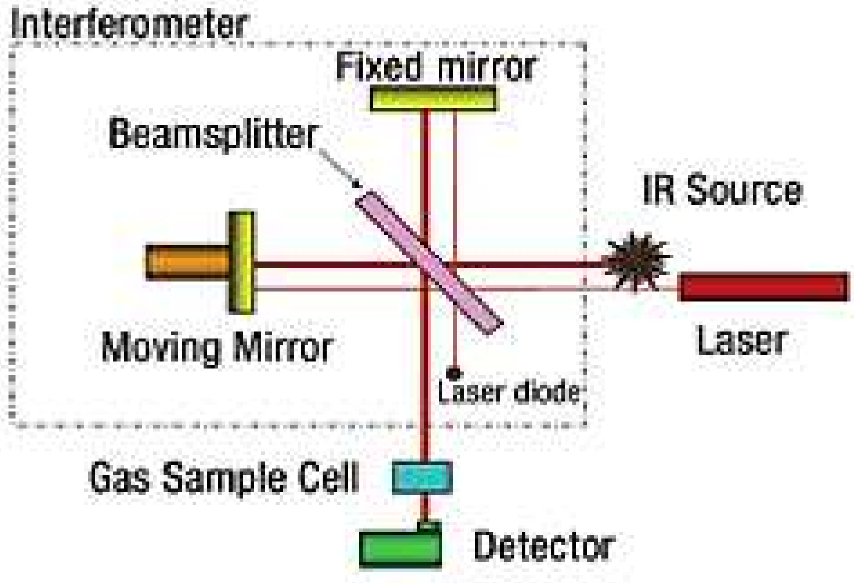


Fig :10

- The Sample :

The Beam enters the sample compartment where it is transmitted through or reflected off the surface of the sample , depending on the type of analysis being accomplished. This is where specific frequencies of energy , which are uniquely characteristic of the sample , are absorbed.

- The Detector :

The beam finally passes to the detector for final measurement . The detectors used are specially designed to measure the special interferogram signal.

- The Computer :

The measured signal is digitized and sent to the computer where the Fourier transformation takes place . The final infrared spectrum is then presented to the user for interpretation and any further manipulation .[24]

4.1.2 Uses of FTIR :

- It is an analytical technique used to identify organic materials .
- Identify contamination on or in a material . e.g., particles, fibers etc.,
- Identify oxidation, decomposition, or uncured monomers in failure analysis investigations.
- This technique measures the absorption of infrared radiation by the sample material thereby identify molecular components and structures.

4.1.3 Advantages of FTIR Spectroscopy :

- FTIR is nondestructive and does not need any sample preparation.
- FTIR is currently the only technique having the capability of identifying synthetic amethyst.
- When conventional gemological methods are inadequate, FTIR spectroscopy at a high resolution (0.5 cm^{-1}) can accurately separate some rare materials and unusual synthetics.

4.1.4 Disadvantages of FTIR Spectroscopy :

- The sampling chamber of an FTIR can present some limitations due to its relatively small size.
- Mounted pieces can obstruct the IR beam. Usually, only small items as rings can be tested.

- Several materials completely absorb Infrared radiation; consequently, it may be impossible to get a reliable result.[25]

4.2 XRD ANALYSIS :

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

Fig :11

4.2.1 XRD INSTRUMENTATION :

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced.

These spectra consist of several components, the most common being K_α and K_β. K_α consists of $K_{\alpha1}$ and $K_{\alpha2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochromators is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha1}$and $K_{\alpha2}$ are sufficiently close in wavelength such that a weighted average of the two is used.

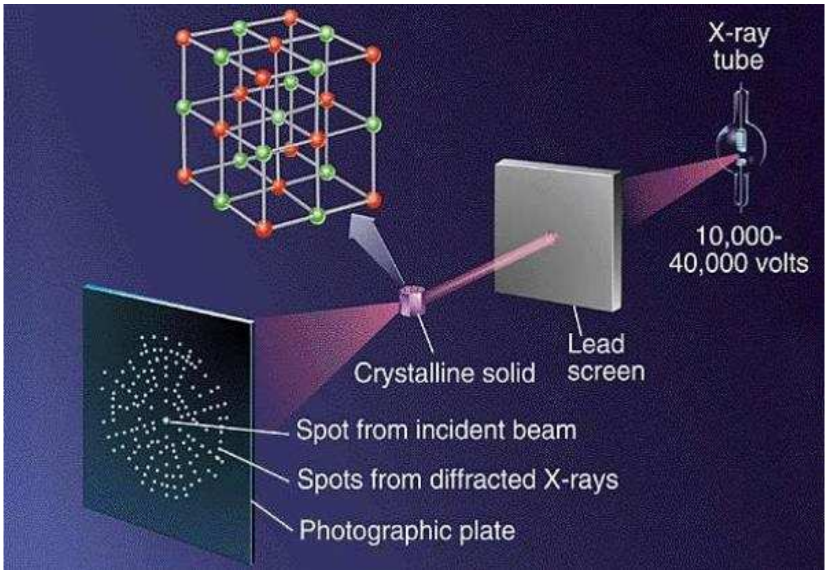


Fig :12

These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a *goniometer*.

When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

4.2.2 APPLICATION OF XRD :

- Its used for characterization of crystalline materials.
- It measures the sample purity.
- For measuring superlattices in multilayered epitaxial structures.
- Determines the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements make textural measurements such as the orientation of grains in a polycrystalline sample.[26]

4.2.3 Advantages Of XRD :

- XRD is the cheap and most convenient method used for determining crystal structure.
- XRD permits non-destructive structure analyses.

4.2.4 Disadvantages of XRD:

- It is relatively low in sensitivity .
- XRD does not interact very strongly with lighter elements . [27]

4.3 FE-SEM :

A Scanning Electron Microscope (SEM) is a type of electron microscope that scans the surface of the sample with a focused beam of electrons whereas in Field Emission Scanning Electron Microscopy (FE-SEM) produces images of the surface of samples using a low energy electron beam obtained from Field Emission Gun. This instrument allows to observe fragile and low melting temperature samples like creams, which is not possible by SEM . [28]

4.3.1 FE-SEM IMAGING PROCESS :

- Electron optical system :

One of the main components in FE-SEM is electron beam that describes the FEG and lenses. Electron optic is used to demagnify the size of electron source to form smallest possible probe for high resolution. A special gun mode was developed to reduce the energy spread of the primary beam to reduce the effect of chromatic aberration. Aberrations are lens imperfections due to spherical or chromatic effects which limit the ability of focusing the electron beam on the surface and thus blur the image. Most FEG is designed to have energy spread as low as 0.35 eV as compared to 1.5 eV for thermionic emitter . The probe current is in the range of 3 pÅ to 100 nÅ. The probe size is another important criterion for high resolution imaging. The demagnification is achieved using a series of lens known as 'probe-firming' lens comprising condenser and objective lens

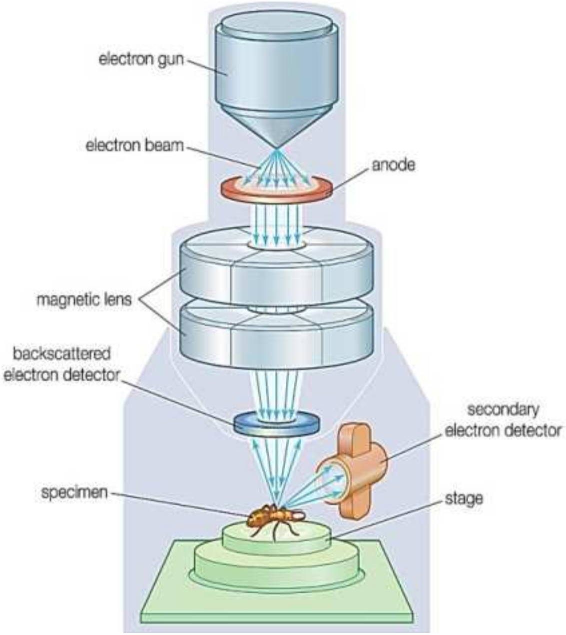


Fig :13

Fig : 14

- Low voltage imaging :

  The high resolution imaging at low voltage is needed to avoid beam damage and to balance the secondary electron (SE) yield and beam current for charge neutrality. The advantage of low voltage imaging is to improve image contrast. The acceleration voltage is from 0.02 to 30 kV. By combining the low probe current with smallest possible probe size and at low acceleration voltage it provides magnification from 20 to 2,000,000 times.

- Detection system :

  Various signals are generated as a result of the impact of incident electrons to the specimen. There are mainly low energy secondary electrons (SE) (energies of < 50 eV), high energy backscattered electrons (BSE) (energies of > 50 eV) and characteristic x-rays .These signals are collected using detectors to form an image or to analyze the sample's surface.. To get high resolution images, the sufficient signals from surfaces are vital. These signals are converted from the electrons that are coming from the surfaces. The types of detectors offered are standard In-Lens SE detector, high efficient Everhart Thornley (ETD) SE detector and angular selective BSE detector.[29]

4.3.2 APPLICATION OF FE-SEM :

- Its used for semiconductor device cross section analyses for gate widths, gate oxides, film thicknesses .
- It includes advanced coating thickness and structure uniformity determination
- Used for small contamination feature geometry and elemental composition measurement.[30]

4.3.3 Advantages of FE-SEM :

- The ability to examine smaller-area contamination spots at electron accelerating voltages compatible with energy dispersive spectroscopy (EDS).
- High-quality, low-voltage images with negligible electrical charging of samples (accelerating voltages ranging from 0.5 to 30 kilovolts).
- There is no need for placing conducting coatings on insulating materials.

4.3.4 Disadvantages of FE-SEM :

- FE-SEM samples must be solid and vacuum-compatible. However, higher pressures can be used for imaging of vacuum-sensitive samples that are nonconductive and volatile .

- Samples that are strong insulators must be coated usually with gold or carbon before testing. However, this process can result in artifacts. [31]

4.4 UV SPECTROSCOPY :

UV spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400 nm) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state.

Fig : 15

4.4.1 Principle of UV spectroscopy :

UV spectroscopy obeys the Beer-Lambert law, which states that, when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution.

The expression of Beer-Lambert law is ,

$A = \log (I_0/I) = Ecl$

Where, A = absorbance .

I_0 = intensity of light incident upon sample cell.

I = intensity of light leaving sample cell.

C = molar concentration of solute.

L = length of sample cell (cm)

E = molar absorptivity.

From the Beer-Lambert law it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. This is the basic principle of UV spectroscopy.

4.4.2 Instrumentation and working of UV spectroscopy :

- Light Source :

  Tungsten filament lamps and Hydrogen-Deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen-Deuterium lamps falls below 375 nm.

- Monochromator:

  Monochromators generally composed of prisms and slits. The most of the spectrophotometers are double beam spectrophotometers. The radiation emitted from the primary source is dispersed with the help of rotating prisms. The various wavelengths of the light source which are separated by the prism are then selected by the slits such the rotation of the prism results in a series of continuously increasing wavelength to pass through the slits for recording purpose. The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism.

- Sample and reference cells :

  One of the two divided beams is passed through the sample solution and second beam is passes through the reference solution. Both sample and reference solution are contained in the cells. These cells are made of either silica or quartz. Glass can't be used for the cells as it also absorbs light in the UV region.

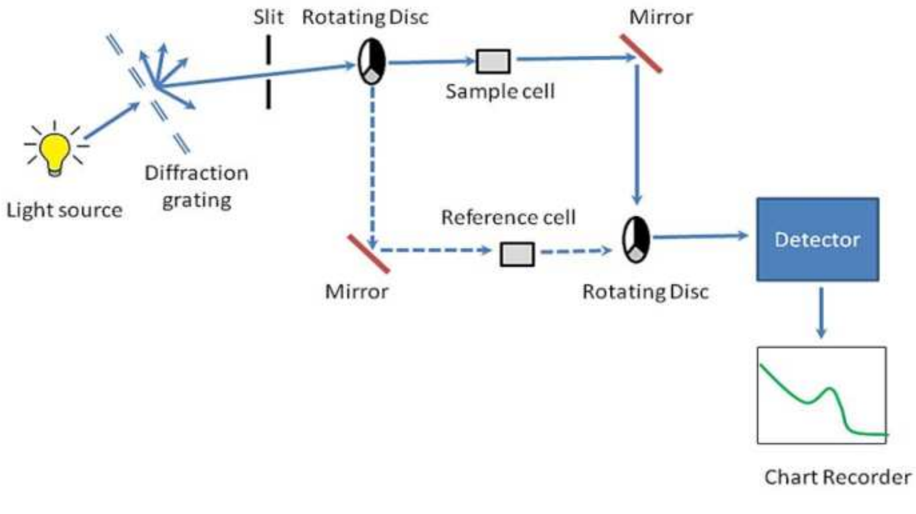


Fig : 16

- Detector :

  Generally two photocells serve the purpose of detector in UV spectroscopy. One of the photocell receives the beam from sample cell and second detector receives the beam from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

- Amplifier :

  The alternating current generated in the photocells is transferred to the amplifier. The amplifier is coupled to a small servo-meter .

- Recording devices :

  Most of the time amplifier is coupled to a pen recorder which is connected to the computer. Computer stores all the data generated and produces the spectrum of the desired compound.[32]

4.4.3 Applications of UV spectroscopy:

- UV spectroscopy is used to detect the presence or absence of chromophore in the compound.
- The extent of conjugation in the polyene can be detected with the help of UV spectroscopy.

4.4.4 Advantages of UV Spectroscopy :

- UV is the simple and inexpensive instrumentation.
- Most Organic compounds absorbs UV light.

4.4.5 Disadvantage of UV Spectroscopy :

- It requires significant sample preparation .
- UV spectra is not highly specific for particular molecule.[33]

4.5 TGA :

Thermogravimetric analysis or Thermal Gravimetric Analysis (TGA) is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. This measurement provides information about physical phenomena, such as phase transitions, absorption, adsorption and desorption ; as well as chemical phenomena including chemisorption , thermal decomposition, and solid-gas reactions like oxidation or reduction .

4.5.1 Thermogravimetric analyzer :

In thermogravimetric analyzer mass, temperature, and time are considered base measurements in thermogravimetric analysis while many additional measures may be derived from these three base measurements. A typical thermogravimetric analyzer consists of a precision balance with a sample pan located inside a furnace with a programmable control temperature. The temperature is generally increased at constant rate or for some applications the temperature is controlled for a constant mass loss to incur a thermal reaction. The thermal reaction may occur under a variety of atmospheres including a high vacuum, high pressure, constant pressure, or a controlled pressure.

The thermogravimetric data collected from a thermal reaction is compiled into a plot of mass or percentage of initial mass on the y axis versus either temperature or time on the x-axis. This plot is referred to as a TGA curve. A TGA can be used for materials characterization through analysis of characteristic decomposition patterns. It is an especially useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films etc.,[34]

Fig : 17

4.5.2 APPLICATION OF TGA :

- TGA is used to decomposite kinetics of material.
- For studying, sublimation behaviour of various substance.

4.5.3 Advantage of TGA :

- A relatively small set of data is to be treated .
- Thermal and Oxidation stability of materials.

4.5.4 Disadvantage of TGA :

- The chemical or physical changes which are not accompained by the change in mass on heating are not indicated in TGA.
- Sensitive to heating rate.[35]

CHAPTER –IV

RESULTS AND DISCUSSION

5.1 FT-IR ANALYSIS :

FT-IR analysis is used to identify the functional group of a system .The IR spectra of Solanum tuberosum with glycerol sample were recorded in the range of 600 – 4000 cm^{-1}. For Manihot esculenta with glycerol , IR spectra is at the range of 600 – 2500 cm^{-1} .The stretching of peaks at 3294.417 cm^{-1} could be assigned as O-H bond .The C-H symmetric bending peaks are at 1342.455 cm^{-1} . CH_2 symmetric deformation peaks are seen at 1440 cm^{-1}. The C-O bending mode peaks associated with OH group are at range 1689 , 1630 cm^{-1}. C-O Stretching of potato and cassava have peak values 2360 ,1890 cm^{-1}.

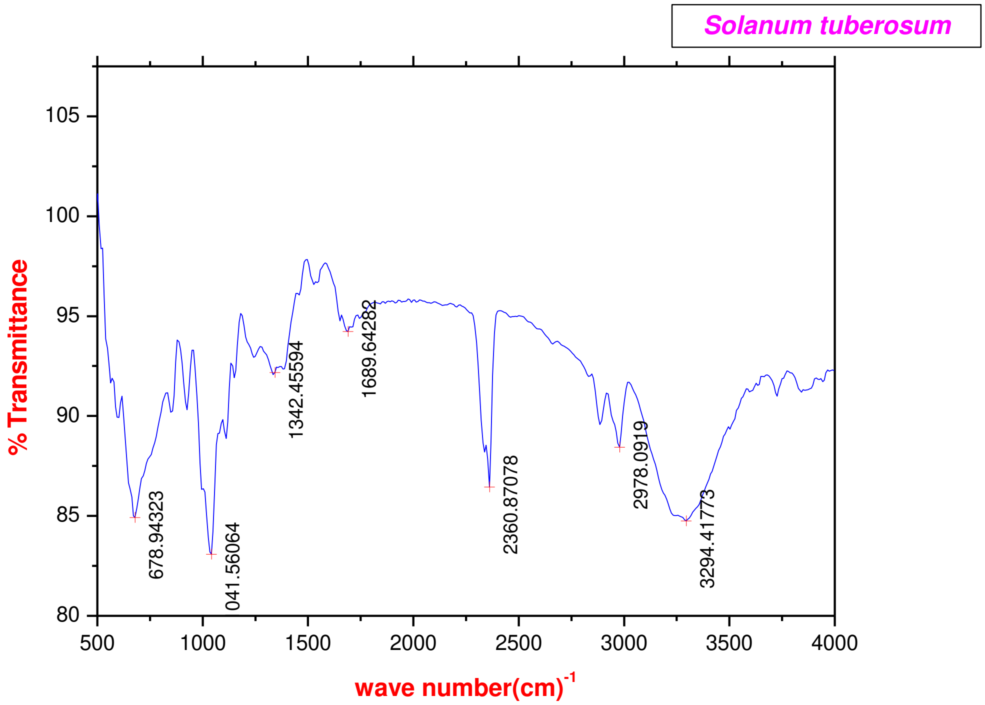
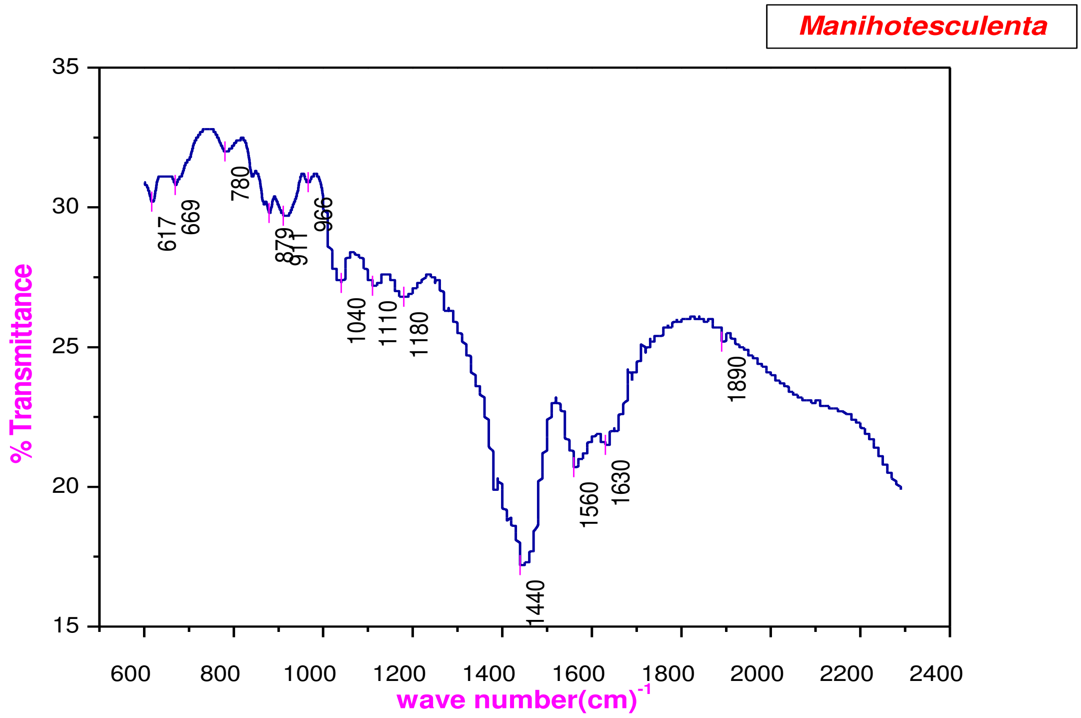


Fig 18.1 FT-IR of Solanum tuberosum with glycerol

Fig 18.2 FT-IR for Manihot esculenta with glycerol



Functional Groups	Solanum Tuberosum (cm^{-1})
C-H Symmetric Bending	1342
C -O Bending associated with OH group	1689
C-O Stretching	2360
O-H Stretching	3294

Table 1 : FT-IR data for sample 1

Table 2 : FT-IR data for sample 2

Functional Groups	Manihot esculenta (cm^{-1})
CH_2 Symmetric deformation	1440
C -O Bending associated with OH group	1630
C-O Stretching	1890

5.2 SEM Characterization :

The morphology and size distribution of Solanum Tuberosum & Manihot esculenta with glycerol can be measured by Field Emission – Scanning Electron Microscope . The fig 19.1 ,19.2 shows SEM magnification images at 500 nm.

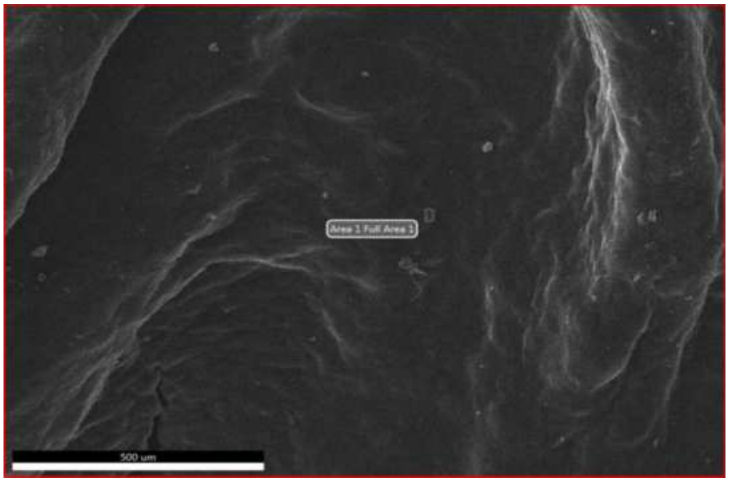


Fig 19.1 SEM behavior of Solanum Tuberosum with glycerol.

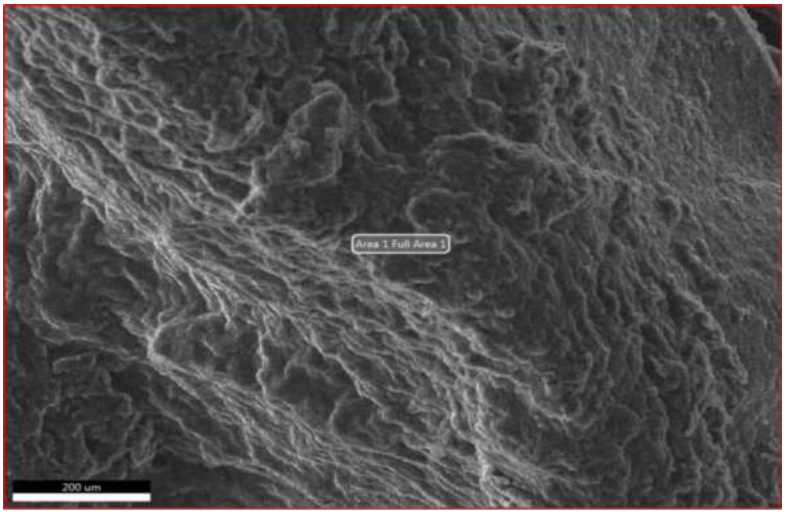


Fig 19.2 SEM behavior of Manihot esculenta with glycerol.

5.3 EDAX Analysis :

The composition of starch with glycerol is given by Energy Dispersive X-Ray Spectroscopy .The result of EDAX clearly indicates the presence of elements like Carbon , Oxygen, Al , Si in sample composition of Solanum Tuberosum with glycerol.

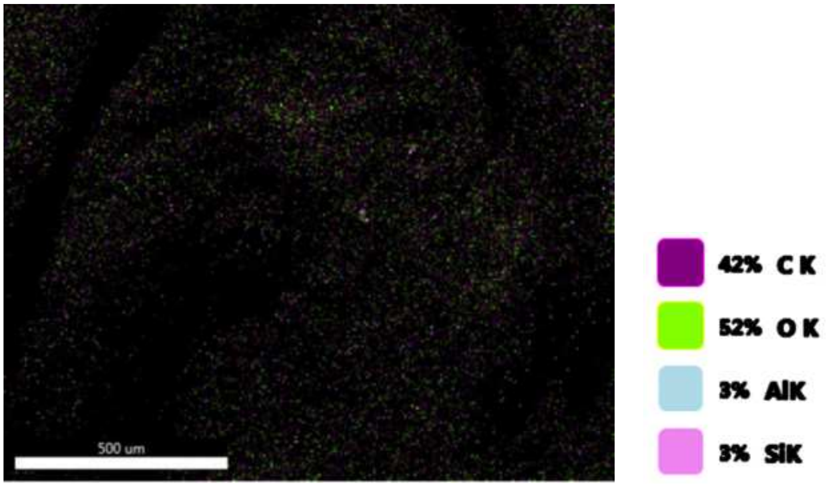


Fig 20.1 Dispersion of Oxygen ,Carbon , Al ,Si

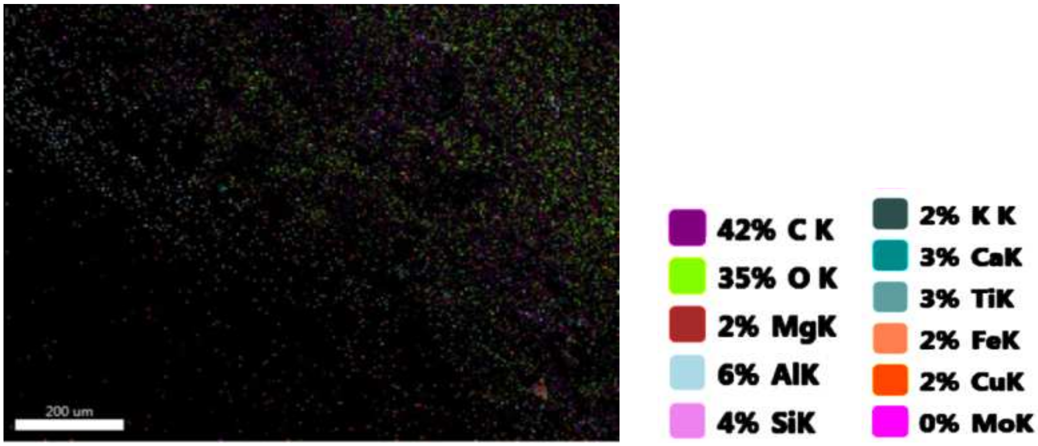


Fig 20.2 Dispersion of Carbon ,Oxygen and other elements .

The result of Manihot esculenta with glycerol sample composition indicates the presence of Carbon ,Oxygen and other elements .

Fig 20.3 EDX image of Solanum Tuberosum with glycerol

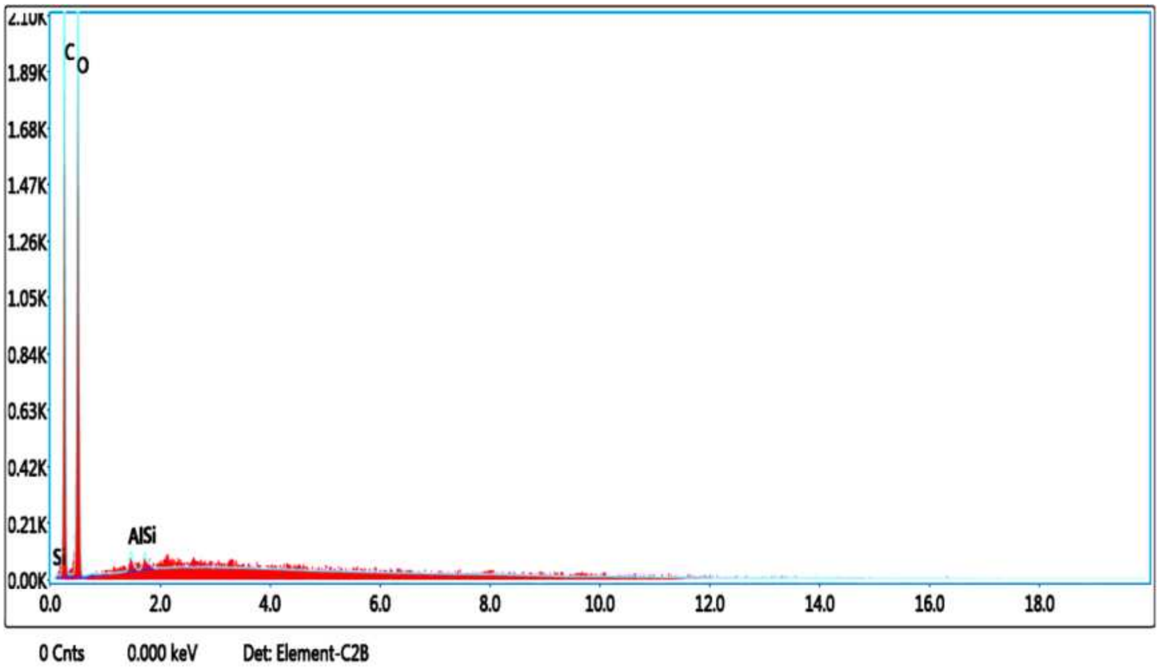


Table 3 : Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %
C K	41.92	49.16	116.65	6.58
O K	57.27	50.42	129.81	9.85
AlK	0.50	0.26	5.57	16.11
SiK	0.31	0.16	4.94	13.83

Fig 20.4 EDX image of Manihot esculenta with glycerol

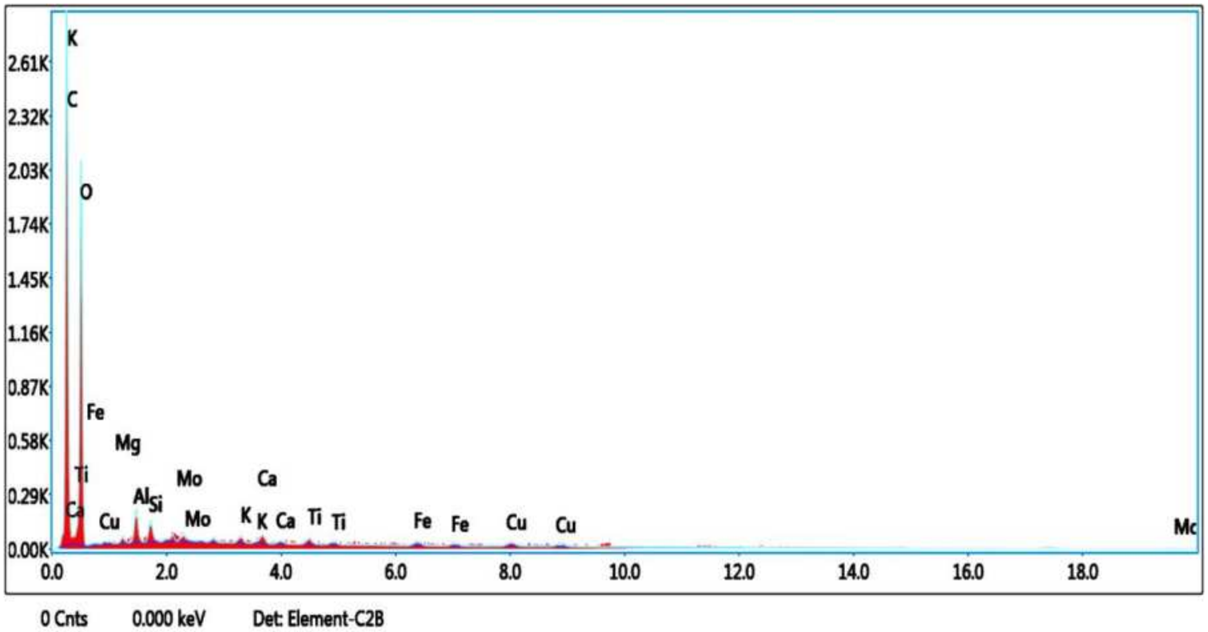


Table 4 : Smart Quant Results

Element	Weight %	Atomic %	Error %
C K	47.5	55.55	6.56
O K	49.13	43.14	10.18
MgK	0.28	0.16	22.64
AlK	0.96	0.5	11.2
SiK	0.47	0.23	12.36
MoK	0.39	0.06	29.89
K K	0.19	0.07	23.81
CaK	0.26	0.09	18.25
TiK	0.23	0.07	20.5
FeK	0.26	0.07	18.49
CuK	0.33	0.07	19.83

5.4 XRD Analysis :

The average crystallite size (D) was calculated using Scherer's Formula ,

$$\mathbf{D = \frac{k\lambda}{\beta\cos\theta}}$$

where , D – average crystalline diameter (nm)

k – Scherer constant (= 0.94)

λ – Wavelength of the X-ray (= 1.5406 Å)

θ – Bragg's diffraction angle.

β – full width at half maxima (FWHM) intensity of the diffraction peak.

$$\boldsymbol{\beta = (\pi/180^\circ)\ \mathrm{x}\ 2\theta}$$

Fig 21.1 XRD image of Solanum Tuberosum with glycerol

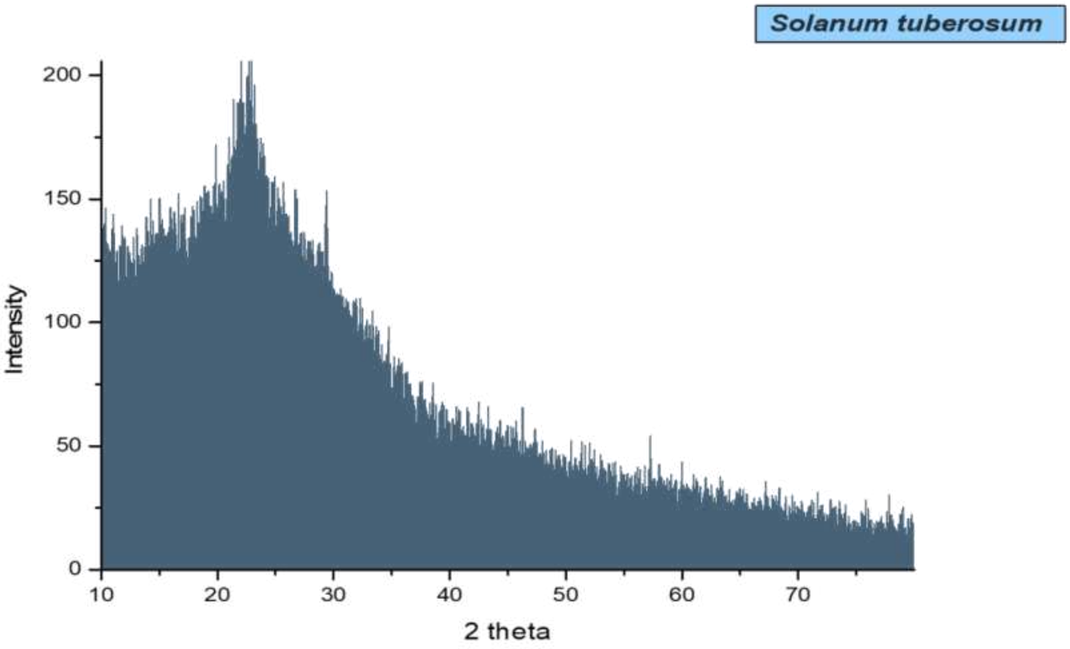


Table 5 : To calculate Average crystallite size (D) for Potato

2θ (deg)	θ (deg)	cos θ (deg)	β	D (nm)
20	10	0.9848	0.3490	4.2133
23	11.5	0.9799	0.4014	3.6816
24	12	0.9781	0.4188	3.5351
27	13.5	0.9723	0.4712	3.1607
30	15	0.9659	0.5235	2.8638

D = 3.4909 nm

Table 6 : To identify lowest common quotient K

θ (deg)	$\sin^2\theta$ (deg)	$\sin^2\theta/2$ (deg)	$\sin^2\theta/3$ (deg)	$\sin^2\theta/4$ (deg)	$\sin^2\theta/5$ (deg)	$\sin^2\theta/6$ (deg)
10	0.0301	0.0150	0.0100	0.0075	0.0060	0.0050
11.5	0.0397	0.0198	0.0132	0.0099	0.0079	0.0066
12	0.0432	0.0216	0.0144	0.0108	0.0086	0.0072
13.5	0.0544	0.0272	0.0181	0.0136	0.0108	0.0090
15	0.0669	0.0334	0.0223	0.0167	0.0133	0.0111

K= 0.0108

Table 7 : To identify Bravais lattice

2θ (deg)	$\mathrm{Sin}^2 \theta$ (deg)	$\mathrm{Sin}^2 \theta / K$	$h^2 + k^2 + l^2$	hkl
20	0.0301	2.7870	3	111
23	0.0397	3.6759	4	200
24	0.0432	4	4	200
27	0.0544	5.0370	5	210
30	0.0669	6.1944	6	211

The lattice value , $a = \frac{\lambda}{2\sqrt{k}}$

$= 1.5406 / 2 \sqrt{0.0108}$

$a = 7.4122$

Fig 21.2 XRD image of Manihot esculenta with glycerol

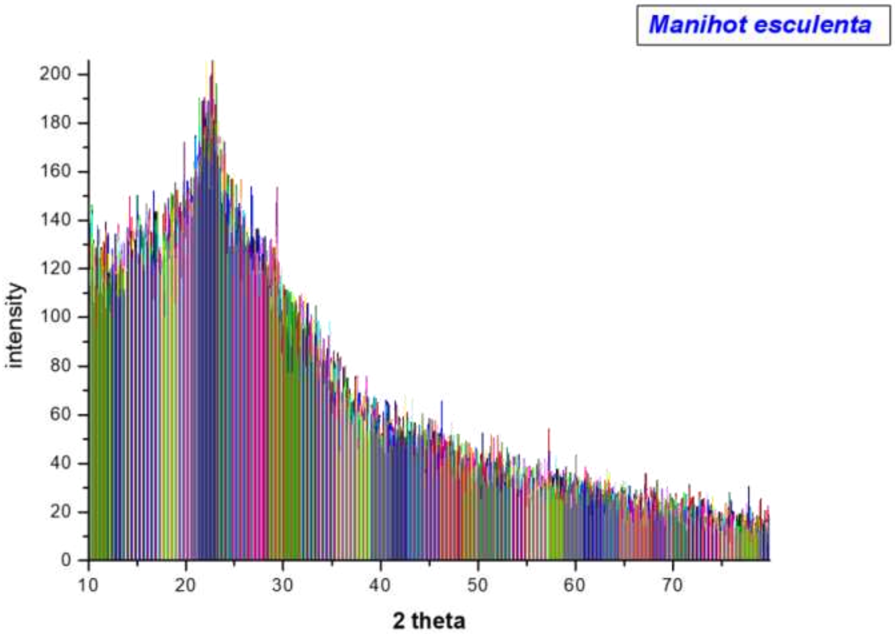


Table 8 : To calculate Average crystallite size (D) for Cassava

2θ (deg)	θ (deg)	cos θ (deg)	β	D (nm)
20.2	10.1	0.9845	0.3525	4.1727
21.5	10.75	0.9824	0.3752	3.9286
23.1	11.55	0.9797	0.4031	3.6668
27.5	13.75	0.9713	0.4799	3.1066
29.8	14.9	0.9663	0.5201	2.8813

D = 3.5512 nm

Table 9 : To identify lowest common quotient K

θ (deg)	$\mathrm{Sin}^2 \theta$ (deg)	$\mathrm{Sin}^2 \theta /2$ (deg)	$\mathrm{Sin}^2 \theta /3$ (deg)	$\mathrm{Sin}^2 \theta /4$ (deg)	$\mathrm{Sin}^2 \theta /5$ (deg)
10.1	0.0307	0.0153	0.01	0.0076	0.0061
10.75	0.0347	0.0173	0.0115	0.0086	0.0069
11.55	0.04	0.02	0.0133	0.01	0.008
13.75	0.0564	0.0282	0.0188	0.0141	0.0112
14.9	0.0661	0.0330	0.0220	0.0165	0.132

K = 0.01

Table 10 : To identify Bravais lattice

2θ (deg)	$\mathrm{Sin}^2\,\theta$ (deg)	$\mathrm{Sin}^2\,\theta$ / K	$h^2 + k^2 + l^2$	hkl
20.2	0.0307	3.07	3	111
21.5	0.0347	3.47	4	200
23.1	0.04	4	4	200
27.5	0.0564	5.64	6	211
29.8	0.0661	6.61	6	211

The lattice value , $a = \frac{\lambda}{2\sqrt{k}}$

$= 1.5406 / 2\,\sqrt{0.01}$

$a = 7.703$

Hence , XRD is employed to identify the crystalline structure of starch . Potato starch have strongest diffraction peak along 24˚ characterize the B- type crystalline structure . For Cassava starch , the diffraction peaks are at 23.1˚ indicates a C- type crystallinity pattern .

5.5 UV Spectral Analysis :

UV absorbance spectra is recorded with the help of UV spectrometer between 200 to 800 nm.

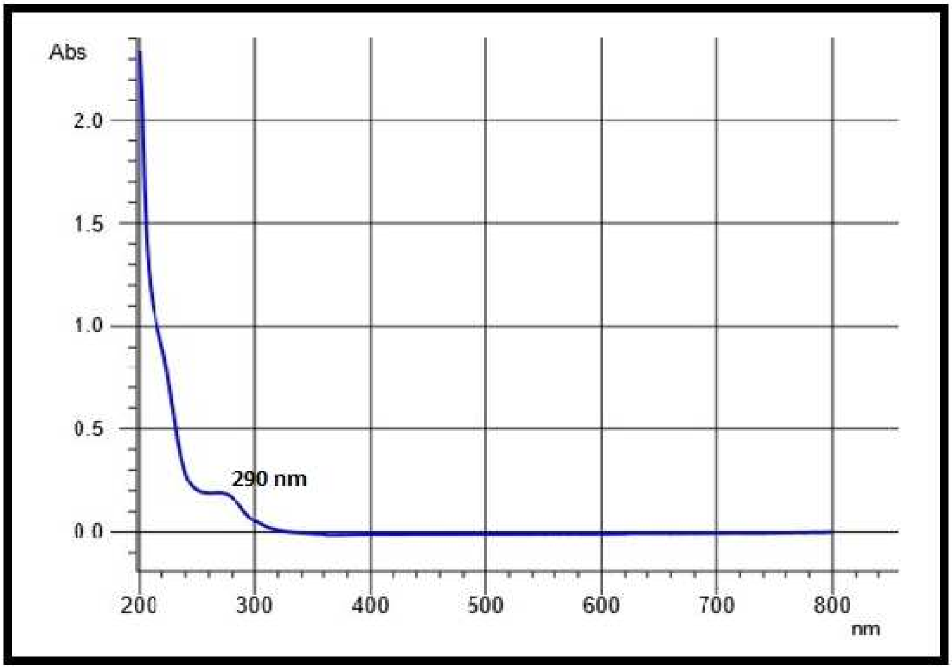


Fig 22 : UV absorbance spectra for Solanum Tuberosum.

Table : 11

Sample	Maximum Absorbance	Wavelength (nm)
Solanum Tuberosum	2.5	290

5.6 TGA Analysis :

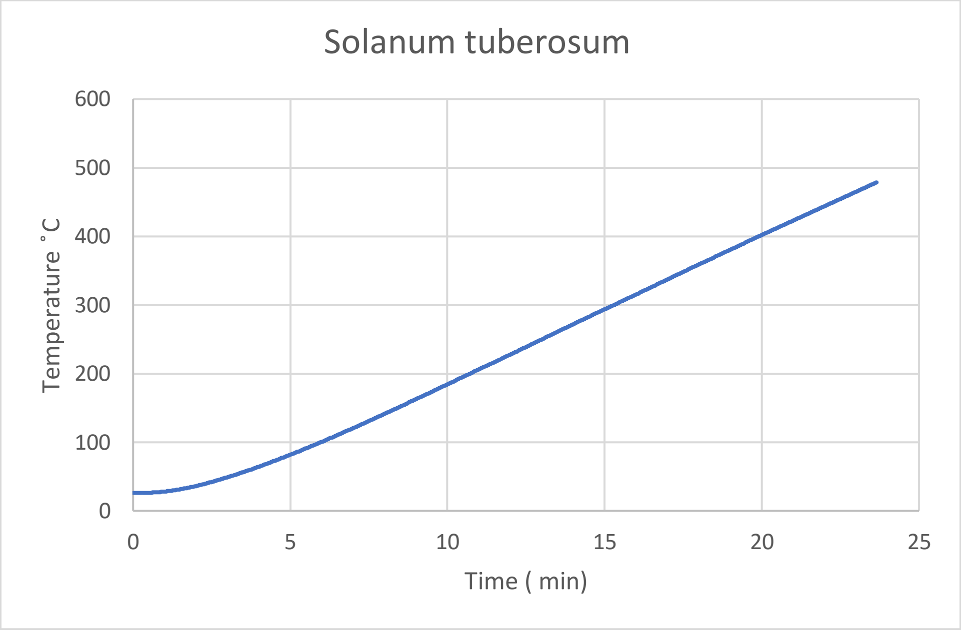
- Sample I - Solanum Tuberosum with glycerol :

Weight of the sample I is 7.881 mg. The graph is plotted against time and temperature. Time starts from (0.0016 -23.6616) min for the corresponding temperature started from (25 ˚C – 500 ˚C) .

Table 12 : TGA data sheet

No	TGA %	Temperature ˚C
1	96.497	55.232
2	27.411	26.00
3	62.448	43.023

Fig 23.1 : TGA for Sample 1



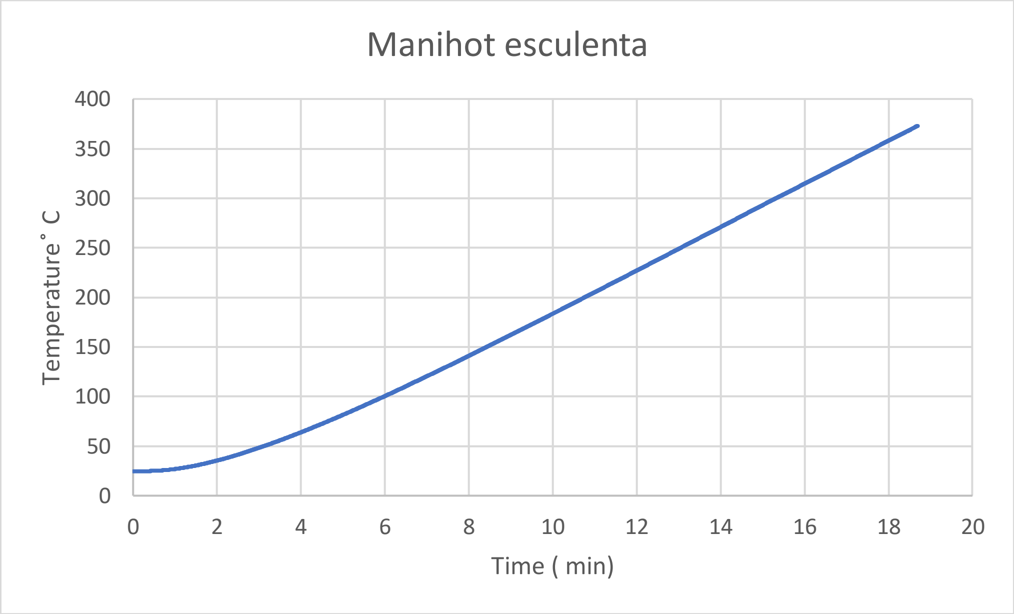
- Sample II – Manihot esculenta with glycerol:

Weight of the sample II is 4.495 mg. The graph is plotted against time and temperature. Time starts from (0.001-18.70167) min for the corresponding temperature started from (25˚C – 400˚C) .

Table 13 : TGA data sheet

No	TGA %	Temperature˚C
1	103.0737	24.893
2	21.804	10.00
3	50.905	18.673

Fig 23.2 : TGA for sample 2



CHAPTER –V

CONCLUSION

- Using Solanum tuberosum and Manihot esculenta polymeric starch film are prepared .
- From FT-IR Spectroscopy, the functional groups and absorbance spectra of synthesized starch material were studied.
- UV -Visible analyze shows peak at 290 nm.
- Optical properties of starch film are studied.
- SEM gives surface morphology of starch film which are rougher.
- Through EDX analysis , the elements present in Solanum tuberosum with glycerol are C , O and Manihot esculenta with glycerol are C, O and other elements .
- TGA (Thermogravimetric analysis) result gives the thermal stability of both samples .

REFERENCE

1. https://www.carboncommentary.com/blog/2011/09/02/bioplastics-an-important-component-of-global-sustainability
2. Renata Ferreira Santana et al., ‘Characterization of starch-based bioplastics from jackfruit seed plasticized with glycerol’ , 2017.
3. S.L Kakani , Amit Kakani ‘Material Science’, New Age International (P)Limited Publishers , pp. 8 – 11, 693 – 698 ,715 – 725 .
4. V.K Ahluwalia , Dr. Anuradha Mishra (2008) ‘ Polymer Science’ , Ane Books Pvt. Ltd.
5. G.S Misra (1993) ‘ Introductory Polymer Chemistry’ , New Age International (P)Limited Publishers , pp . 221 – 222 .
6. https://en.m.wikipedia.org/wiki/Potato
7. https://en.m.wikipedia.org/wiki/cassava
8. https://biologydictionary.net/glycerol/
9. Fatma Masmoudi et al., ‘Biodegradable packaging materials conception based on starch and polylactic acid (PLA) reinforced with cellulose’, 3 Aug 2016.
10. A.C. Souza et al., ‘Cassava starch biodegradable films: Influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature’, 27 October 2011.
11. M. F. Shukur et al., ‘Ionic conductivity and dielectric properties of potato starch-magnesium acetate biopolymer electrolytes: the effect of glycerol and 1-butyl-3-methylimidazolium chloride’ , 27 Dec 2015 .
12. S. Ramesh et al., ‘Ionic Transport and FTIR Properties of Lithium Iodide Doped Biodegradable Rice Starch Based Polymer Electrolytes’, Centre for Ionics University of Malaya, Department of Physics, Malaysia. 1 July 2013.

13. S. Ahmad Khiar et al., ‘Conductivity studies of starch-based polymer electrolytes’, 28 May 2009.
14. M.A. Hannaa et al., ‘Chitosan–starch composite film: preparation and characterization’, Department of Food Science and Technology, Industrial Agricultural Products Center, University of Nebraska,USA ,17 March 2004.
15. Y M Yusof et al., ‘Conductivity and electrical properties of corn starch–chitosan blend biopolymer electrolyte incorporated with ammonium iodide’, Institute of Graduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia ,6 February 2014.
16. N. G. Olaiya et al., ‘Properties and Characterization of a PLA–Chitin–Starch Biodegradable Polymer Composite’, 11 October 2019.
17. Neelam Srivastava et al., ‘Electrical transport behaviour of bio-polymer electrolyte system: Potato starch +ammonium iodide’, Physics Department, MMV, Banaras Hindu University, Varanasi 221005, UP, (India) , 26 November 2011.
18. Renata Ferreira Santana et al., ‘Characterization of starch-based bioplastics from jackfruit seed plasticized with glycerol’, Association of Food Scientists & Technologists (India) 2017.
19. Fakhoury FM et al., ‘Edible films made from blends of manioc starch and gelatin—Influence of different types of plasticizer and different levels of macromolecules on their properties’, LWT Food Sci Technol 49:149–154 , 2012 .
20. Laohakunjit N et al., ‘Effect of plasticizers on mechanical and barrier properties of rice starch film’, 2004.
21. Mbey JA et al.,‘ Cassava starch–kaolinite composite film. Effect of clay content and clay modification on film properties’, Carbohydrate Polymer 88:213–222 , (2012).

22. Singh N et al., ‘ The effects of iodine on kidney bean starch: films and pasting properties’. Int J Biol Macromol 45:116–119 ,(2009).
23. Shimazu AA et al.,‘ Plasticizing and antiplasticizing effects of glycerol and sorbitol on biodegradable cassava starch films’. Semin Cienc Agr 28:70–88 ,(2007).
24. https://rtilab.com/techniques/ftir-analysis/
25. https://agta.org/advantages-and-disadvantages-of-raman-fourier-transform-infrared-spectroscopy-ftir-in-the-gemological-field/
26. https://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html
27. https://www.slideshare.net/saqib16/xray-diffraction-technique-xrd
28. https://en.wikipedia.org/wiki/Scanning_electron_microscope
29. https://inis.iaea.org/collection/NCLCollectionStore/_Public/47/111/47111897.pdf
30. https://photometrics.net/field-emission-scanning-electron-microscopy-fesem/
31. https://www.innovatechlabs.com/newsroom/2083/advantages-disadvantages-scanning-electron-microscopy/
32. https://www.indiastudychannel.com/resources/146681-Principle-working-and-applications-of-UV-spectroscopy.aspx
33. https://www.slideshare.net/nandakumar711/u-v-visible-spectroscopy
34. https://en.wikipedia.org/wiki/Thermogravimetric_analysis
35. https://www.slideshare.net/AmrutaBalekundri/thermo-gravimetric-analysistga

ULTRASONIC STUDIES ON DIFFERENT ALCOHOLS AT 308K

A project report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI

In partial fulfillment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

K.LEONSHIYA

Reg. No: 19SPPH04

Under the supervision and guidance of

Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this project work entitled **"ULTRASONIC STUDIES ON DIFFERENT ALCOHOL AT 308K"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** in partial fulfillment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the year 2020-2021 by

K.LEONSHIYA **Register No: 19SPPH04**

Signature of the Guide

Signature of the SSC Coordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

A. Nirmala Shirley

Signature of the Examiner

ACKNOWLEDGEMENT

"GIVE THANKS TO THE LORD FOR HE IS GOOD"

First of all, I thank the Lord Almighty for his blessing and grace to complete this comprehension work.

I am deeply indebted to our Principal **Rev. Dr. Sr. A. S. J. LUCIA ROSE M. Sc., PGDCA., M. Phil., Ph. D.,** for the encouragement she bestowed upon us.

I wish to express my sincere thanks to our Director of SSC, **Rev. Sr. F. MARY JOYCE BABY M.A., M.Phil.,** for her support in my work.

I would like to express my special thanks of gratitude to **Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D.,** Head of the Department, for her inspirational words and encouragement to complete this project.

I am thankful to **Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,** SSC Coordinator, and my guide , for the continuous support, , patience, motivation, and immense knowledge. Her guidance had encouraged me to do this project successful.

I am grateful to my parents who have provided me through moral and emotional support to complete my work.

An endeavor over a long period can be successful only with the advice and supports of many well-wishers. I take this opportunity to express my gratitude and appreciations to all these people.

Abstract:

The density, ultrasonic velocity and viscosity have been measured for methanol, ethanol, iso- propyl alcohol and tert - butanol at the temperature 308K. The experimental data have been used to calculate some acoustic and thermodynamic parameter such as adiabatic compressibility, free length, free volume and internal pressure. Some probable reasons on the increase or decrease of decrease of acoustic and thermodynamics parameter are presented.

LIST OF CONTENTS

Chapter No. **Title** **Page No**

I **The Liquid State**

III **materials and methods**

V REFERENCE

List of table

Symbols, Abbreviations & Nomenclature	**Meanings**
H^E	Excess of mixing for several alcohols
U	Velocity
K	Wave number
K_s	Adiabatic bulk modulus
ρ	Density
ρ_0	Ambient hydrostatic pressure
ρ_{mix}	Density of binary mixtures
P	Acoustic pressure
α	Cubical expansion coefficient
β^{α}	Adiabatic compressability
γ	Ration of specific heats
ω	Angular frequency
ξ	Particle displacement
ξ_0	Peak value of the particle displacement
m	Molecular weight
U_T	Isothermal sound velocity

R	Gas constant

Symbols, Abbreviations & Nomenclature	**Meanings**
T	Temperature
N_A	Avogadro number
R_m	Molar refraction
Z_i	No. of atoms in the i^{th} molecules
A_i	Additive volume
W	Sound velocity
T_c	Critical Temperature
T_0	Melting point
V_0	Volume per mole
V_f	Free volume
V_a	Available volume
V_{OA},V_{OB}	Molar volume of the components A, B
L_f	Free length
L_{mix}	Free length in binary mixtures

CHAPTER - 1

THE LIQUID STATE

1.1 INTRODUCTION

While it is often said that a liquid is intermediate in its properties between a solid and a gas, this statement should not be understood to mean that every property of a liquid is intermediate in value between those of the other two states. If the actual figures are compared, it is found that in the great majority of cases the value of any property of a liquid is approximately equal either to that of the solid or to that of the gas. The intermediateness, then, is a statistical one-a liquid has some of the properties of a solid, and some of the properties of gas. The most obvious resemblance between liquids and gases is their lack of rigidity neither offers permanent resistance to a shearing stress. The immediate consequence of this is that neither a liquid nor a gas possesses shape of its own, but always offer a resistance to shearing stress.

Between liquids and solids, the most prominent resemblance is that both possess cohesion, which enables each to maintain a free surface, whereas a gas will always completely fill any container. A second, and hardly less fundamental, property common to liquids and solids, is their relative incompressibility compared to gases. While the compressibility of solids are usually of the order or of10^{-6} atm^{-1}, those of liquids are only slightly larger (about10^{-5} atm^{-1}).

The compressibility of a gas, on the other hand, is roughly equal to the reciprocal of the pressure, or, at a pressure of one atmosphere, about 10^{5} times great as that of liquid. Closely allied to the second similarity between liquids and solids is the third: their similarity in density. The density change which takes place when a solid melts is usually of the order of 10 to 50 percent, but on vapourization the density decreases by a factor of 100 or 1,000.

From these simple facts considerable information can be obtained about the nature of the molecular arrangement in liquids. From the density, for example, the mean distance between molecules can be calculated. Taking Argon as a typical example, the molar volumes of the solid, liquid and gas at the boiling point are respectively 24.3 cc, 28.1 cc and 7.050 cc. As a first molecules of the liquid and gas are arranged like those of the solids in a face centered cubic lattice. To obtain the correct densities it is then necessary to assume that the distance between nearest neighbours is 3.84 A° in the solid 4.03 A° in the liquid 25.4 A° in the gas. In the solid, the molecules are in contact. In the liquid, there is a little space (about 5 percent of the molecular diameter) between molecules is about six times the molecular diameter.

Since the forces between molecules are short range forces, and act through a distance of only two or three times the molecular diameter, it is immediately obvious that in the gas these forces are of little importance. Any such regular arrangement of molecules as that we have assumed will therefore be destroyed by the thermal motions of the molecules, and the usual assumption that the molecules of a gas are arranged in space and are randomly distributed.

In the solid, on the other hand, the close-packed arrangement of the molecules prevents any molecule moving from moving far from its original position, which results in turn in the rigidity of the crystal. At the same time the low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must be accomplished by reducing the size of the molecules themselves. If the liquid maintains the arrangement we have assumed, it is difficult to see how to explain its fluidity. The molecules are packed so closely together that no interior molecule can change its position by much more than can the molecule of the solid. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane molecule. Such a motion, however, would require the simultaneous lengthening of a great number of intermolecular distances and hence a large energy of activation for the flow process. To avoid this difficulty it is obviously necessary to assume that a few molecules move at a time, but this in turn implies that it must be relatively easy for molecules to become displaced from the regular lattice.

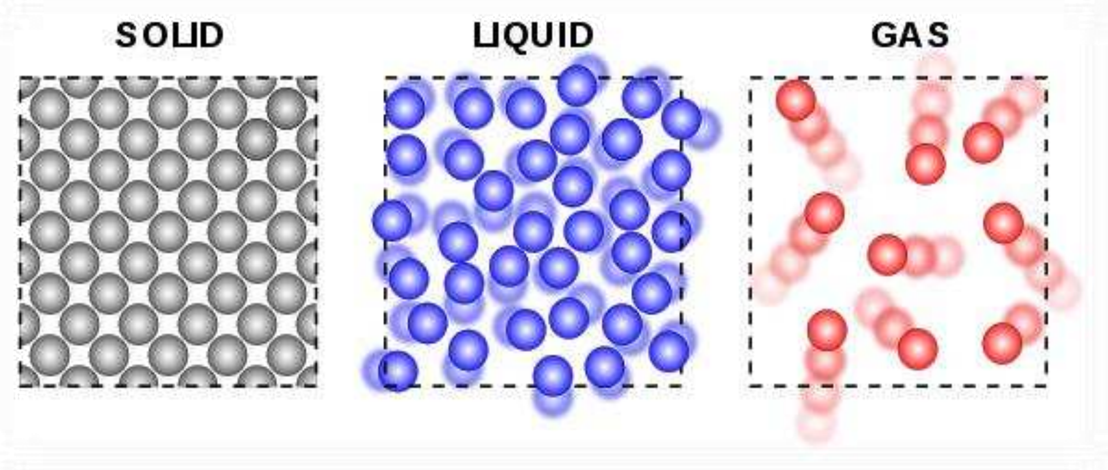


Fig1.1Relative spacing of molecules in solid, liquid and Gaseous Phases

On the other hand, the problem of packing so many spheres into a given volume does not permit any great variation from the regular closed packed structure. In fact the only reasonable modifications which can be made are two in number. First, there may be local irregularities caused by groups of molecules coming closer together, leaving wider spaces elsewhere in the structure. Second, there may be gradual distortion of the structure as we go from molecule to molecule, so that although the pattern in the immediate neighbourhood of a given molecule be quite regular, the pattern is irregular at a distance.

1.2 SHORT AND LONG RANGE ORDER

The tendency of a liquid molecule to surround itself with a more or less definite number of neighbouring molecules at a near a definite distance shows that if we consider a region in the liquid so small that it contain only a few molecules, - say about 20 – these molecules must be arranged very nearly in as regular fashion as in the corresponding crystal. On the other hand, if the size of the region is enlarged, the irregularities mount up, and the positions of the molecule no longer can be related to a lattice of the type occupied by the molecules in the crystal. The regularity exhibited by the crystal is now generally referred to as long range order, since the positions of molecules many diameters away from a central molecule can be predicted from a knowledge of the position of the central molecule and the molecules immediately surrounding it.

In the liquid, on the other hand, this long range order has disappeared. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite, we can say that the liquid still possesses short range order. The crystal, of course, has short range order as well as long range order, but in the gas phase even the short range order has disappeared.

We can, therefore, state as an experimental fact that the melting of a crystal is accompanied by the disappearance of long range order, and the evaporation of a liquid is accompanied by the disappearance of short range order.

1.3 THE LOOSE PACKING OF RIGID SPHERES

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied a minimum, them a regular crystal-like lattice-either hexagonal or cubic is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of the structure will disappear. This has been demonstrated in two dimensions by a number of experimenters[1] who have studied the distribution of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by Morrell and Hildebrand[2] by suspending hard gelatin spheres in a solution of the same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

It would appear from this experimental evidence that the principal factor in the determination of the radial distribution function in a liquid is the volume occupied by the molecules themselves, that is to say, the repulsive forces between the molecules rather that their attraction.

1.4 THEORIES OF LIQUID STATE

The readiness with which liquids flow and diffuse suggests a random molecular structure analogous to the gas. On the other hand the cohesion and compactness exhibited by liquids indicate a structure resembling that of a solid. The similarities between a liquid and a solid make one to consider the two states of matter collectively as a "condensed matter" while the properties of fluidity shared by liquid and gas connect them collectively as "fluids". Hence liquid state theories are broadly of two types.

1. Considering it as a condensed gas so that the interaction between the neighbouring molecules may be calculated through "pair potential functions" and
2. Considering it as a disordered solid lattice.

1.5 MOLECULAR INTERACTION IN LIQUIDS

There are two kinds of interaction

1. Dispersion interaction and
2. Dipole-dipole interaction in liquids.

In the case of non polar molecules the average dipole moment averaged over all phases of electronic motions is zero while the instantaneous dipole moment is never zero.

If two non-polar molecules are placed near each other, the instantaneous dipole moment will interact and will produce some potential energy, which may be positive (or) negative.Such interaction between the molecules is termed as dispersion interaction and is present in all the aggregates of molecules irrespective of the nature of the atoms and molecules.

The second category of interaction is specific. It requires a Hydrogen atom attached to a fairly high electronegative atom and an atom at an optimum distance with non bonded electrons (ion-pairs). This results in the formation of complexes between molecules while the dispersion interaction leads to positive contributions to excess thermodynamic quantities, the latter category makes negative contribution.

The determination of sound velocity, density, viscosity etc., leads to an understanding of the nature and type of molecular interactions especially in binary mixtures of liquids through the excess thermodynamic quantities. Normal liquids obey certain empirical rules such as Trouton's rule, The heat of vaporization at the boiling point is nearly equal to $85 \pm 10\, JK^{-1} mole^{-1}$, the associated liquids (having hydroxyl group), do not obey these empirical rules. The deviation is due to association of molecules found in the vapor to form larger molecules in liquids. In the case of alcohols and acids, the links between the individuals are provided by hydrogen bonds.

The protic dipolar liquids are ordinarily intermolecular hydrogen bonded. This class of liquids has been extensively studied, the best example being water. Aliphatic and aromatic alcohols and amines, carboxylic acids and amides are typical representatives of this class of liquids.

The liquids of this class possess an entropy of vaporization which is 30% higher than for normal non-associated liquids. A notable exception is the carboxylic acids.

The alcohols show regularly changing liquid properties as the aliphatic chain length is increased (or) as the number of hydroxyl groups is increased. For example, the di-electric constant drops as the chain length increases, but increases with the increase in number of hydroxyl groups.

When two liquids are mixed, the solution is said to be ideal if there is no volume change (or) enthalpy change on mixing. But in practice, solutions of liquids are never ideal. The deviation from ideality is much more marked in the case of associated solutions. The thermal energy is less than the interaction energy. The thermal perturbation cannot disturb the association very much. In a binary system of associated liquids, a distortion occurs depending on the concentration. The distortion in the structure of the associated molecules leads to large changes in the physical properties such a dielectric constant, viscosity, free volume etc. Considerable dissociation must occur when alcohols are mixed with diluents, the hydrogen bonds are broken and this explains the positive heats of reactions.

Self associations in alcohols are shown on fig 1.2. The earliest model of self association in alcohols is that of Oster and Kirkwood[5], which assumed long chain association with free rotations of the O.H. around the H-bond in such a situation,

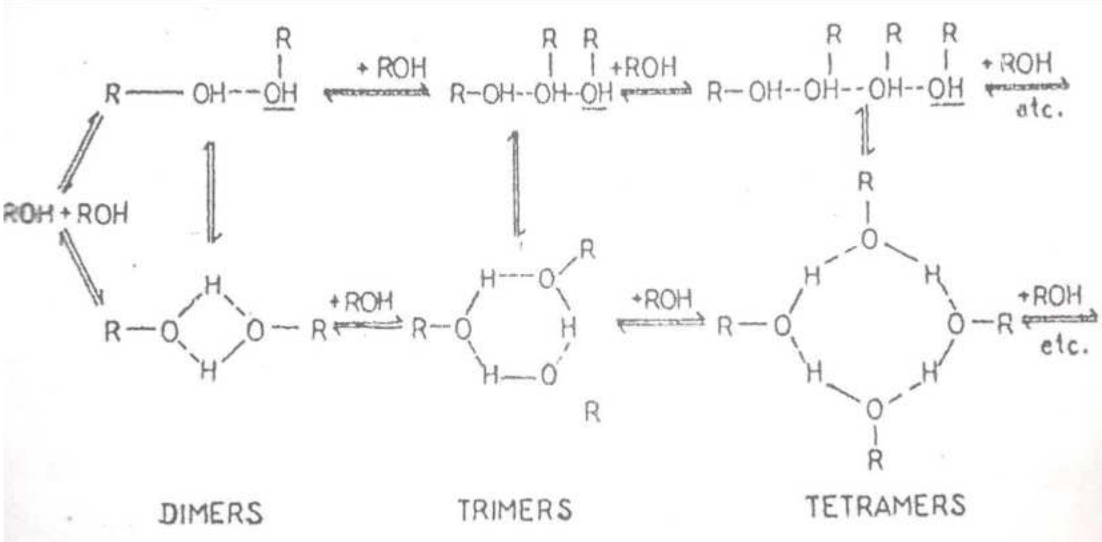


Fig: 1.2 POSSIBLE EQUILIBRIA IN THE SELF-ASSOCIATION OF ALCOHOLS

Dipole moment of the alcohol solution should be greater than that of its monomer unit, which is not the case always[6, 7]. In the most alcohols, dilution with non polar solvents resulted in a dip in dipole moment at a definite concentration[8], which means qualitatively that dilution leads to the formation of cyclic multimers of lesser dipole moment. Bellamy and Pace[9] and Coburn Oxrunwald[10] were of the view that such cyclic structures must be multimers and not dimmers because of unfavourable bonding angles in dimers. Since the cyclic form possesses one additional H-bond compared to the open (or) linear form, the change in enthalpy AH^o for cyclic form should be greater than that corresponding to the open structure.

Hence it is possible to look for specific information from the experimental studies of enthalpy and entropy. Such studies[11, 12] also do not provide sufficient data to permit a decision in favour of or against a particular model. Bordewijk[13], from his dielectric studies showed in mono alcohols, the large multimers are cyclic, probably tetramers, without of plane Oxygen and Hydrogen atoms.

Though there are plenty of data available on the ultrasonic behavior of mono alcohols[14-19] and in mixtures with inert solvents, they do not provide enough information on the model of mono alcohols.

Since the ultrasonic velocity is very sensitive to change in the free volume, it is desirable to look at the data on ultrasonic compressibility's of liquids from the thermo-dynamic point of view. The change in free volume results in a large change in the internal pressure of the liquids and hence the enthalpy of the system. The ease with which one can distort the fluid structure is determined by the energy holding the lattice together. In H-bonded liquids, it is reasonable to assume that this internal energy is related directly to the number of H-bonds per unit volume. The ultrasonic wave propagation in such liquids should result on the distortion of the fluids structures. Based on this concept, Sabesan et.al[20] studied the internal pressure and excess of mixing (H^E) for several alcohols including cyclo hexanol, amyl alcohol, Isoamyl alcohol, Isopropanol, n-butonol, 2-butonol, Isobutanol and tert-butanol in dioxin at different concentrations at 303, 308 and 313K. The positive values of H^E for the systems reported was explained as arising due to the stronger, self associations that was broken, rather strongly by dioxin compared to n-heptane (or) n-hexane.

Among that the isomer alcohols, the n-compounds were found to have less H^E at a given concentration and temperature, than the corresponding isomer.

The role of free volume in systems involving propylene, glycol in several interacting systems was analyzed by Varadarajan and Bharathi[21]. The length of the side chain of hexanols was found to have a definite influence on the excess enthalpy values, on mixing with the interacting solvents [22].

1.6 VELOCITIES OF ULTRASONIC WAVES IN LIQUIDS

The first extensive measurements of ultrasonic velocity in organic liquids were done by Parthasarathy. He arrived at the assumptions that the aromatic compounds usually have higher velocities than the corresponding aliphatic compounds, although their densities are higher velocity in liquids of high density is low, but not in proportion, the increase in density being to some extent set off by an accompanying decrease in compressibility, polar molecules favour high velocities, long molecules give rise to higher velocity, a double bond of unsaturation tends to lower velocity and in similar derivatives changes from a light to a heavy atom lowers velocity. The results in many organic liquids indicate that as a rule an increase in density is to some extent balanced by an accompanying increase in β_0[23]. Nevertheless, since a number of inconsistencies developed from some of these rules, no quantitative derivations were possible[24]. However, Schaaffs had contradicted Parthasarathy's rule arguing that the aromatic substances have generally higher velocities than aliphatics. Increasing density through a homologous series ought to decrease u, but, in fact does not. In halogen compounds the abnormal in molecular weight accounts for the observed fall in U through a series. Increase in molecular volume and the density go hand in hand. These are the factors, which cause the increase of U when heavier atoms are substituted and not increased in molecular weight per sec. There is real evidence that dipole moment is of important in this connection[25].

The velocity of ultrasonic waves in liquids varies from about 900 to $2000ms^{-1}$. The value of U also depends on the temperature and pressure. For most pure liquids at temperatures far from the critical values the value of U decreases as the temperature increases. Water is an exception to this general rule and in this case U increases by about 2 ms^{-1} for each Kelvin rise in temperature and reaches a maximum at 346 mK, above this temperature, U decreases as the temperature rises further. As far as pressure changes are concerned, the velocity U increases in an approximately linear way with pressure for all liquids. This is simply as consequence of the fact that the bulk modulus increases as the molecules are squeezed closer together. For water U increases by about 0.2 ms^{-1} for every increases of one atmosphere[26].

In ultrasonic work, it is convenient to work with plane waves of small amplitude. When an ultrasonic waves passes through a liquid, the pressure and density of an element of liquid vary periodically with time. The variations in P and ρ may be assumed reversible and adiabatic. An ultrasonic wave is propagated as a longitudinal wave in a liquid because the particles of the liquid oscillate in the same direction in which the wave is moving. This is because the liquid possesses only one elastic modulus, the bulk modulus K. The propagation velocity, U, of the wave depends on this modulus and on the density ρ_0 of the liquid according to the equation,

$$U = \sqrt{\frac{Ks}{\rho_0}} \qquad (1.1)$$

where K_s is the adiabatic bulk modulus. The above equation holds for small excess pressure amplitudes for which ρ_0 can be considered to remain a constant. This excess or acoustic pressure P is equal to the difference between the instantaneous pressure P and the ambient hydrostatic pressure ρ_0 i.e.,

$$P = P - \rho_0 \qquad (1.2)$$

Let us consider a plane wave traveling in a liquid in the x-direction. Its propagation is given by the well known equation,

$$\frac{\partial^2 p}{\partial t^2} = U^2 \frac{\partial^2 p}{\partial X^2} \qquad (1.3)$$

As the wave proceeds, each particle of the liquids sutlers a certain displacement from its mean position, we denote this particle displacement we denote this particle displacement by 'ξ'. The corresponding particle velocity v in the medium is given by v $=\frac{\partial \xi}{\partial t}$ and the particle acceleration by

$$a = \frac{\partial v}{\partial t} = \frac{\partial^2 \xi}{\partial t^2} \qquad (1.4)$$

In equation (1.3), the propagation of sound wave has been described in terms of the acoustic pressure, p. This equation is also satisfied by other quantities such as velocity potential cp, particle displacement ~ and particle acceleration

$$\frac{\partial^2 \xi}{\partial t^2} = U^2 \frac{\partial^2 \xi}{\partial X^2} \qquad (1.5)$$

We consider the typical solution

$$\xi = \xi_0 . \exp j\ (\omega t - kx) \qquad (1.6)$$

In this equation ξ_0 represents the peak value of the particle displacement, $\omega = 2\pi f$ f is the angular frequency and k $=\frac{\omega}{U} = 2\frac{\pi}{\lambda}$ is the wave number[27, 28].

CHAPTER-2

LITERATURE SURVEY

2.1 REVIEW

Dash Ashok Kumar et al.,(2014)[29] proposed that the ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of binary mixture of dimethyl acetamide (DAMC) and diethyl ether at temperature 308K have been measured at different frequencies (2MHZ, 4MHz 6MHZ and 8MHZ). Adiabatic compressibility (K_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and their respective excess values have been computed for entire range of concentration and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time (τ), excess enthalpy (H^E) and absorption coefficient (α/f2) have been calculated and discussed. On the basis of the experimental values of density, ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixture, it is concluded that there exists dipole-dipole, dipole-induced dipole and dispersion interactions in the binary liquid mixture of DMAC diethyl ether.

D. Ubagaramary et al.,(2018)[30] discovered that the functions of ultrasonic velocity, density and viscosity for ternary liquid mixtures of 1-proponol, 1- butanol and 1-pentanol with tetra hydro furan are determined by 303.15 K-313.15 K. This data is used to calculate various parameters like the excess free volume, excess internal pressure and Gibb’s free energy, which is used to discuss molecular interactions in the ternary liquid mixtures.

Nabaparna Chakraborty et al.,(2020)[31] revealed that the Velocity of sound and density of binary liquid mixture of Dichloromethane with Ethanolamine have been calculated at different range of temperatures for various concentrations. Liquid-liquid interaction is confirmed by obtaining experimental values of fundamental parameters; ultrasonic velocity and density. Then these parameters are used to determine various other dependent parameters such as acoustic impedance (Z), intermolecular free length (Lf), adiabatic compressibility (β), Rao's constant (R), Wada's constant (W), Vander Waal's constant (b), effective molecular weight and Relative strength. Graphs are plotted for all parameters versus mole fraction. The linear variation of most of the acoustical parameters shows the absence of complex formation in the mixture. The decrease in ultrasonic velocity indicates that there is weak interaction between the molecules of the mixture. The solution tested, consisting of Dichloromethane and Ethanolamine, was selected in order to obtain data on the molecular interaction between their constituent particles.

R. K. Kolhe et al.,(2020)[32] proposed that the viscosity (η**),** density (ρ) and ultrasonic velocity (U) of dimethylsulphoxide with 1-Octanol have been measured at different concentrations and temperatures from 303.15K to 318.15K. Above measured data is used to calculate the parameters like adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), free volume (V_f), and available molar volume (Vα). These calculated parameters are helpful to explain the strength of interaction among the molecules of liquid binary mixture under investigation. From observed values of ultrasonic speed, viscosity and density of mixture, other parameters such as adiabatic compressibility, acoustic impedance, free length, free volume and available volume for binary mixtures of dimethylsulphoxide with 1-Octanol at various temperatures, it is found that, molecular association is present among the molecules of liquid combinations.

Nabil M. Abdel Jabbar et al.,(2017)[33] proposed that the ultrasonic velocities have been measured for different binary mixtures of common choline chloride-based deep eutectic solvents (DESs), namely, reline, glyceline and ethaline with water, in the range of temperature: 303.15–353.15 K. The experimental data measurements with different mole fractions of DES–water solutions were utilised in fitting four different models for speed of sound. These models correlate the speed of sound with some physical properties such as molar volumes, molar components sound velocity, densities, molecular weights, collision factors etc. A close match was obtained with these models with an average relative error of less than 4% for all data points used. It was observed that the ultrasonic velocity increases with the concentration of DES solvent and decreases with temperature. Moreover, this study roughly indicated that the intermolecular interactions in reline and ethaline aqueous mixtures exist in the form of disruption of dipole–dipole interactions (that varies considerably as a function of DES mixture composition and solution temperature). On the other hand, the interactions on the molecular level in glyceline aqueous solution are mainly due to dipole–dipole intermolecular forces. The speed of sound and density data of different aqueous solutions of three common choline chloride-based DESs were measured as a function of temperature within the range 323.15–353.15 K.

K. P. Singh et al.,(2018)[34] the work presented in this paper deals with the study of thermodynamic properties of new working fluids for absorption machines, mainly for characterization of absorbent–refrigerant pairs that could improve the cycle performance. The study of atomic motion in liquids plays an important role in understanding the solid-like behaviour of liquids. The accurate measurement of the energy changes due to scattering can be used to study the dynamical behaviour of liquids. Measurements of the ultrasonic velocity (u), density (ρ) and viscosity (η) for binary mixtures of polyethylene glycol 250 dimethyl ether with 1-propanol and 1-butanol have been made at three temperatures (T = 293, 303 and 313 K) over the entire composition range in order to investigate the nature of intermolecular interactions between the components of these liquid mixtures. Non-linear variation of derived quantities with the mole fraction supports the molecular interaction occurring between component molecules. From above studies, it is concluded that presence of strong interaction through hydrogen bonding between unlike molecules is characterised by non-linear behaviour of excess values of Gibbs's free energy of activation for viscous flow (ΔG^{*E}) and internal pressure (π_i^E).

N. P. Mohabansi et al.,(2020)[35] discovered that the Density(ρ), Viscosity(η), Ultrasonic Velocity(U) and Surface Tension(γ) of an aqueous-consolute, Na2SO4 solution of [2-(dimethylamino)-1-(4-methoxyphenyl) ethyl] cyclohexan-1-ol (Venlafaxine) 0.0201,0.0402,0.0804,0.1608 mol/kg were measured at 293.15, 303.15 and 313.15K. The resulting data were used to calculate various acoustical parameters, acoustic impedance (Z), adiabatic compressibility (β), Intermolecular free length (L_f), Wada's Constant (W), Rao's Constant (R), free volume (V_f), Relative Association (RA) were calculated which provides valuable information regarding drug-electrolyte (Na2SO4) interaction. The excess parameters viz. partial molar volume and excess adiabatic compressibility (β^E), excess inter molecular free length (L_f^E), excess free volume (V_f^E) were also calculated. These calculations help in predicting the intermolecular interactions. In an aqueous 2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]cyclohexan-1-ol and co-solute Na2SO4 solution, ultra-sonic velocity, density, viscosity and surface tension are measured at 293.15, 303.15 and 313.15K.

S. R. Dandwate et al.,(2018)[36] in the present studyattempt has been made to determine acoustic and thermodynamic parameters for binary liquid mixture of DMSO with methanol at 295.15 K, 300.15 K, 305.15 K, 310.15 K and 315.15 K temperatures. The excess values of isentropic compressibility, acoustic impedance, and internal pressure have been calculated using experimental data of ultrasonic velocity, density and viscosity. Molecular interactions in mixture form have been discussed depending upon deviations in excess values. Experimental data have been validated using Redlich-Kister polynomial equation. The values of excess isentropic compressibility have been found negative over entire concentration range at all temperatures.

P. S. Syed Ibrahim et al.,(2019)[37] deal the values of ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary liquid mixtures containing meta methoxy phenol and 1-propanol in n-hexane at different temperature 303 K,308 K and 313 K at a fixed frequency of 2MHz., experimentally. Using the experimental data of velocity, density and viscosity, various acoustical and thermodynamical parameters like Gibb's free energy, entropy, molecular interaction parameter, stability constant and excess property like solvation number are either calculated or computed. All these parameters have been discussed to throw light on intermolecular interactions between the component of ternary mixtures. The dependence of excess property in particular solvation number of the ternary mixture is compared and discussed in the context of intermolecular interaction and other factors. The result is interpreted in terms of molecular interactions under the influence of ultrasonic sound. From this present study it is concluded that the values of solvation number support the molecular reactions rather than the ionic reactions and henceforth interaction will be allowed due to dipole-dipole interactions and dipole – induced dipole interactions and nature of the hydrogen bonding and some extent due to steric effect of the substituent present in the benzene ring between MMP and 1- propanol in n hexane and these facts are substantiated by the values of thermodynamic properties such as ΔG^0 & ΔS.

V. Vanathi et al.,(2019)[38] proposed that the ultrasonic velocity (U), density (ρ), viscosity (η) for the ternary mixture of benzene þ chloroform þ cyclohexane in the whole range of composition has been carried out at various temperatures 303.15, 308.15 and 313.15K. From the measured parameters U, ρ and η, some derived parameters β, Lf, Vf, πi, Z, R,W with molar enthalpy (Hm) and apparent molar volume (ϕv) are also estimated. The decreasing trend of η, R,W, Hm, and ϕv with concentrations and other parameters are in increasing trend were observed. The trend of acoustical and physico-chemical parameters confirm the dynamics of molecules at higher temperature and the magnitude of intermolecular interactions among the constituents of the mixtures always reflects the nature of substance. The role of enthalpy and apparent molar volume has been used to determine their thermal response. The sign and magnitude of these properties are evident for the nature of interactions between component molecules. In summary, the ultrasonic velocity, density and viscosity measurements on ternary organic mixtures at various temperatures are carried out.

Sudhir P. Dange et al.,(2020)[39] reported that the Ultrasonic velocity (u), density (ρ) and viscosity (η) at 2 MHz in the binary mixtures of Riboflavin with methanol in the concentration range (0 to 0.1 M) and at temperature of 298K using ultrasonic interferometer technique. The experimental parameters, ultrasonic velocity, density and viscosity were used to calculate various acoustic and thermodynamic parameters. The obtained results support the nature and strength of molecular interaction, Physico-chemical behaviour in the binary liquid mixture of Riboflavin and Methanol. The Non-linear variation of thermo-acoustical parameters with molar concentration reveals that, there exist intermolecular forces in the binary liquid mixture of Riboflavin and methanol.

Pallavi B. Nalle et al.,(2019)[40] discovered that the ultrasonic velocity, density and viscosity of drug *Piperine* with MgCl2 have been measured as a function of number of moles n = (0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) at 323.15 K, 328.15 K and 333.15 K. The experimentally collected data have been used to calculate various acoustical, thermodynamic and excess

parameters such as excess values of adiabatic compressibility, excess intermolecular free length, excess specific acoustic impedance, excess relaxation amplitude and excess relaxation time have been calculated. Above excess

parameters are fitted to the Redlich-Kister equation. The results of acoustical, thermodynamic and excess properties reveal the existence of strong molecular interaction in the mixtures. The drug works as a structure breaker (it breaks the structure of MgCl2) and there is ion formation in the system. Acoustic, thermodynamic and excess parameter of mixture reflects the structural deformation in terms of intermolecular interaction. As the isentropic compressibility goes on increasing in a negative manner, the prepared solvent mixture maleic acid and methanol (60/40) can be used for the bleaching purpose of coconut coir fibres.

T Karunakar et al.,(2013)[41] revealed that the ultrasonic velocity and density measurements for binary mixtures of aniline + 1-butanol at T= (303.15 – 318.15) K, are conducted at atmospheric pressure. Some thermo acoustical parameters like adiabatic compressibility (β), molar volume (V_m), inter molecular free length (L_f) and acoustic impedance (Z) have been calculated from experimental measurements. The results have been used qualitatively to explain the molecular interaction between the components of these mixtures. Further, the results are further supported by FT-IR spectra. From the data of ultrasonic velocity and density various acoustical parameters of the mixtures of aniline with 1-butanol at 303.15, 308.15, 313.15 and 318.15 K were calculated.

R. C. Verma et al.,(2014)[42] proposed that Density, Ultrasound velocity and viscosities of Ethyl propionate with butanol-1 and pentanol-1 have been measured over entire range of composition at 308 K and atmospheric pressure. The computed acoustic and thermodynamic properties of Ethyl propionate in higher alcohols will give the excess values of issentropic compressibility, molar volume and viscosity. The excess value will decided the nature and extent of molecular interaction of Ethyl propionate in butanol-1 and pentanol-1.

L. Palaniappan et al.,(2020)[43] proposed that the ultrasonic velocity, density and viscosity measurements carried out for the binary mixtures of toluene, m-xylene with some butanols at 303 K. Various theoretical models have been applied to these binary systems; evaluate the sound velocity values and compared with the experimental values. The validity of Nomoto theory (NT), Van Deal-Vangeal (IMR) and Free length theory (FLT) is checked and a comparative study of the above models is made. The non-ideal behaviour of the system is explained in terms of molecular interactions of the constituents of the mixture. The interactions further, evident with percentage deviation, molecular interaction parameter and goodness fit test. Among the three theories taken up for the prediction of sound velocity, Namoto Relation is found to yield excellent comparison with the experimental value for the systems investigated.

Sk. Md Nayeem et al.,(2015)[44] proposed that the ultrasonic velocities, u, and densities, q, of binary liquid mixtures of dimethyl sulphoxide (DMSO) with ketones such as acetophenone (AP), cyclohexanone (CH), and 3-pentanone (3P), including pure liquids, over the entire composition range have been measured at 308.15 K. Using the experimental data, deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess molar volume, V_m^E, excess intermolecular free length, L_f^E and excess acoustic impedance, Z^E, partial molar volumes, $V_{m,1}$, $V_{m,2}$, and excess partial molar volumes, $V^E_{m,1}$, $V^E_{m,2}$, have been calculated. Molecular interactions in the systems have been studied in the light of variation of excess/deviation values of calculated properties and these properties have been fitted to Redlich–Kister type polynomial equation. The observed positive values of V_m^E, Δk_s, L_f^E and negative values of Δu, Z^E for all the binary liquid mixtures studied clearly indicate the presence of the dominance of weak physical interactions between the components of molecules. Further, FTIR spectra support the conclusions drawn from deviation/excess properties. Moreover, theoretical values of ultrasonic velocity in the mixtures have been evaluated using various theories and such values were compared with experimental velocities to verify the applicability of such theories to the systems investigated.

Subhraraj Panda(2020)[45] proposed that the measurement of ultrasonic velocity is helpful to interpret solute-solute, solute-solvent interaction in aqueous medium. The ultrasonic speed (U), density (ρ) and viscosity (η) at 313 K have been determined using ultrasonic interferometer at four different frequencies *i.e.* 1MHz, 5MHz, 9MHz and 12 MHz, pycnometer and Ostwald's viscometer of dextran in aqueous medium respectively. All the three measurements were carried out in a water bath of constant temperature with an uncertainty of ±0.1 0C. The derived acoustical parameters such as free volume (Vf,), internal pressure (πi), absorption coefficient (α), molar sound velocity (R) and molar sound compressibility (W) have been determined from experimental data. The outcomes are described in terms of molecular interaction between the solution components. Ultrasonic speed, density and viscosity have been measured for aqueous dextran solution at different frequencies in constant temperature.

R. Chithra Devi et al.,(2019)[46] proposed that the density (ρ), viscosity and ultrasonic velocity (u) in ternary liquid mixture of acrylonitrile (AN) with benzene in N-N-di methyl aniline have been measured at (303,308 and 313)K respectively, over the entire composition range by using an ultrasonic interferometer for measuring velocity at 2MHz frequency. From the experimental data various acoustical and thermodynamical parameters such as; adiabatic compressibility(β), Intermolecular free length (Lf), Specific acoustic Impedance (Z), relative association(RA) and molar sound velocity have been computed using the standard relations. The results have been analysed on the basis of variation in thermodynamic parameters. These parameters are found to be very sensitive in exploring the interaction between the component molecules, which enable to have better understanding of the liquid mixtures. Since the system show similar trends for evaluated parameter so the constituent ternary mixture at different temperatures. The results have been interpreted in terms of dipole induced dipole interaction. The results obtained for the present study indicates that the molecular interaction is present in the liquid mixtures.

Chapter III

Materials and Methods

3.1 Introduction:

Ultrasonic, thermo-physical and thermodynamic properties of liquid mixtures are of great significance in obtaining an in depth knowledge of inter and intra-molecular interactions, structural and physiochemical behavior and also in verifying various liquid state theories which attempt in estimating the properties of liquid mixtures. Systematic study of thermodynamic properties of solutions with a new type of multi-frequency ultrasonic interferometer is done for precise measurement of the velocity of sound in liquids. The path length in the cell is varied by motion of a reflector, at the electrical reaction of the cell upon the oscillator is used to fix standing wave position at a standard frequency, and their locations are determined with a suitable cathetometer.

An investigation in the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been found to be an excellent quantitative way to elicit information about molecular structure and intermolecular forces in liquid mixtures. This has given impetus to the theoretical and experimental investigation of excess thermodynamic properties of liquid mixtures. Measurement of physiochemical properties such as density and ultrasonic velocity of pure components and their binary mixtures are being increasable used as tools for investigations of the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures. The significance reasons for the study of thermo-physical and thermodynamic properties of multi-component liquid mixtures are as follows:

- They provide way for studying the physical forces acting between molecules of different species.
- The study of liquid mixtures provides appearance of new phenomena, which are absent in pure liquids. The most interesting of these are the new types of phase equilibria, which are introduced by the variation in the promotion of the pure components.
- Liquid mixtures are the most direct source for studying the various parameters. The study of thermo-physical and thermodynamic properties of liquid mixtures helps in obtaining in depth knowledge about molecular interactions.

3.2. Theory:

Ultrasonic interferometer is a simple and direct device which yields accurate and consistent data, from which one can determine the velocity of ultrasonic sound in a liquid medium with a high degree of accuracy. A crystal-controlled interferometer (model M-83S) supplied by Mittal Enterprises, New Delhi, operating frequency 2 MHz has been used to measure the ultrasonic velocity.

3.3. Ultrasonic:

Ultrasonic sound refers to sound pressure with a frequency greater than the human available range (20 Hz to 20 KHz). When an ultrasonic wave propagates through a medium, the molecules in that medium vibrate over short distance in a direction parallel to the longitudinal wave. During this vibration, momentum is transferred among molecule. This causes the wave to pass through the medium.

3.4. Ultrasonic Interferometer:

An Ultrasonic Interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy.

Fig 1: Experimental setup for ultrasonic interferometer.

The salient features of ultrasonic interferometer are given below:

- It is a simple in design, rugged and gives very accurate and reproducible results.
- Experiments may be performed over a wide range of temperature from -30 ^{0} C to +80 ^{0} C on all liquids except those which reacts with the plating of cell and crystal.
- Nearly 10 ml of experimental liquid is required.
- There is no danger of any change such as depolymerisation, due to ultrasonic effect since a very small ultrasonic energy is required.

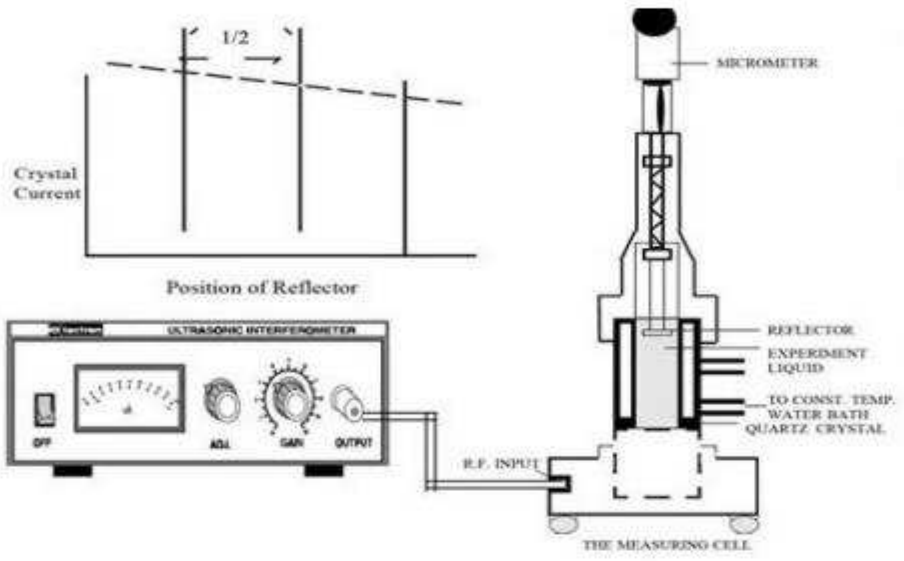


Fig 2: Cross section of the liquid cell and graph plotted position of reflector versus crystal current.

In an ultrasonic interferometer, the ultrasonic waves are produced by the piezoelectric methods. At a fixed frequency variable path interferometer, the wavelength of the sound in an experimental liquid medium is measured, and from this one can calculate its velocity through that medium. The ultrasonic cell consists of a double walled brass cell with chromium plated surfaces having a capacity of 10 ml. The double wall allows water circulation around the experimental liquid to maintain it at a known constant temperature. The micrometer scale is marked in units of 0.01 mm and has an overall length of 25 mm. Ultrasonic waves of known frequency are produced by a quartz crystal which is fixed at the bottom of the cell. There is a movable metallic plate parallel to the quartz plate, which reflects the waves. The waves interfere with their reflections, and if the separation between the plates is exactly an integer multiple of half wave length of sound, standing waves are produced in the liquid medium. Under these circumstances, acoustic resonance occurs. The resonant waves are a maximum in amplitude, causing a corresponding maximum in the anode current of the piezoelectric generator. The ultrasonic interferometer consists of the following mainly two parts:

3.4.1. The high frequency generator.

3.4.2. The measuring cell.

3.4.1. The high frequency generator

The high frequency generator is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the "measuring cell". A micrometer to observe the changes in current two controls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the high frequency generator.

3.4.2. The measuring cell

The measuring cell is specially designed for maintaining the temperature of the liquid constant during the experiment. A fine digital micrometer screw (LC 0.001 mm) has been provided at the top, which can lower or raise the reflector plate in the liquid within the cell through a known distance. It has a quartz crystal fixed at its bottom.

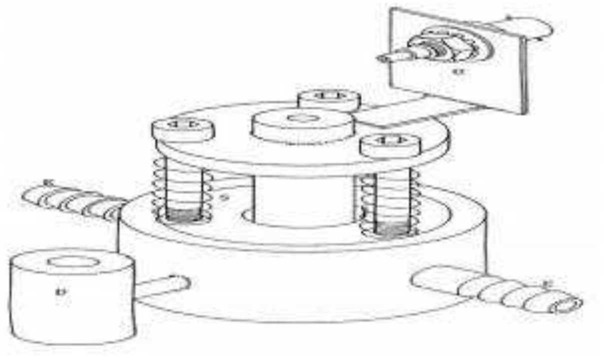


Fig 3: Ultrasonic interferometer cell liquid mixtures.

3.5: Working principle

The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ)in the medium. Ultrasonic waves of known frequency (f) are produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator become a maximum. If the distance is now increased or decreased and the variation is exactly one-halfwavelengths$(\lambda/2)$ or multiple of it, anode current become maximum from the knowledge of wavelength (λ) the velocity (U) can be obtained by the relation:

Velocity = Wavelength × Frequency $U = \lambda \times f$ (1)

3.6: Adjustment of ultrasonic interferometer

For initial adjustment two knobs are provided on high frequency generator, one is marked with "ADJ" to adjust the position of the needle on the ammeter and the knob marked "GAIN" is used to increase the sensitivity of the instrument for greater deflection, if desired. The ammeter is used to notice the number of maximum deflection while micrometer is moved up or down in liquid.

3.7. Procedure

- Unscrew the knurled cap of cell and lift it away from double walled construction of the cell. In the middle position of it pour experimental liquid and screw the knurled cap. Wipe out excess liquid overflowing from the cell.
- Insert the cell in the heavy base socket and clamp it with the help of a screw provided on its side. 7.3 Connect the high frequency generator with cell by coaxial cable provided with the instrument. In ultrasonic interferometer frequency selector knob should be positioned at desired frequency (same frequency as that of liquid cell chosen).
- Move the micrometer slowly in either clockwise or anticlockwise direction till the anode current on the ammeter on the high frequency generator shows a maximum or minimum.
- Note the reading of micrometer corresponding to the maximum or minimum (which is sharper) in micro ammeter. Take about 50 reading of consecutive maximum or minimum and tabulate them. 7.6 Take average of all differences ($\lambda/2$).
- Once the wavelength (λ) is known the velocity (U) in the liquid can be calculated with the help of the relation.

3.8. Sample calculations Sample:

Water Average ($\lambda/2$): 0.375mm.

Ultrasonic velocity in sample: $U = \lambda \times f = 1480$ m/sec.

Density of the liquid = 996.458 Kg/m3

Adiabatic compressibility (ŧad) = 1/ρv2 = 1/996.458 ×(1480)2

ad = 4.58 × 10-10 N/m2 .

3.9. Measurement of the density:

The density (ρ) of the liquid mixture was determined by a specific gravity bottle of 25ml capacity .The specific gravity bottle with the liquid mixture was immersed in a temperature controlled water bath. The density was determined using the relation:

$\rho_2 = (w_2/w_1)\rho_1$

where w_1,w_2,ρ_1 , and ρ_2 are masses of distilled water, mass of the liquid mixture, density of distilled water , and density of liquid mixture ,respectively.

. Measurement of viscosity

The viscosity measurements were done through Ostwald’s viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. The water in the viscometer is allowed for some time to attain the experimental temperature. Using a suitable arrangement, the water is sucked above the marked level and then it is allowed to flow freely. The time taken for the flow of water is noted. The water is replaced with a mixture, whose viscosity is to be determined. Using the same procedure, the time taken for flow of liquid mixture at the experimental temperature was determined. Using the time taken for the distilled water and mixture, the viscosity of unknown liquid mixture is determined:

ϥs / ηw = ρs/ ρw × ts/ tw (2)

Where ηw, ρw and tw are the viscosity, density and time flow of water respectively and ɋs, ρs and ts are the viscosity, density and time flow of unknown liquid mixture respectively. Viscosity is an important transport property for process design in petroleum, petrochemical, chemical and other chemical industries involving fluid transportation, mixing agitation, heat exchange and concentration. The estimation of the viscosity of a mixture is more difficult than of the pure compound. The prediction of the viscosity of liquid mixtures is a goal of long standing with both experimental and theoretical importance. Many industrial, chemical processes or laboratory works need experimental data of viscosity at any given temperature and composition for the liquid mixtures

3.9 Theoretical methods for the estimation of acoustical thermodynamic parameters of liquid and liquid mixtures

3.9.1Adiabatic Compressability (β_a)

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation;[47]

$\beta_{ad} = 1/\nu[\partial\partial\nu/\partial\partial p]$ (3.3)
It can also be calculated from the speed of sound (U) and the density of the medium (ρ) using the equation of Newton Laplace as;
$\beta_{ad} = 1/u\rho_2 Kg_{-1}\, ms_2$ (3.4)

3.9.2.**Ultrasonic velocity(U)**

characterizing of thermodynamic and physio-chemical aspects of ternary liquid mixtures. A variety of empirical,semi-empirical and statistical theories in liquid are available in the literature for evaluating ultrasonic velocity in liquids and liquid mixtures.

3.9.3.Free volume (v_f)

Free volume is one of the significant factors in explaining the variation in the physio-chemical properties of liquid and liquid mixture. The free space and its dependence properties have close connection with molecular structure and it may show interesting features about interaction, which may occur when two or more liquids are mixed together .This molecular interaction between like and unlike molecule are influenced by structural arrangements along with shape and size of the molecules.

A liquid may be treated as if it were composed of individual molecules each moving in a volume V_f in an average potential due to its neighbors. That is, the molecules of a liquid are not closely packed and there are some free spaces between the molecules for movement and the volume V_f is called the free volume. Eyring and Kincaid defined the free volume as the effective volume in which particular molecule of the liquid can move and obey perfect gas laws. Free volume in terms of Ultrasonic velocity (U) and the Viscosity of the liquid (η) as,

$V_f = [M_{eff}U/K\eta]^{1/2}$ (29)

Where

M_{eff} is the effective molecular weight.

$M_{eff} = M_iX_i$ in which M_i and X_i are the molecular weight and the mole fraction of the individual constituents respectively.

K is a temperature independent, constant which is equal to 4.28×10^9 for all liquid.

3.9.4.Intermolecular free length (L_f)

The intermolecular free length is the distance covered by sound wave between the surfaces of the neighboring molecules. It is measure of intermolecular attractions between the components in binary mixture .The increases or decrease in free length indicates weakling and strengthen of intermolecular attraction .As the ultrasonic velocity increase due to the increases in concentration , the interaction free length has to decrease and vice-versa .It is related to ultrasonic velocity and density as;

$L_f = K/(\rho U)^{1/2}m$ (27)

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surface of the neighboring molecules and is given by the relation ,

$L_f = K_T \beta^{1/2}$ (28)

Where , $K_T = (93.875 = 0.345T) \times 10^{-8}$

3.9.5.Relaxation time (τ)

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on the temperature and on impurities .The dispersion of the Ultrasonic velocity in binary mixture reveals information about the characteristic time of the relaxation process that causes dispersion .The relaxation time(τ) can be calculated from the relation

$\tau = 4/3\beta\eta$ (30)

Methanol

Molecular weight – 32.04g/mol

Molecular formula-CH3OH

Density-771.4kg/m^3

Uses

- Methanol is a polar liquid at room temperature
- It is used as antifreeze ,solvent, fuel and as a denaturant for ethanol
- The chemical is also used to produce biodiesel via transesterification reation

Ethanol

Molecular weight -46.07g/mol

Molecular formula –C2H5OH

Density -771.8kg/m^3

Uses

- Ethanol is used extensively as a solvent in the manufacture of varnishes and perfumes.
- In the preparation of errences and flavorings.
- Ethanol is used in many medicines and drugs.

Isopropyl Alcohol

Molecular weight-60.1g/mol

Molecular formula –C3H8O

Density –772.2kg/m^3

Uses

- It's used to treat heart problem ,help with anxiety and prevent migraines
- Used to treat high blood pressure

Test-Butanol

Molecular weight -74.121g/mol

Molecular formula-C4H10O

Density –759.8

Uses

- butanol is used as a solvent for a wide variety of chemical and textile processes.
- It is also used as a paint thinner and a solvent in other coating application.
- It is also used as a base for perfumes but on its own has a highly alcoholic aroma.

CHAPTER-4

RESULT AND DISCUSSION

Table 4.1: Values of ultrasonic velocity (U),Density(ρ),viscosity(η) for methanol ,ethanol, iso propyl alcohol, tert butanol at 308K

Alcohol	Velocity (ms$^{--1-)}$	Density (Kg m^{-3})	Viscosity (×10^{-4})Nsm^{-2}
Methanol	1076.8	771.4	4.1656
Ethanol	1118.4	771.8	6.5828
Iso-Propyl	1115.2	772.2	12.766
Tert-Butanol	1090	759.8	19.062

Table 4.2: Values of adiabatic compressability (β_{ad}),free length (L_f) ,free volume (V_f),internal pressure(Πi) for methanol,ethanol,iso-propyl alcohol, tert-butanol for 308K.

Alcohol	Compressibility ($\times 10^{-09}$)m^2N^{-1}	Free Length ($\times 10^{-11}$)m	Free Volume ($\times 10^{-8}$) m^3	Internal Pressure ($\times 10^8$) Nm^{-3}
Methanol	1.11802	7.00084	8.5126	9.7072
Ethanol	1.03586	6.73869	7.8206	7.8409
Propanol	1.04127	6.75627	4.2954	8.0231
Butanol	1.10777	6.96865	3.1162	7.6799

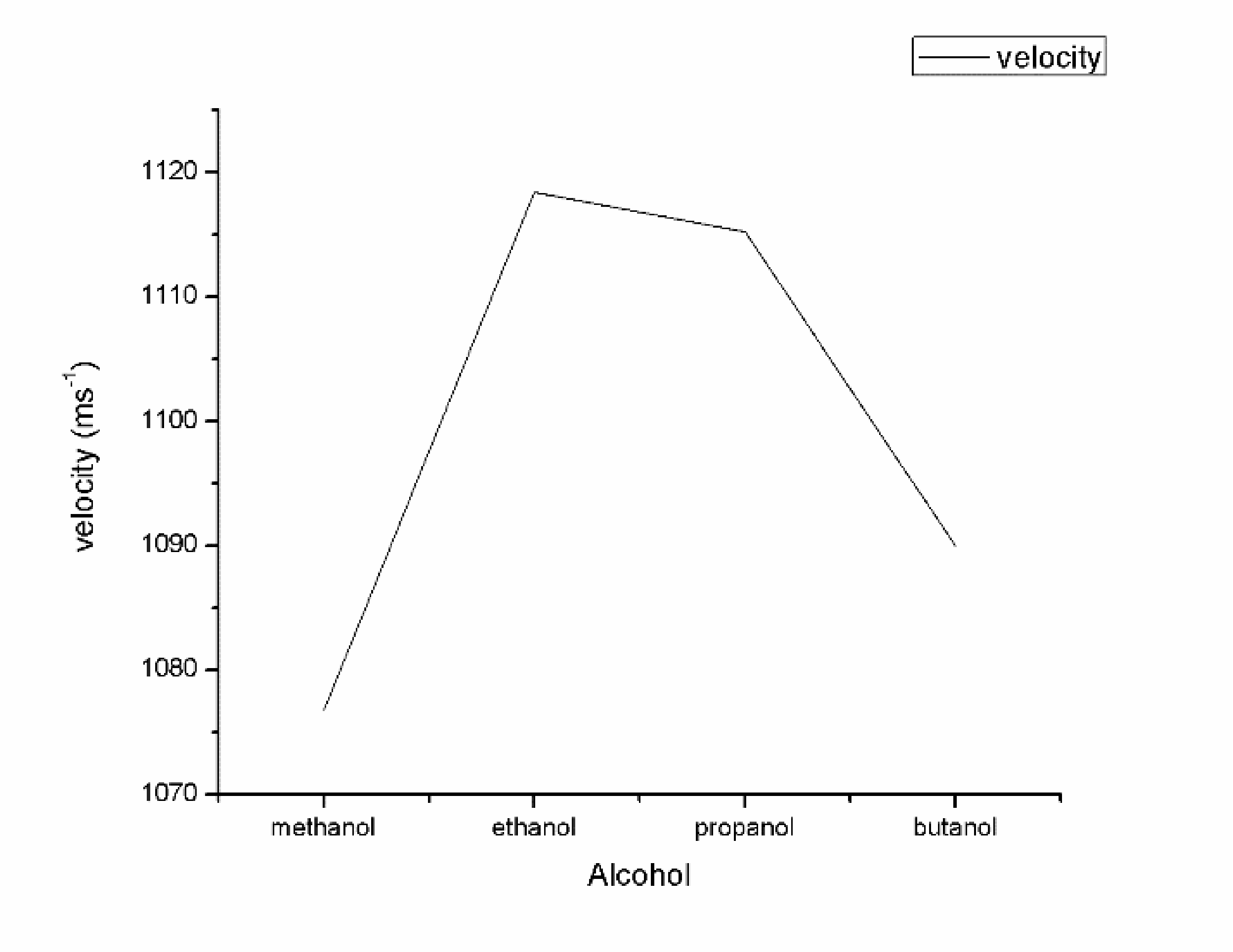


Fig4.1:Alcohol vs velocity

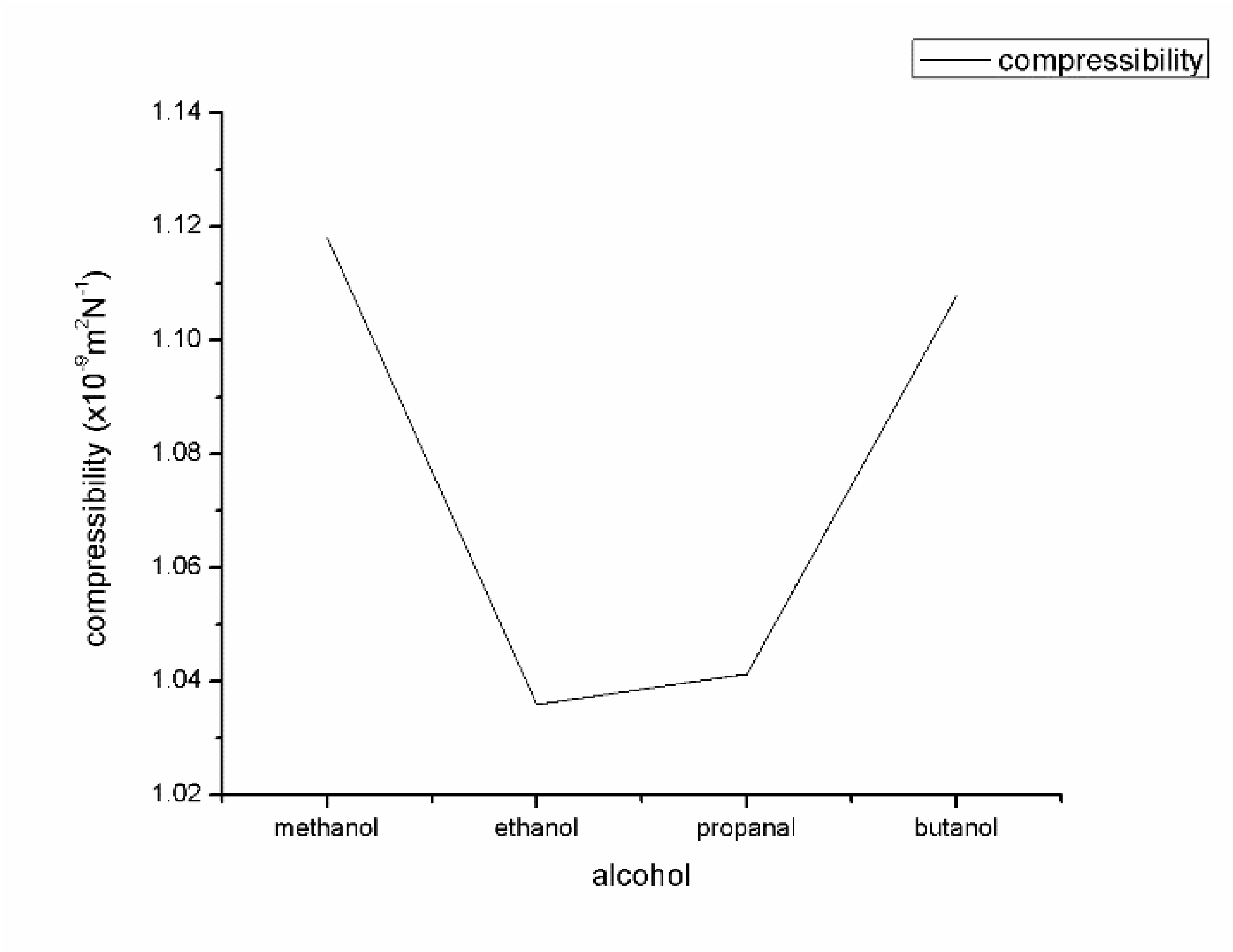


Fig4.2:Alcohol vs compressibility

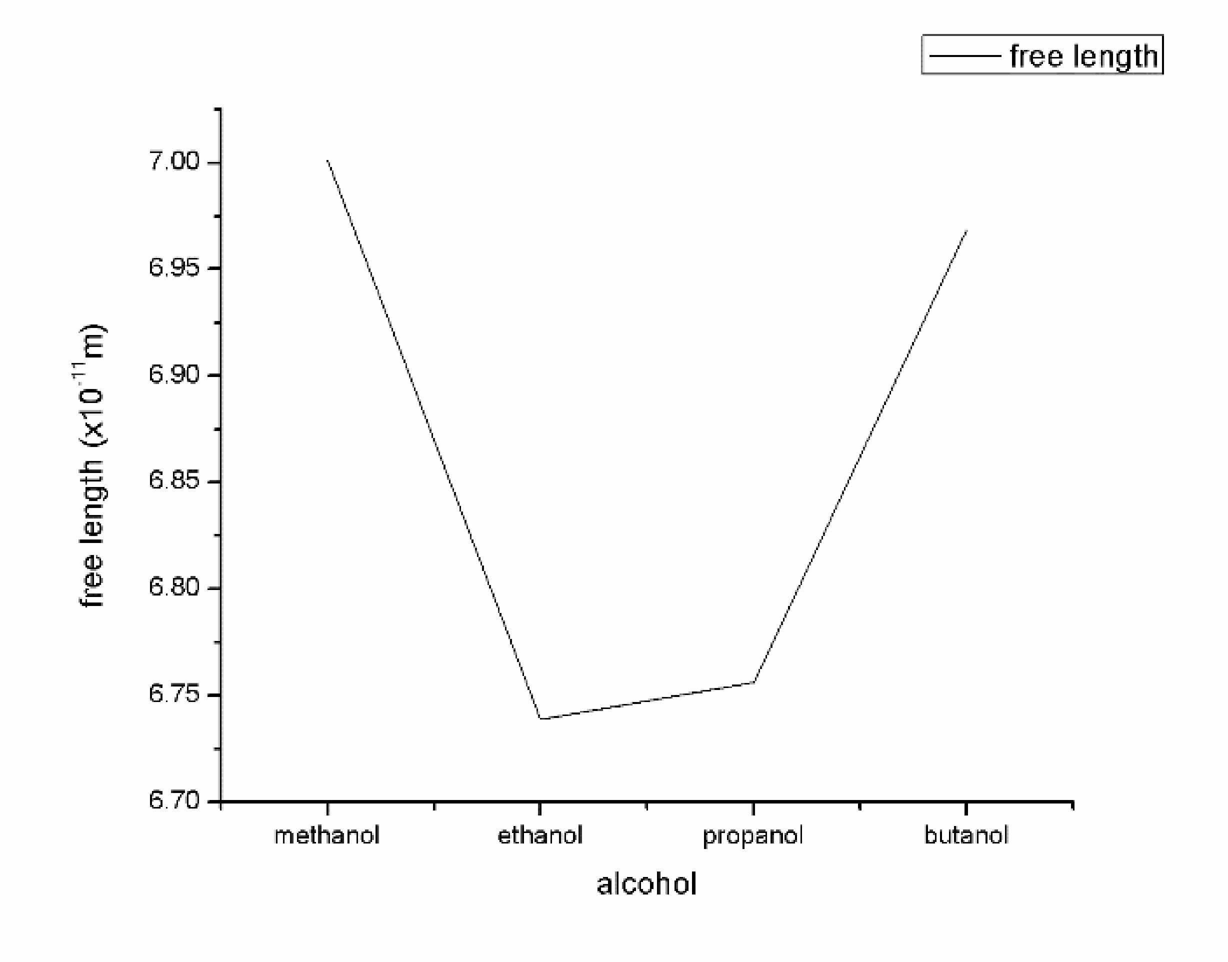


Fig4.3Alcohol vs free length

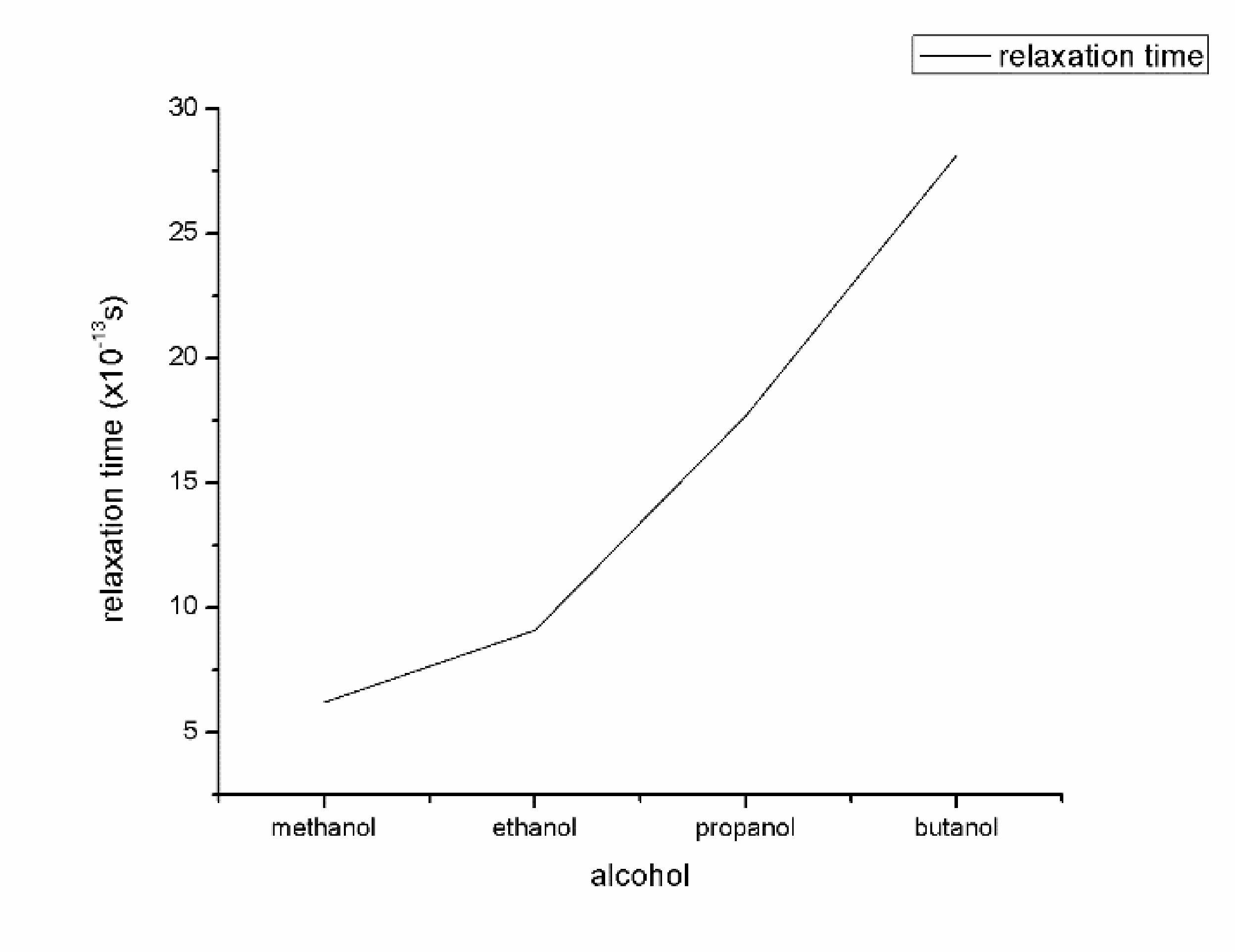


Fig4.4:Alcohol vs relaxation time

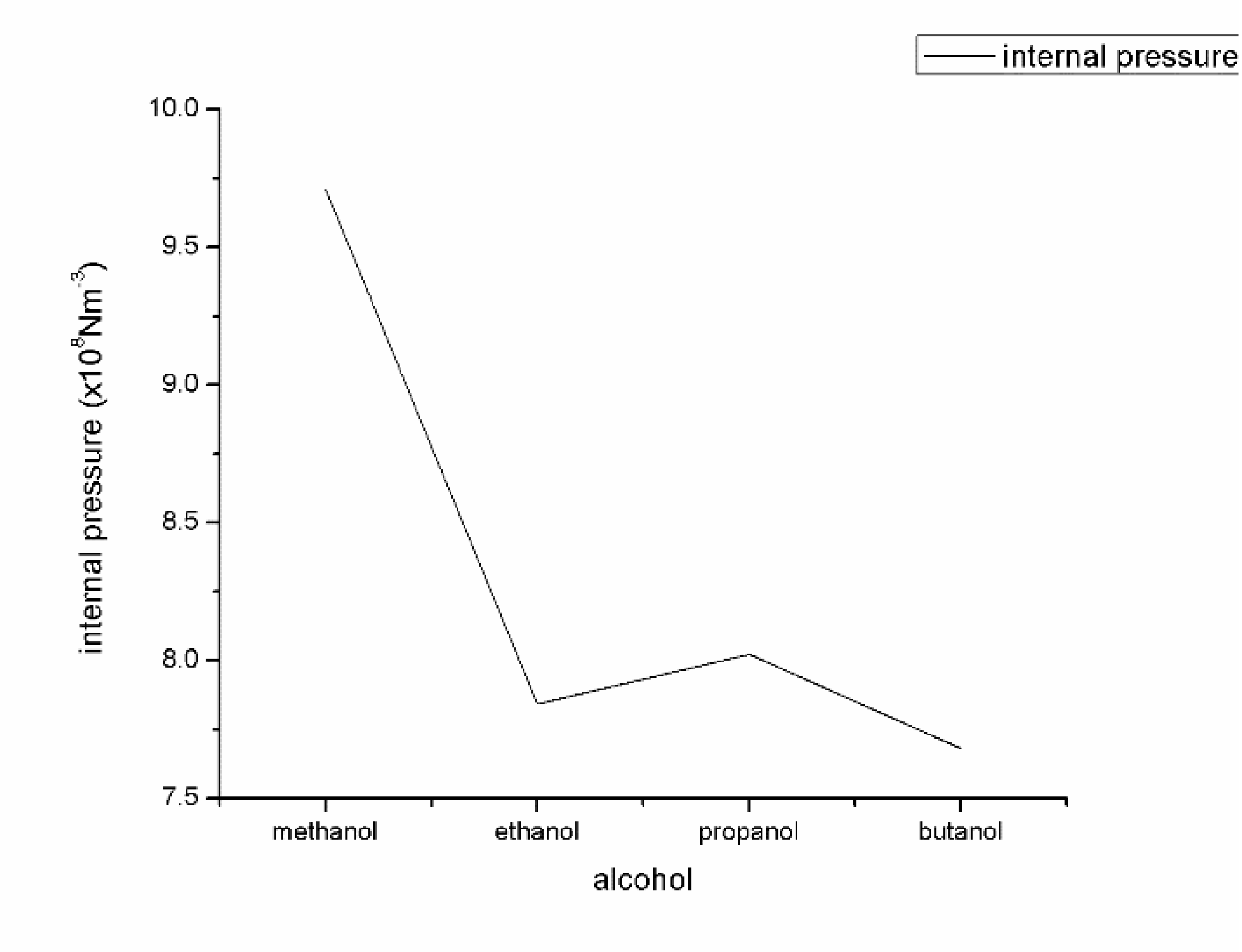


Fig 4.5:Alcohol vs internal pressure

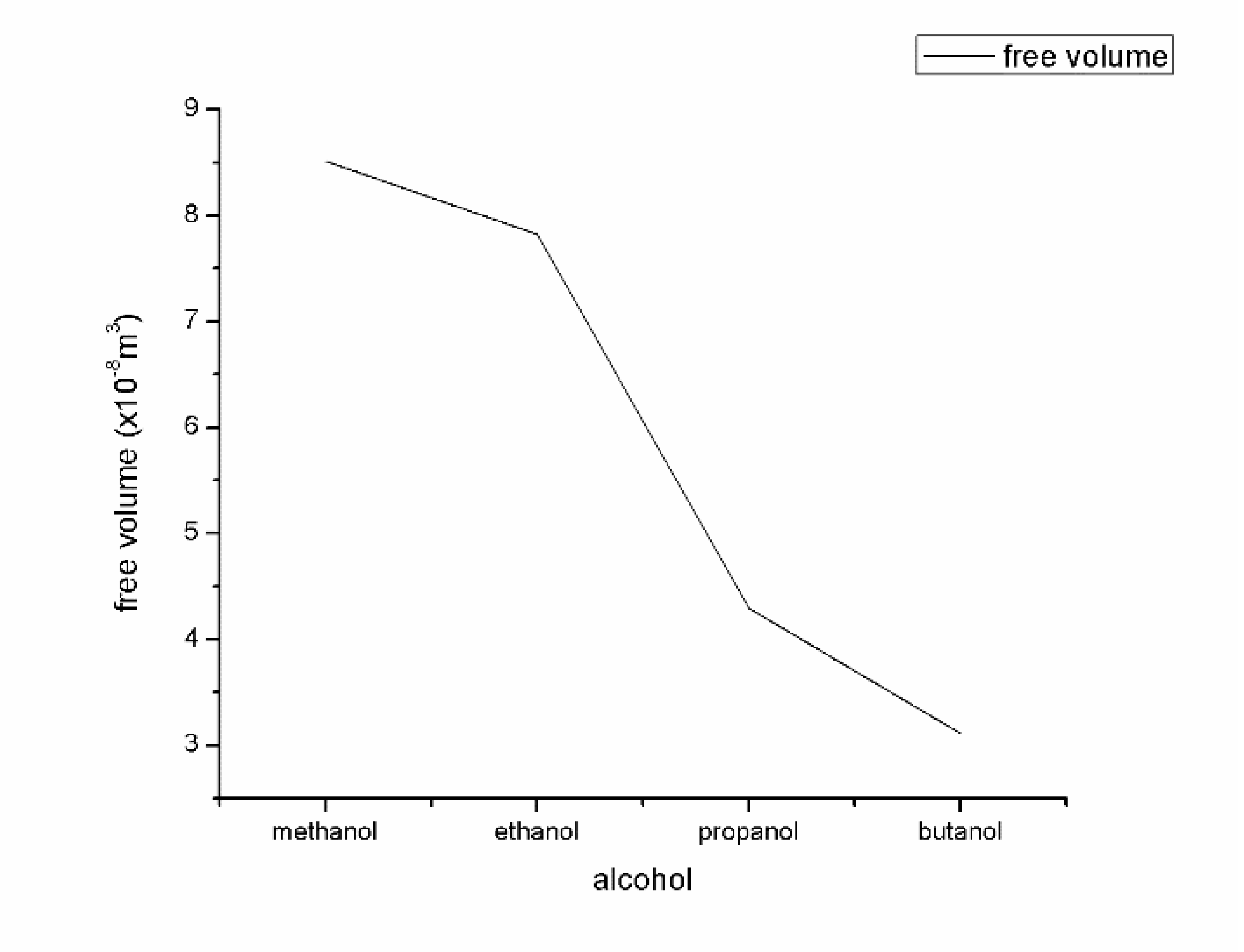


Fig4.6: Alcohol vs free volume

The experimental value Ultrasonic velocity , viscosity , and density at temperature 308K for the liquids methanol, ethanol, iso-propyl alcohol and tert-butanol given in table 4.1. The calculated values of adiabatic compressability, free length ,free volume ,internal pressure are represented in the table 4.2

Fig (4.1) clearly shows that U maximum for ethanol and it is minimum for methanol among the four alcohols. The increase in velocity shows that the molecules are tightly packed.

The variation in adiabatic compressability and free length are represented in fig (4.2&4.3). Further compressability and free length shows an inverse behaviour as compared to the U . It is primarily the compressability that change with the structure and this leads to the change in U.

Among the four alcohols relaxation time is maximum for tert-butanol. It indicates that, when the hydrocarbon molecules increased the relaxation time also increased which is represented in the fig (4.4)

Fig (4.5) gives variation in internal pressure for different alcohols. The internal pressure is a measure of cohesive forces between the constituents molecules in liquids. The internal pressure describes the molecular arrangement in the liquid medium. The internal pressure increase or decrease due to the various degrees of dispersive interaction existing between the component molecules. The internal pressure maximum for methanol

The reverse trend is observed in free volume. Free volume is lesser for tert –butanol and it is higher for methanol which is shown in fig (4.6)

Conclusion:

Acoustic properties of adiabatic compressability, free length, relaxation time, free volume, are determined which explain how these interaction occur &responsible for breaking and making of the structure in the solution . The trends in the variation of parameter derived from ultrasonic velocity, density, viscosity at temperature 308K. Over entire composition range suggest existence of molecules interaction in the chosen binary mixture.

REFERENCE:

1. Warren, B. E. (1937), J. Applied Physics, 8,645.

2. Compton, A. H. And Allison, S. K. 'X-rays in Theory and Experiment' (Newyork: D. Van Nostrand Co., Inc., 1935), pp. 781-782.

3. G. W. Stewart, Phys. Rev., 37, 9(1931); E. Amaladi, Phuysik. Z., 32, 914(1931); H. H. Meyer, Ann. Physek, 5,701(1930); S. Katzoff, J. Chem. Phys; 2, 841(1934); J. D. Bernal and R. H. Fowler, ibid, 1,515(1933); J. Morgan and B. E. Warren, ibid; 6,666(1938).

4. A. Joffe, Ann. Physik, 72, 461 (1923); J. Frenkel, Z. Physik, 35,652 (1926).

5. Oster, G., and Kirkwood, J. G., J. Chem., Phys., II (1943), 175.

6. Smyth, C. P., and Stoops, W. N., J. Am. Chem. Soc., 51(1929), 3330.

7. Philippe, R., and Piette, A. M., Bull Soc. Chem., Belg., 64(1995), 600.

8. Malecli, J., J. Chem., Phys., 43(1965), 1351.

9. Bellamy, L. J., and Pace, R. J., Specitrochim Acta, 22(1966), 525.

10. Copurn, W. C., and Grunwald, E. J., Am. Chem. Soc., 81(1959),6145.

11. Brown, I. Fock, W., and Smit, F., Aust. J. Chem., 17(1964), 1106.

12. Haskell, R. W., Hollinger, H. B and Van Ness, H. C., J. Phys., Chem., 72(1968), 4534.

13. Bordewijk, P., "Fluid Structure and Dielectric behaviour of the mono alcohols", Ph.D., thesis, University of Leiden, 1968.

14. Reddy, K. S., and Naidu, P. R., J. Chem. Thermodynamics(1976), 1208.

15. Prakash, S., Srivastau, S. B., and Prakash, O., Ind. J. Pure and Apopld. Phys., 13(1975), 19.

16. Ravindraa Prasad, K., Ravimahar, E. L., and Reddy, K. G. Acoust, Lett., 4(1981), 170.

17. Subba Rao, S., and Gobala Krishnan, R. Acoust, Lett., 2(1978), 69.

18. Gopal K. And Prabhakara Rao, N. Acoust Lett., 4(1981), 164.

19. Ramanjappa, T., and Raja Gopal, K., Proc. Latl. Sympoium on Acoustis(1986), 57.

20. Sabesan, R., Ramadurai, R and Rangan, R., J. Acoust. Soc. (India), 11(1983), 5.

21. Vradarajan, R., and Bharathi, G., J. Pure and Appl. Ultrasonics, 9(1987), 15.

22. Sabesan, R., Vradarajan, R., and Natarajan, M., Proc. Natl. Symposium on Acoustic, Tiruchy, 1987, 282.

23. P. Vigoureux, Ultrasonics, Chapman and Hall Ltd, London (1952).

24. T. Robert Beyer, V. Stephen Letcher, Physical ultrasonics Academic Press, New York (1969).

25. E. G. Richardoss, Ultrasonic Physics, Elseveir, London (1952).

26. N. V. Temperley and D. H. Trevena, Ellis Horwood Ltd, Liquids and other properties, John wiley and sons, England (1978).

27. A. B. Bhattia, Ultrasonic Absorption , Oxford (1967).

28. Chandra Bhan Singh, Avanesh Kumar and Soran Singh (2012).

29. Dash Ashok Kumar and Paikaray Rita (2014) 'Study of Molecular Interaction in Binary mixture of Dimethyl Acetamide with Diethyl Ether using Ultrasonic and Viscosity probes', Research Journal of Chemical Science vol. 4, No. 3, pp. 45-53

30. Ubagaramary .D, Muthu Vijayan Enich, Mullainathan .S and Kesavaswamy (2018) 'Acoustical properties of molecular interactions in 1-propanol, 1-butanol and 1-pentanol with tetrahydrofuran in cyclohexaone at various temperatures', vol. 29, No. 17, pp. 3276-3281.

31. Nabaparna Chakraborty, Monika Rani and Juglan .K.C (2020) ‘Ultrasonic Investigation of Dichloromethane with Ethanolamine at various temperatures’, vol. 20, pp. 2825-2829.

32. Kolhe .R.K and Bhosale .B.B (2020) ‘Molecular Interaction study in Binary mixtures of DMSO and 1-octanol using ultrasonic method at various concentrations and temperatures’ vol. 11, No. 5, pp. 750-757.

33. Nabil M. Abdel Jabbar and Farouq S. Mjalli (2017) ‘Ultrasonic study of binary aqueous mixtures of three common eutectic solvents’, An International Journal of Physics and Chemistry of Liquids, pp. 1-18.

34. Singh K.P and Singh .S (2018) ‘Thermodynamic and acoustic properties of binary mixtures of PEGDME 250 with 1-propanol and 1-butanol at 293, 303 and 313 °K’, An International Journal of Physics and Chemistry of Liquids, pp. 1-21.

35. Mohabansi N.P, Satone A.K, Gulafsha A.I. Sheikh and Komal Vairagade (2020) ‘Excess Thermodynamic Parameters of 1-[2-(Dimethylamino)-1-(4-Methoxyphenyl)Ethyl] Cyclohexan-1-ol in aqueous Na_2SO_4’, International Journal of Researches in Biosciences, Agriculture and Technology, vol. 3, No. 8, pp. 26-34.

36. Dandwate S.R and Deshmukh S.B (2018) ‘Excess Thermodynamic properties of Binary liquid mixtures of DMSO with Methanol at different temperatures’, International Journal of Universal Print, vol. 4, No. 4, pp. 196-201.

\

Syed Ibrahim P.S, S. Chidambaravinayagam, J. Senthil Murugan and J. Edward Jeyakumar (2019) ‘Studies on some Acoustical and Thermodynamic properties of Ternary liquid mixtures of Meta Methoxy Phenol (MMP), 1-propanol and n-Hexane at different temperatures using ultrasonic techniques’, Journal of Information and Computational Science, vol. 9, No. 7, pp. 391-399.

37. V. Vanathi, S. Mullainathan, S. Nithiyanatham, V. Ramasamy and L. Palaniappan (2019) ‘Ultrasonic velocity, density, viscosity for the ternary mixture of (benzene+Chloroform+Cyclohexane) at different temperatures’, pp. 1-6.

38. Sudhir P. Dange and Omprakash P. Chimankar (2020) ‘Molecular Interaction study in Binary mixture of Riboflavin with Methanol at 298K’, vol. 7, No. 2, pp. 555-557.

39. Pallavi B. Nalle, R.G. Dorik and K.M. Jadhav (2019) ‘Acoustical and excess parameter studies of piperine with $MgCl_2$’, Journal of Pure and Applied Ultrasonics, vol. 41, No. 2, pp. 27-35.

40. T Karunakar, CH Srinivasu and K Narendra (2013) ‘Thermo Acoustic and Infrared study of Molecular Interactions in Binary mixture Aniline+1-butanol’, Journal of Pure and Applied Physics, vol. 1, No. 1, pp. 5-10.

41. R.C. Verma and Vinod Kumar Yadav (2014) ‘The study of Excess molar volume and deviation in viscosity of binary mixtures of Ethyl Propionate.

42. L. Palaniappan and S. Nithiyanantham (2020) ‘Molecular Interactions from the Experimental and Validation with Estimated Theoretical sound velocity’, pp. 277-285.

43. SK. Md Nayeem, M. Kondaiah, K. Sreekanth and D. Krishna Rao (2015) ‘Acoustic and volumetric investigatuins in aromatic, cyclic and aliphatic ketones with dimethyl sulphoxide at 308.15K’, Arabian Journal of Chemistry, pp. 1-12.

44. Subhraraj Panda (2020) ‘Ultrasonic study on dextran in aqueous media at 313K at different frequencies’, Adalya Journal, vol. 9, No. 3, pp. 456-462.

45. R. Chithra Devi and R. Mathammal (2019) ‘Thermodynamic Behaviour of Ternary mixtures of Acrylonitrile in Benzene with N-N-dimethyl aniline at 303K, 308K and 313K’, vol. 8, No. 12, pp. 158-165.

46. Nikam PS and Hasan Mehdi ‘Ultrasonic velocity and adiabatic compressability of Monochloric acetic acid in aqueous ethanol at various temperatures’, Journal of Chemical and engineering Data. 1988; 88: 165-169.

47. Nikam PS and Hasan Mehdi ‘Ultrasonic velocity and apparent molar compressability of trichloroacetic acid in aqueous ethanol’, Asian Journal of Chemistry, 1993; 5(02): 319-321.

48. Venkateswarlu .P and Raman GK. 'Sound velocities and isentropic compressabilities of 1,2-dibromethane+Ketone at 303.15K', Journal of Pure and Applied ultrasonics, 1985; 7(02): 31-34.

49. Reddy Raveendranatha .K, Rama Murthy .S, Moorthy Rama .L 'Free volume and internal pressure study in aqueous solutions of methylene blue and auramine', The Journal of Acoustical society of India, 1991; 19(4): 22-25.

50. Kumar Naidu Vijaya .B, Rao Sadasiva .A and Rao Chowdoji 'Polyglycols in formamide solutions', Journal of Acoustical society of India, 2000; 28(1-4): 297-300.

51. Reddy Raveendranatha .K, Rama Murthy .S, Moorthy Rama .L 'Free volume and internal pressure study in aqueous solutions of methylene blue and auramine', The Journal of Acoustical society of India, 1991;

FABRICATION OF NANOCOMPOSITE USING POLYPYRROLE/TITANIUM DIOXIDE

A project report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

A.MAHA SORNA

Reg. No: 19SPPH05

Under the supervision and guidance of

Mrs. L. SMILA M.Sc., M. Phil.,

DEPARTMENT OF PHYSICS

ST.MARYS'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to verify that this project work entitled **"FABRICATION OF NANOCOMPOSITE USING POLYPYRROLE/TITANIUM DIOXIDE "** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year 2020 -2021 by

A.MAHA SORNA **Register No: 19SPPH05**

Signature of the Guide

Signature of the SSC Coordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomo
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21

Signature of the Examiner

DECLARATION

I hereby state that the field project report entitled, **"FABRICATION OF NANOCOMPOSITE USING POLYPYRROLE/TITANIUM DIOXIDE"** is submitted to **ST.MARYS'S COLLEGE(AUTONOMOUS),THOOTHUKUDI.** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY TIRUNELVELI ,** for the award of the Degree of Master of Science in Physics is my unique work and no part of this project has been submitted for any Degree, Diploma or other similar titles.

Station : Thoothukudi **A.MAHA SORNA**

Date : **Signature of the student**

CONTENTS

ABSTRACT

Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost.Pyrrole and its derivatives are widely used as an intermediate in synthesis of pharmaceuticals,medicines,agrochemicals,dyes,photographicchemicals, perfumes and other organic compounds. Titanium dioxide (TiO_2) is mostly introduced into the environment as nanoparticles via wastewater treatment plants.Cosmetic pigments including titanium dioxide enter the wastewater when the product is washed off into sinks after cosmetic use.Polypyrrole-TiO_2 nano composite samples were synthesized by chemical oxidative method at room temperature. The samples were characterized by Fourier transforms infrared (FTIR), SEM with EDAX, UV vis Spectrum, X-ray diffraction (XRD). The doped H_2SO_4 may interact with PPy by donating either hydrogen sulfate (HSO_4) ions as dopants. XRD results demonstrate the amorphous nature of Ppy, however, its composites with TiO_2 exhibit powder nature. FT-IR spectroscopy reveals the presence of interaction between conducting Ppy and TiO_2.SEM images confirm that introduction of higher content of TiO_2 leads to the formation of nanocomposite. UV–Vis study show changes in spectra of Ppy in presence of TiO_2 with a slight increase in the band gap.

Keywords: Polymeric materials,PPy,TiO_2,Nanocomposite.

CHAPTER I

INTRODUCTION

Nanocomposites materials have been widely reported in the scientific literature to provide substantial properties enhancements, even at low nanoparticles content. In nanotechnology, polymer nanocomposites are defined as solids consisting of a mixture of two or more phase separated materials, where one or more dispersed phase is in nanoscale and a polymeric major phase. Materials can be referred to as nanoscaled when their size, meaning at least one of the three external dimensions range from approximately 1 nm to 100 nm . Nanocomposites can be processed by conventional wet and dry processing techniques, yet in adjusted conditions vs. their neat counterparts. Polymer nanocomposites and nanoparticles can also be applied as nanocoatings, meaning a deposited nanoscale layer on selected substrates to reach specific surface behavior. [1]

1.1 NANOSCIENCE:

The word **Nanoscience** refers to the study, manipulation and engineering of matter, particles and structures on the nanometer scale (one millionth of a millimeter, the scale of atoms and molecules). Important properties of materials, such as the electrical, optical, thermal and mechanical properties, are determined by the way molecules and atoms assemble on the nanoscale into larger structures. Moreover, in nanometer size structures these properties often different then on macroscale, because quantum mechanical effects become important.[2]

1.2 NANOTECHNOLOGY:

Nanotechnology is the application of nanoscience leading to the use of new nanomaterials and nanosize components in useful products. Nanotechnology will eventually provide us with the ability to design custom-made materials and products with new enhanced properties, new nanoelectronics components, new types of “smart” medicines and sensors, and even interfaces between electronics and biological systems. These new born scientific disciplines are situated at the interface between physics, chemistry, materials science, microelectronics, biochemistry, and biotechnology. Control of these disciplines therefore requires an academic and multidisciplinary scientific education.[3]

1.3 POLYMERS:

The word "polymer" is derived from two Greek words, polys (= many) and mers (= parts or units). A polymer is a large molecule which is formed by repeated linking of small molecules called "monomers". Example: Polyethene is a polymer formed-by linking together of a large number of ethene (C2H4) molecules. Thus, small molecules which combine with each other to form polymer molecules, are termed monomers.and the "re-peat unit" in a polymer is called mer. **Polymerization**, any process in which relatively small molecules, called monomers, combine chemically to produce a very large chainlike or network molecule, called a polymer. The monomer molecules may be all alike, or they may represent two, three, or more different compounds. Usually at least 100 monomer molecules must be combined to make a product that has certain unique physical properties such as elasticity, high tensile strength, or the ability to form fibres that differentiate polymers from substances composed of smaller and simpler molecules. often, many thousands of monomer units are incorporated in a single molecule of a polymer. The formation of stable covalent chemical bonds between the monomers sets polymerization apart from other processes, such as crystallization, in which large numbers of molecules aggregate under the influence of weak intermolecular forces.[4]

1.3.1 CHARACTERISTICS OF POLYMERS:

Polymeric molecules are very big molecules. There average molecular weights may approach 105 or more. That's why, they are also known as macromolecules.

Polymers are semi-crystalline materials. It means they have both amorphous and crystalline regions. In fact, polymers have regions of crystallinity, called crystallites, embedded in amor- phous regions. Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material.

The intermolecular forces in polymers can be Vander Waals' forces, dipole-dipole attractions or hydrogen bonding. These intermolecular forces are in addition to covalent bonds which connect the repeating units into a macromolecule.

The chemical, electrical, optical, mechanical and thermal properties of polymers depend on size and shape of polymers, and the presence or absence of characteristic intermolecular forces.[5]

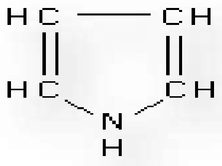
These parameters not only determine the properties of the polymers, but also the performance of these materials in a given applications.

- Polymers show time-dependent properties
- Polymers are combustible materials.
- Polymers have low densities and they show excellent resistance to corrosion.
- Generally, polymers are thermal and electrical insulators.
- Polymeric materials are easily mouldable even into complex shapes with reproducible dimensions with a minimum of fabrication and finishing cost.[6]

MATERIAL IMPORTANCE

1.4 PYRROLE:

Pyrrole is a heterocyclic aromatic organic compound, a five membered ring with formula C4 H4 NH. It is a colorless volatile liquid that darkens readily upon exposure to air. The existence of pyrrole in coal tar, bone oil, and in general, in products obtained by the dry distillation of proteins was first surmised by Runge in 1834. The discovery that pyrrole ring was an integral part of heme and of chlorophyll molecules not only created intense interest in the chemistry of pyrrole and its derivatives, but also resulted in the majority of investigations conducted during the latter part of the nineteenth century and the early years of the twentieth century being dominated by this relationship of pyrrole with naturally occurring compounds.[7]



Pyrrole

Pyrrole is very much less basic than secondary amines but much more acidic. Pyrrole is, however, still a very weak acid (pKa = 17.5).The nitrogen-bound proton can be abstracted from pyrrole by the use of strong bases such as sodium amide in liquid ammonia and n-butyl lithium in hexane.[8]

Table 1.1 PROPERTIES OF PYRROLE

IUPAC name	1H-pyrrole
Molecular formula	C_4H_5N
Appearance	Colourless
Molar mass	67.09g mol^{-1}
Melting point	23°C,250K,-9°F
Boiling point	129-131°C,402-404°K,264-268°F
Density	967.00 kg /m^3
Solubility	Water – sparingly Organic solvents – easily soluble

1.4.1 APPLICATIONS:

- Pyrrole and its derivatives are widely used as an intermediate in synthesis of pharmaceuticals,medicines,agrochemicals,dyes,photographicchemicals, perfumes and other organic compounds.
- They are used as catalysts for polymerization process, corrosion inhibitor,
- Preservatives and as solvents for resin and terpenes.
- They are used as the standard of chromatographic analysis.
- They are used also in many organic synthesis.[9]

1.5 AMMONIUM PER SULFATE

Ammonium per sulfate (APS) is the inorganic compound with the formula $(NH_4)_2S_2O_8$. It is a colourless (white) salt that is highly soluble in water, much more so than the related potassium salt. It is a strong oxidizing agent that is used in polymer chemistry, as an etchant, and as a cleaning and bleaching agent.[10]

Ammonium per sulfate is white, odorless single crystal, the formula is (NH4) 2S2O8, it has strong oxidation and corrosion, when heated, it decomposes easily, moisture absorption is not easy, it is soluble in water, the solubility increases in warm water, it can hydrolyze into ammonium hydrogen sulfate and hydrogen peroxide in an aqueous solution. The dry product has good stability, storage is easy, and it has the advantage of convenience and safety and so on. When heated to 120 °C, it can decompose, it is easily damped and it can cake in moist air. It is mainly used as an oxidizing agent and the preparation of hydrogen peroxide, potassium persulfate and other persulfate. It can be used as free initiator of polymerization reaction, particularly vinyl chloride emulsion polymerization of polymerizable compound and redox polymerization. It can be used as bleaching agent in grease, soap industry. It can be used to prepare dyes and dye oxidation and electroplating industry, photographic industry and chemical analysis.[11] Ammonium per sulfate is non-flammable, but it can release of oxygen, so it has the role of combustion-supporting, storage environment must be dry and clean, and well-ventilated. People should pay attention to moisture and rain, it should not be transported in rain. Keep away from fire, heat and direct sunlight. It should keep sealed packaging, clear and intact labels. It should be stored separately with flammable or combustible materials, organic compounds, as well as rust, a small amount of metal, and other reducing substances, it should avoid be mixed toprevent the decomposition of ammonium per sulfate and cause explosion.[12]

1.5.1 APPLICATION:

♣ It can be used as analytical reagents, photographic fixing agent and reducing agent.

♣ It can be used as food preservative, oxidizing agent and initiator molecular polymer.

♣ It can be used as raw material of producting per sulfate and hydrogen peroxide in chemical industry, inhibitor of polymerization organic polymer, initiator of during the polymerization of vinyl chloride monomer.

♣ It can be used as bleaching agent in grease, soap industry.

♣ It can also be used as corrodent in plate metals cutting eclipse and oil extraction in oil industry. For food-grade, it can be used as modifier of wheat, brewer's yeast mildew.[13]

1.6 TITANIUM DIOXIDE

Titanium dioxide (TiO_2) is mostly introduced into the environment as **nanoparticles** via wastewater treatment plants.Cosmetic pigments including titanium dioxide enter the wastewater when the product is washed off into sinks after cosmetic use. Once in the sewage treatment plants, pigments separate into sewage sludge which can then be released into the soil when injected into the soil or distributed on its surface. 99% of these nanoparticles wind up on land rather than in aquatic environments due to their retention in sewage sludge. In the environment, titanium dioxide nanoparticles have low to negligible solubility and have been shown to be stable once particle aggregates are formed in soil and water surroundings. In the process of dissolution, water-soluble ions typically dissociate from the nanoparticle into solution when thermodynamically unstable. TiO_2 dissolution increases when there are higher levels of dissolved organic matter and clay in the soil. However, aggregation is promoted by pH at the isoelectric point of TiO_2 (pH= 5.8).[14]

Table 1.2 PROPERTIES OF TIO$_2$

Molar mass	79.866 g/mol
Appearance	White solid
Odour	Odorless
Density	4.23 g/cm^3 (rutile) 3.78 g/cm^3 (anatase)
Melting point	1,843 °C (3,349 °F; 2,116 K)
Boiling point	2,972 °C (5,382 °F; 3,245 K)
Solubility in water	Insoluble

1.6.1 APPLICATION

- The most important application areas are paints and varnishes as well as paper and plastics, which account for about 80% of the world's titanium dioxide consumption.
- Other pigment applications such as printing inks, fibers, rubber, cosmetic products, and food account for another 8%.
- The rest is used in other applications, for instance the production of technical pure titanium, glass and glass ceramics, electrical ceramics, metal patinas, catalysts, electric conductors, and chemical intermediates.[15]

OBJECTIVES

- The main objectives of the present study are to prepare the polymer nanocomposite using polypyrrole and Titanium Dioxide.
- To analyse the functional groups of synthesized polymer nanocomposite by FT-IR spectroscopy.
- To study the optical properties of polymer nanocomposite by UV Vis analysis.
- To study the surface morphology as prepared sample using Field Emission Scanning Electron Microscopy.
- To find the crystallographic structure of a polymer nanocomposite by XRD analysis.

CHAPTER II

LITERATURE REVIEW

Manik A. Chougule, et al ., reported that the Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer pyrrole and ammonium per sulphate as an oxidant in a ratio of 1:1. Thin films of polypyrrole were prepared by dissolving polypyrrole in m-cresol and cast using spin coating technique on glass substrates. Thin films of polypyrrole were characterized by X ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infra red spectroscopy (FTIR), UV visible spectroscopy and electrical resistivity by four probe method. The XRD spectra showed that the polypyrrole is amorphous in nature. SEM studies revealed a uniform granular structure of PPy. The FTIR spectra shows that the presence of all characteristics absorption peaks of polypyrrole that is, 890 cm–1 (=C–H out-of-plane vibration), 1040 cm–1 (=C–H in-plane vibration), 1170 cm–1 (N–C stretch bending) and 1410 cm−1 (pyrrole ring vibration). UV visible study shows PPy films exhibit absorption peak at 446 nm (2.77 eV). Room temperature electrical resistivity of PPy is in the critical regime of the metal –to –insulator (M-I) transition.[16]

S. Deivanayaki, et al ., reported that the Polypyrrole-TiO2 nano composite samples with various dopant percentages of TiO2 were synthesized by chemical oxidative method at room temperature. The samples were characterized by Fourier transforms infrared (FTIR), SEM with EDAX, UV vis Spectrum, X-ray diffraction (XRD), Photoluminescence (PL) and Conductivity measurements. Electrical conductivity measurements indicate that the conductivity of nano composites increases with TiO2 content. The doped H2SO4 may interact with PPy by donating either hydrogen sulfate (HSO4) or sulfate (SO4 2-) ions as dopants. SEM images confirm that introduction of higher content of TiO2 leads to the formation of nano spheres.[17]

Vanja Gilja, et al., reported that the great advantage of conductive polymers is that their chemical, physical and optical properties can be adjusted according to the demand of application. In this study the structure of conductive polymer polypyrrole (PPy) was studied during the chemical synthesis. It is of great importance to explore the appropriate structure of polypyrrole that can induce activation of TiO2 photocatalysts since the synthesis of organic/inorganic hybrid materials can result in a synergistic and complementary feature, increasing TiO2 photocatalytic efficiency. As conductive polymers are also photosensitive, they can be activated by light absorption, which starts the transition of electrons from a conductive polymer by injection in the conductive band of TiO2. However, despite intensive research, the relationship between structure and conductivity is still not completely understood. It is assumed that the conductivity increases with a higher degree of crystallinity but this is not confirmed for all conducting polymers, only for some of them. In this paper different conditions of synthesis of pure polypyrrole and titanium dioxide/polypyrrole (TiO2/PPy) composites were studied. Samples of polypyrrole and TiO2/PPy composites were characterized by Fourier transform infrared spectroscopy (FTIR) and cyclic voltammetry (CV). The results show that due to the changes in the fraction of oxidant during the synthesis of PPy its structure was changed and thus the conductivity. The photocatalytic activity of the samples was tested by the decomposition of the dye Reactive Red 45 (RR45)[18]

Trong Tung Nguyen, et al., reported that the Polypyrrole/titanium dioxide nanocomposite (PPy/TiO2) was synthesized by in situ chemical polymerization of pyrrole (Py) monomer in colloidal suspension of TiO2 rutile. TEM and SEM images show that the TiO2 is covered by PPy forming a coreshell structure. The PPy/TiO2 core-shell will create n-p junction and bring in an inversion layer on the PPy-shell surface. The feature is accounted for the modification in electrical properties of the PPy/TiO2 nanocomposite. On the exposure to oxygen the conductivity of the nanocomposite exhibits an increase in 16–18-folds that are accounted for the interaction between oxygen (an electron acceptor) and the inversion layer. The cyclic voltammetry diagrams have shown that at around 15% TiO2 and scan rate 100 mV/s the nanocomposites can reach a specific capacitance about 176 F/g.[19]

M.q.he, et al., reported that the highly selective molecularly imprinted nanocomposites MIPRhB-PPy/TiO2 were successfully prepared by surface molecular imprinting technique with rhodamine B (RhB) as template molecule. The prepared MIPRhB-PPy/TiO2 coated with a thin imprinted layer could respond to visible light. The static and dynamic binding experiments revealed that MIPRhB-PPy/TiO2 possessed strong affinity, high adsorption capacity and fast adsorption rate for RhB. The selectivity experiments indicated that MIPRhB-PPy/TiO2 had excellent recognition selectivity for RhB. Selective photocatalytic degradation experiments indicated that the apparent rate constant (k) for the photodegradation of RhB over MIPRhB-PPy/TiO2 is 0.0158 min–1, being 3.6 times of that over non-imprinted nanocomposites NIP-PPy/TiO2 (0.0044 min–1). Compared with the NIP-PPy/TiO2, MIPRhB-PPy/TiO2 showed higher photocatalytic selectivity toward RhB under visible light, which was attributed the introduction of the imprinted cavities on the surface of MIPRhB-PPy/TiO2. Moreover, MIPRhB-PPy/TiO2 exhibited high reusability and stability. The results indicate that molecularly imprinted nanocomposites MIPRhB-PPy/TiO2 have a promising perspective in industrial wastewater treatment.[20]

Sobhan Bahraeian, et al., reported that the Conductive polypyrrole (PPy) was synthesized using a chemical polymerization method in aqueous solution. A series of reactions were carried out with different reaction times of 240 mins and 20 mins. All results were compared to find the highest conductivity and yield. The formation of PPy was verified with Fourier transform infrared (FTIR) analysis which has detected the C-N and pyrrole stretching peaks at 1462 cm-1 and 1169 cm-1, respectively, while the x-ray diffraction (XRD) study has shown a broad halo pattern around 25° related to PPy. The PPy particles sizes of 5-20 microns were measured from the scanning electron microscope (SEM) image. It was found that in the presence of sodium dodecylbenzene sulfonate (DBSNa) as surfactant, the highest conductivity value of 3.18 S/cm and yield of 68% were achieved at 20 mins reaction time and temperature of 0°C.[21]

Wei Shi , et al., reported that the vapor phase polymerization (VPP) method is a conventional strategy for synthesizing conducting polymers (CPs) on the surfaces of various materials. However, the current VPP method performed on a metal surface usually requires harsh reaction conditions, such as high temperature and low vacuum. In this paper, a polypyrrole (PPy) and vanadium pentoxide (V2O5) composite film was synthesized on the surface of Mg using a mild VPP method. Here, V2O5 was used as an oxidant, and it was found that the oxidation of pyrrole (Py) vapor on the surface of V2O5, which had been previously coated on the surface of Mg, could be performed at room temperature under normal atmospheric pressure. The formation of the PPy/V2O5 composite was verified by Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray (EDX) spectroscopy. A thermogravimetric analyzer (TGA) was used to study the thermal stability of the composite. Subsequent corrosion tests showed that the PPy/V2O5 composite film could slow down the corrosion of Mg in 3.5 wt% NaCl. It is expected that the mild VPP method may find great potential in the fields of synthesis of CPs and the corrosion protection of reactive metals.[22]

Chepuri R.K.Rao, et al., reported that a new complex is synthesized from FeCl3 and lauryl sulphate and used as oxidizing agent for the synthesis of polypyrrole. This process yields highly conducting polypyrrole (50 S/cm). The polymer is characterized by FT-IR, UV-vis, conductivity measurements and electrochemical and thermal analyses. Cyclic voltammetry of the polymer suggests moderate specific capacitance values.[23]

Mostafizur Rahaman, et al., reported that in this article, iota-carrageenan (IC) and kappa-carrageenan (KC) are used as dopants for the chemical and electrochemical synthesis of polypyrrole (PPy). The composites of chemically synthesized PPy with multi-walled carbon nanotubes (MWNTs) were prepared using an in situ technique. Both the dialyzed and non-dialyzed IC and KC were used as dopants for electrochemical polymerization of pyrrole. Chemically synthesized PPy and PPy/MWNTs composites were studied by ultraviolet visible (UV-vis) absorption spectra to investigate the effect of the concentration and the incorporation of MWNTs. In addition, the electrical, thermal, mechanical, and microscopic characterizations of these films were performed to examine the effect of the dopants and MWNTs on these properties, along with their surface morphology. The films of electrochemically polymerized PPy were characterized using UV-vis absorption spectra, scanning electron microscopy, and cyclic voltammetry (CV). The results were then compared with the chemical polymerized PPy.[24]

Ayaz Mahmood Dar,et al., reported that the Pyrrole is the special class of heterocyclic compounds with a broad spectrum of biological activities such as anti-inflammatory, antiproliferative, antihistaminic, anti-HIV, antifungal, antihelmintic and antiviral agents. Pyrrole is a five membered ring structure, with formula C4 H4 NH. The heterocyclic pyrroles are the ideal building blocks for different biologically efficient molecules including porphyrins and bile pigments. Therefore researchers are synthesizing these heterocycles through multi-stepped or single stepped pathways as target structures for biological studies. In this review, different synthetic protocols/methodologies are shown in which different entry molecules are converted into pyrrole derivatives, which are important from medicinal and pharmaceutical points of view.[25]

Abdirahman Yussuf ,et al., reported that the Conductive polymer, polypyrrole (PPy), was synthesized by chemical oxidative polymerization technique for a period of four hours at room temperature using pyrrole monomer (mPPy) in aqueous solution. Different oxidants such as ferric chloride (FeCl3) and ammonium per sulphate (N2H8S2O8) and surfactant sodium dodecyl sulphate (C12H25NaO4S) were used. The produced PPy samples were characterized by using different techniques such as the electrical resistivity by four probe technique, thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The performance of the oxidants has been investigated and compared. It was found that both oxidants, FeCl3 and N2H8S2O8, have decreased electrical resistivity as a function of temperature, which means increased conductivity. However, FeCl3 has achieved better performance than N2H8S2O8, where it has achieved a lower resistivity of about 60 ohms at room temperature, which indicates higher conductivity of PPy samples with FeCl3 as an oxidant. Similarly, further investigation of FeCl3 oxidant has been conducted by varying its concentration, and its influence on the final properties was reported. It has been observed that the morphology of PPy samples has a significant influence on the conductivity. It was found that 0.1 M and 0.05 M concentrations of FeCl3 oxidant and monomer, respectively, have achieved better thermal stability, which is FeCl3/mPPy ratio of 2 as an optimum value. FTIR and XRD results confirmed the structural formation of polypyrrole from pyrrole monomer during the synthesizing process.[26]

Rezaansari, et al., reported that the paper deals with a fundamental review of preparation methods, characterizations, thermal and environmental stabilities and practical applications of polypyrrole (PPy) conducting electroactive polymers. In this article some of the most important factors affecting the electrical, electrochemical, thermal and environmental stabilities of polypyrrole conducting polymers have also been reviewed.[27]

Behzad Rezaei,et al., reported that Metal oxide semiconductors, such as TiO2 nanoparticles are frequently used as photocatalyst due to nontoxicity, chemical stability, and the ability to possess relatively high photocatalytic activity of TiO2. Laboratory studies have demonstrated that organic compounds such as alcohols, carboxylic acid, phenolic derivatives, and chlorinated aromatics can be readily mineralized by TiO2 into harmless carbon dioxide, water and simple mineral acids, using molecular oxygen as the primary oxidant.[28]

Andrea Leon, et al., reported that the aim of this study was to prepare a novel targeting drug delivery system for 2-Methoxyestradiol (2ME) in order to improve the clinical application of this antitumor drug. It is based in nanoparticles (NPs) of titanium dioxide (TiO2) coated with polyethylene glycol (PEG) and loaded with 2ME. A complete IR and Raman characterization have been made to confirm the formation of TiO2–PEG–2ME composite. Vibrational modes have been assigned for TiO2, PEG, and 2ME and functionalized TiO2–PEG and TiO2–PEG–2ME. The observed variation in peak position of FTIR and Raman of each for these composites has been elucidated in terms of intermolecular interactions between PEG–2ME and TiO2, obtaining step-by-step the modification processes that were attributed to the conjugation of PEG and 2ME to TiO2 NPs. Modifying TiO2 NPs with PEG loaded with the 2ME drug revealed that the titanium dioxide nanocarrier possesses an effective adsorption capability, and we discuss their potential application as a system of drug delivery.[29]

Ziyang Li, et al., reported that the Simultaneous formation of polypyrrole (PPy) and metal (or metal oxide) on a single electrode is particularly challenging because the electrodeposition of PPy and metal (or metal oxide) usually requires opposite potentials. Namely, the preparation of PPy needs an oxidation potential while the metal (or metal oxide) needs a reduction potential. In the present work, nanocomposites of PPy and metal (or metal oxide) were prepared successfully on the cathode by a one-step process, in which V2O5 coated titanium sheet was applied as cathode. In fact, two chemical reactions happened here at the same time. The first reaction was the chemical preparation of PPy on the cathode by the use of V2O5 as oxidant and the second reaction was the electrochemical formation of metal (or metal oxide) on the surface of the same cathode. As a result, nanocomposites of PPy and metal (or metal oxide) were one-step prepared on a single electrode. The morphology, composition and structure of nanocomposites were investigated via field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) and Xray diffraction (XRD). Furthermore, PPy-Ag nanocomposite was prepared and used as a sensor to evaluate the electrocatalytic performance of H2O2. It was found that the sensor displayed excellent H2O2-sensing properties and a feasibility for practical applications. These results imply that the present one-step process not only presents a simple, facial and efficient way for the formation of PPy-based nanocomposites but also exhibits great potential to improve the application performance and broaden the applied fields of the nanocomposites. [30]

J.Y.Lee, et al ., reported that the soluble polypyrrole(PPy) was synthesized chemically by using ammonium persulfate and dodecylbenzene sulfonic acid as an oxidant and a dopant, respectively. It was found that the soluble PPy powder as well as the cast film contained a high concentration of free radicals detected by an electron paramagnetic resonance spectrometer. The polymer solution was cast into a film with a very fine reflective surface. A thin film with the light transmittance of 80% showed the surface resistivity of 25 kΩ/square displaying an increase in the resistivity only by 20 kΩ/square compared to the resistivity of a thick film. DC conductivity of the PPy film fitted nicely the quasi-one-dimensional variable range hopping model. The bulk electrical conductivity of the cast film increased by one order during initial heating to 200°C in air and changed little during isothermal heating at 200°C for 120 minutes. The conductivity kept a half of the initial increase after cooling from 200°C to room temperature. The surface resistivity of the film, however, was found to increase dramatically on heating at 200°C in air. Since the surface resistivity showed no change on heating in nitrogen atmosphere at 200°C, oxidation during heating caused the decrease in the conductivity of the polymer.[31]

CHAPTER III

EXTRACTION METHODS

3.1 CHEMICAL OXIDATION METHOD:

The aim of chemical oxidation is to oxidise organic pollutants to less dangerous or harmless substances. In the best case scenario, complete oxidation of organic substances will result in CO_2 and H_2O. This technique can also be used to remove inorganic components (e.g. oxidation of cyanide). Chemical oxidation can also be used in combination with biological purification. In this case, we refer to partial oxidation. The purpose of chemical oxidation as a pre-treatment technique is to either break down difficult to degrade components and make them suitable for biological degradation or to limit sludge production by partly oxidating the sludge.

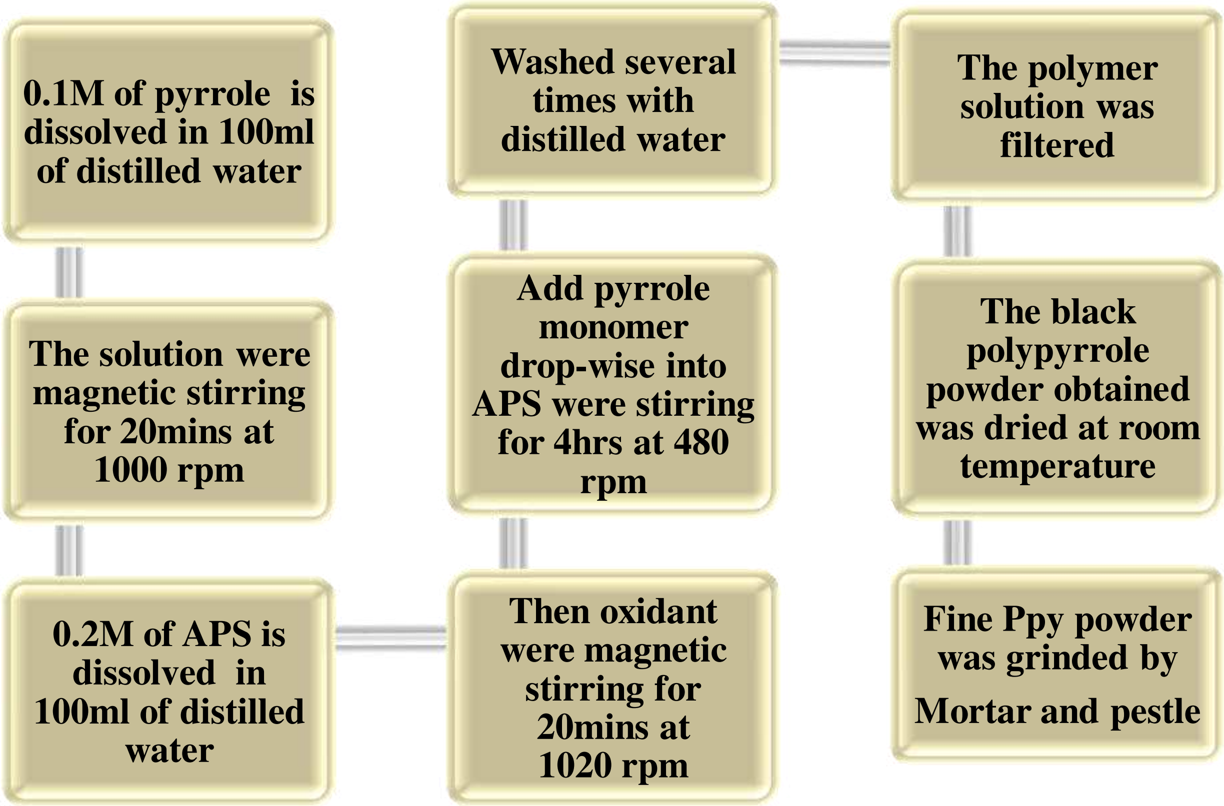
Chemical oxidation involves adding or generating oxidants in the waste water.Below is a brief description of some examples of chemical oxidation:

- Treatment of groundwater for the removal of cyanides, PAH, BTEX, phenols and other organic micro-pollutants.
- Chemical oxidation of percolation water as post-biological purification. The aim of this is to further oxidise certain residual pollutants (persistent COD or AOX).[32]

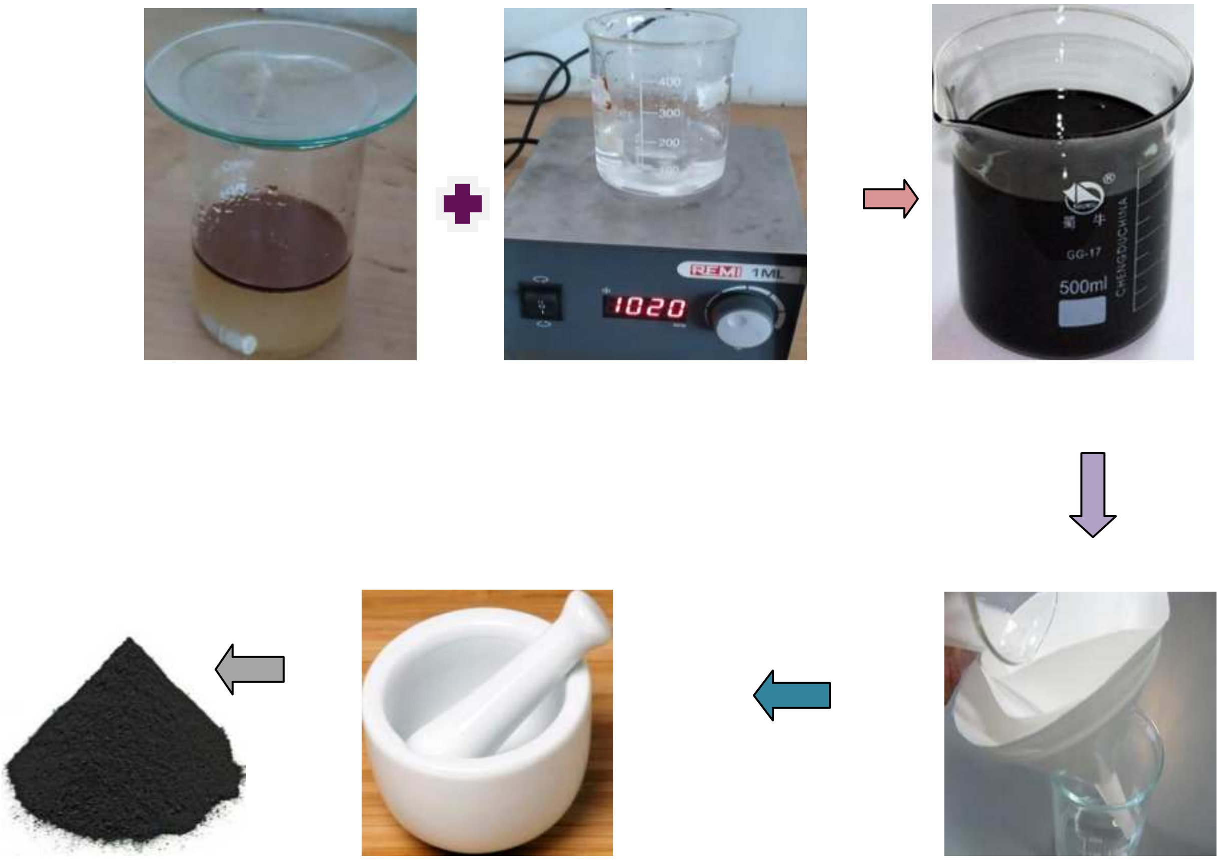
3.1.1 SYNTHESIS OF POLYPYRROLE BY CHEMICAL OXIDATION METHOD:

Polypyrrole is a conducting polymer that has attractive characteristics for the use as a radar absorbing material. The polymer's conductivity can be varied over several orders of magnitude, covering a range that is suitable for microwave absorption. In the science behind the formation of polypyrrole are reviewed along with the published literature investigating the use of PPy as a radar absorbing material.Polypyrrole (PPy) can be formed chemically or electrochemically through oxidative polymerization of pyrrole monomer.[33]

FLOW CHART



3.1.2 IMAGE OF PYRROLE MONOMER & APS (CHEMICAL OXIDATION METHOD)



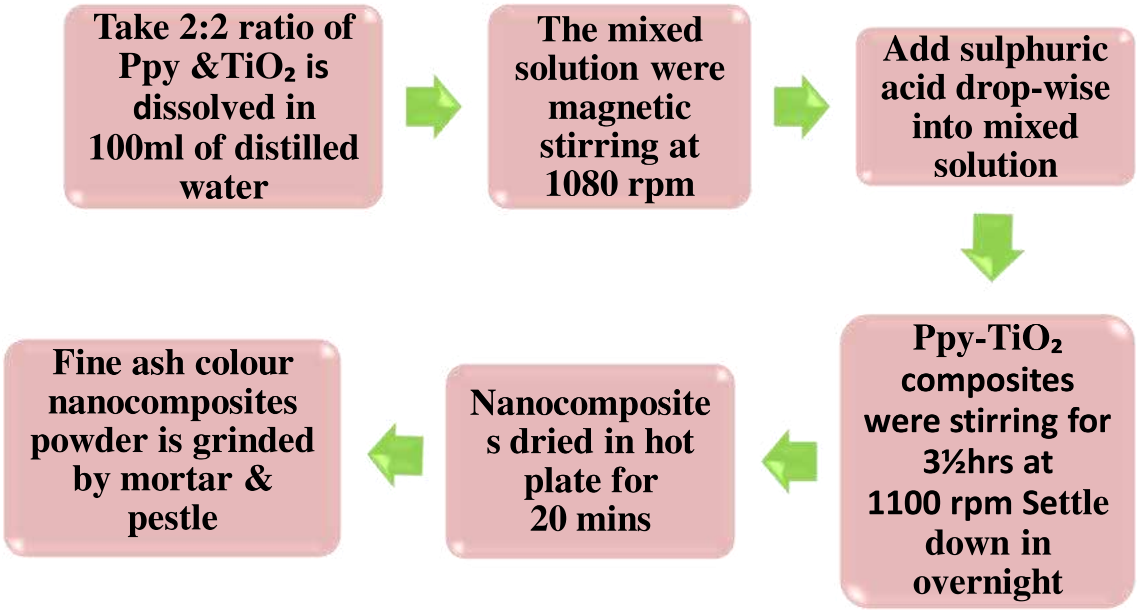
3.2 NANOCOMPOSITES

Nanocomposites have been studied for nearly 50 years. They were first referenced as early as 1950 . Polyamide nanocomposites were reported in 1976. It was the efforts of Toyota research group that laid the foundation stone for the interest in this area. Nanocomposites are a combination of two or more phases containing different compositions or structures where at least one of the phases is in the range of 10 to100 nm. Fillers with a particle size in the nano metre range have a small number of atoms per particle and for this reason may have different properties than the bulk material and strong interactions with the matrix. The separation of filler particles is of the order of molecular dimensions, which may modify the properties of polymers. In polymer nanocomposites research, the primary goal is to enhance the strength and toughness of polymeric components using molecular or nano scale fillers. Composites that exhibit a change in composition and structure over a nano metre scale have shown remarkable property enhancements relative to conventional composites.

3.2.1 PREPARATION OF PPY & TIO_2 OF NANOCOMPOSITIES:

A polymeric particle polymer nanocomposite contains a rigid polymer component dispersed within a flexible polymer matrix on a nanoscale level. The rigid polymer, with high modulus and high strength, usually has high melting temperature, is insoluble in organic solvents, and combining it with the flexible polymer is thermodynamically unfavourable. Therefore it is very difficult to prepare a nanocomposite, and phases may undergo segregation during processing and end use. Hydrodynamic effects and physic or chemi-sorption of matrix at filler surface governs the reinforcement. The most common applications, this review focus more in-depth on the properties and materials of relevance in three target sectors: packaging, solar energy and automotive. In terms of advances in the processing of nanocomposites, this review discusses various enhancement technologies such as the use of ultrasounds for in-process nanoparticles dispersion. In the case of nanocoatings, it describes the conventionally used processes as well as nanoparticles deposition by electro-hydrodynamic processing.[34]

FLOW CHART


Take 2:2 ratio of Ppy &TiO_2 is dissolved in 100ml of distilled water

The mixed solution were magnetic stirring at 1080 rpm

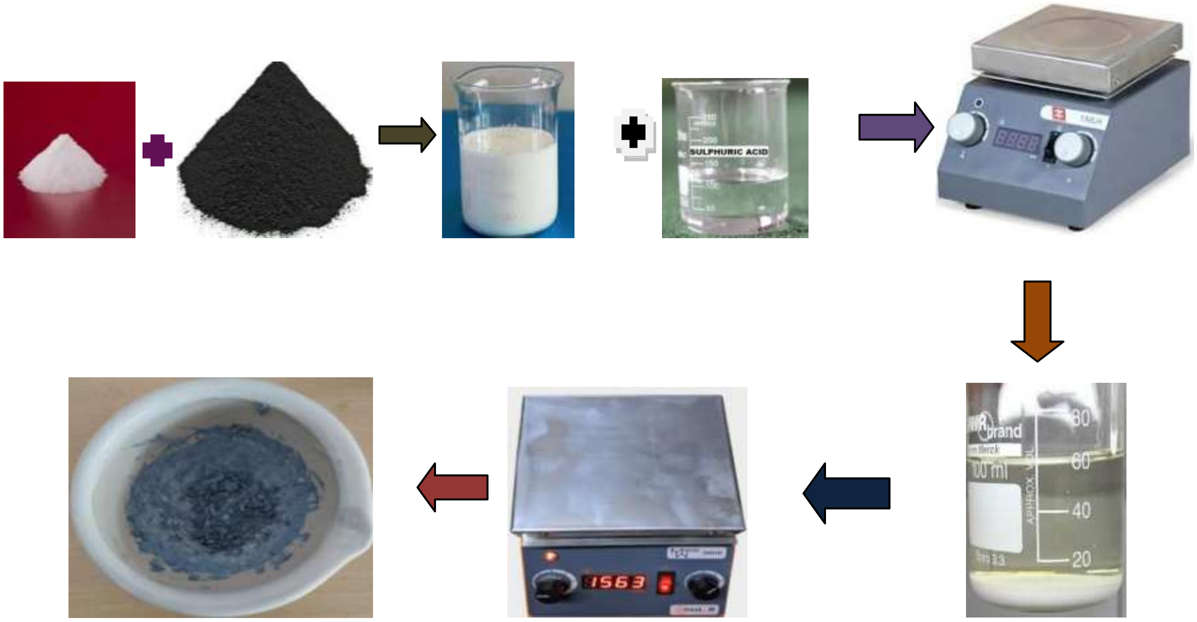
Add sulphuric acid drop-wise into mixed solution

Ppy-TiO_2 composites were stirring for 3½hrs at 1100 rpm Settle down in overnight

Nanocomposites dried in hot plate for 20 mins

Fine ash colour nanocomposites powder is grinded by mortar & pestle

3.2.2 IMAGES FOR PPY-TIO_2 NANOCOMPOSITES:



CHAPTER IV

EXPERIMENTAL METHODOLOGY

4.1 FIELD EMISSION SCANNING ELECTRON MICROSCOPE:

The field emission scanning electron microscope (FESEM) is suitable for observing structures as small as 1 nm on the surface of material. The magnification of observation can be adjusted and considered based on the requirements. A few examples of objects that are studied with a FESEM in practice are organelles and nuclei of cells, synthetical polymers, and coatings, but it is also suitable for characterizing the morphology and geometry of electrospun nanofibers. The FESEM is one microscope that works with electrons with a negative charge instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern.

4.1.1 FESEM ANALYSIS:

Electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column, these so-called primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relate to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal. This signal is amplified and transformed to a monitor or to a digital image that can be saved and processed.

The FESEM looks like a cylindrical column mounted on a desk. The column hosts the electron beam. Knobs for the regulation of the electron beam can be found at various levels on the column. The microscope is operated from the steering panel. A copy of this panel has been used for the simulations.[35]

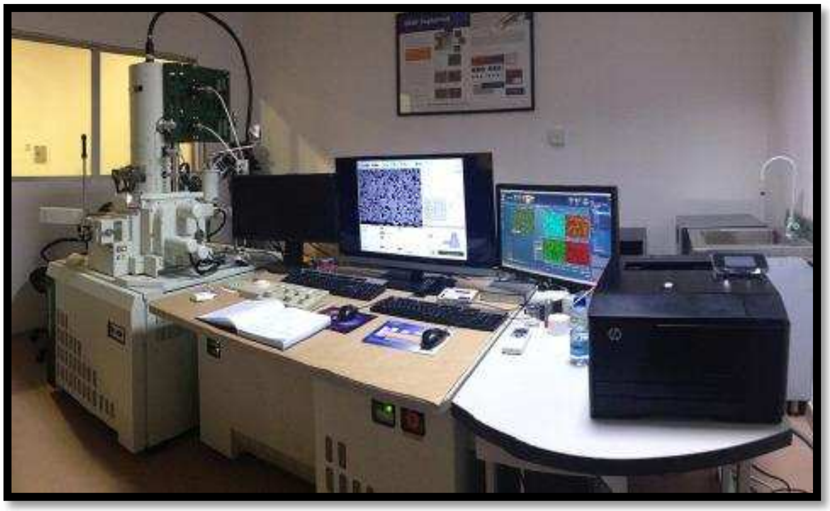


Fig 4.1 Instrumentation of FESEM

4.1.2 APPLICATION OF FESEM:

- Semiconductor device cross section analyses for gate widths, gate oxides, film thicknesses, and construction details
- Advanced coating thickness and structure uniformity determination
- Small contamination feature geometry and elemental composition measurement

4.1.3 ADVANTAGES OF FESEM:

- The ability to examine smaller-area contamination spots at electron accelerating voltages compatible with energy dispersive spectroscopy (EDS).
- Reduced penetration of low-kinetic-energy electrons probes closer to the immediate material surface.
- High-quality, low-voltage images with negligible electrical charging of samples (accelerating voltages ranging from 0.5 to 30 kilovolts).
- Essentially no need for placing conducting coatings on insulating materials.

4.1.4 DISADVANTAGES OF FESEM:

- FESEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference.
- Maintenance involves keeping a steady voltage, currents to electromagnetic coils and circulation of cool water.[36]

4.2 ULTRA VIOLET SPECTROSCOPY:

Ultraviolet–visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible regions of the electromagnetic spectrum. This means it uses light in the visible and adjacent ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the spectrum, atoms and molecules undergo electronic transitions. Absorption spectroscopy is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions of electrons from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.[37]

4.2.1 UV ANALYSIS:

Molecules containing bonding and non-bonding electrons (n-electrons) can absorb energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons , the longer the wavelength of light it can absorb. There are four possible types of transitions (π–π^*, n–π^*, σ–σ^*, and n–σ^*).[38]

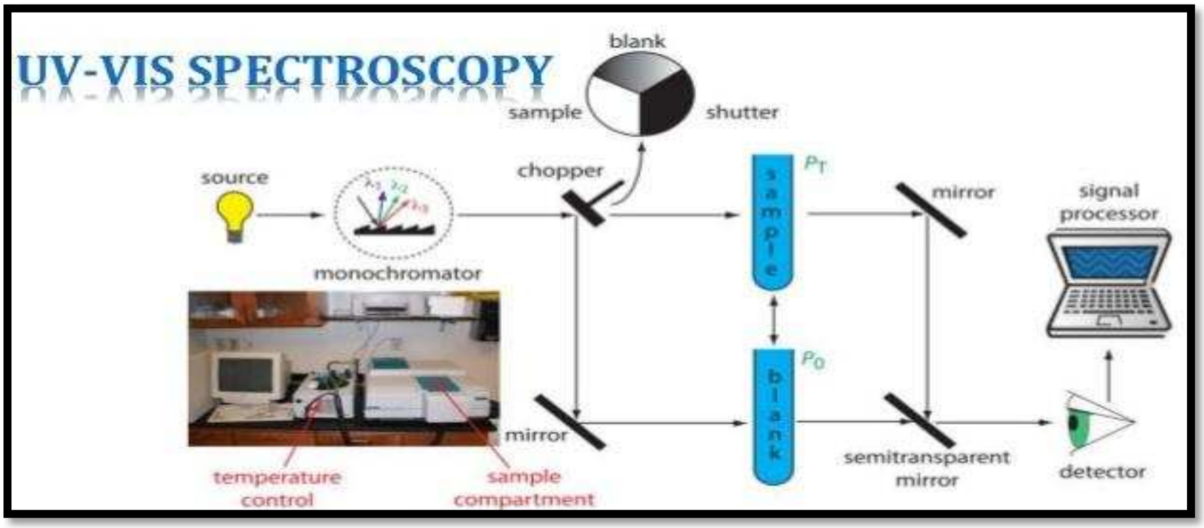


Fig 4.2 Instrumentation of UV Spectroscopy

4.2.2 APPLICATION OF UV SPECTROSCOPY:

- UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.
- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

4.2.3 ADVANTAGES OF UV SPECTROSCOPY:

- UV-VIS Spectroscopy is the accuracy of the device. Even small UV-VIS spectrometers can give extremely accurate readings, which is crucial when you are preparing chemical solutions or recording the movement of celestial bodies.

- UV-VIS spectroscopy are easy to use. Most UV-VIS spectroscopy used in astronomy attach to telescopes. Most of the ones used in chemistry are comparable in size to electron microscopes and require the same basic skills to use.

4.2.4 DISADVANTAGES OF UV SPECTROSCOPY:

- UV-VIS spectrometer is the time it takes to prepare to use one. With UV-VIS spectrometers, setup is key. You must clear the area of any outside light, electronic noise, or other outside contaminants that could interfere with the spectrometer's reading.
- If the space has been properly prepared ahead of time, UV-VIS spectrometers are simple to use and give accurate results. However, if the space has not been properly prepared, even a small bit of outside light or vibration from a small electronic device could interfere with the results you are hoping to achieve in using a UV-VIS spectrometer.[39]

4.3 FOURIER TRANSFORM INFRARED SPECTROSCOPY:

Fourier-transform infrared spectroscopy (**FTIR**) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.[40]

4.3.1 ANALYSIS OF FTIR:

FTIR is less sensitivity to stray light, that is radiation of one wavelength appearing at another wavelength in the spectrum. In dispersive instruments, this is the result of imperfections in the diffraction gratings and accidental reflections. In FT instruments there is no direct equivalent as the apparent wavelength is determined by the modulation frequency in the interferometer.[41]

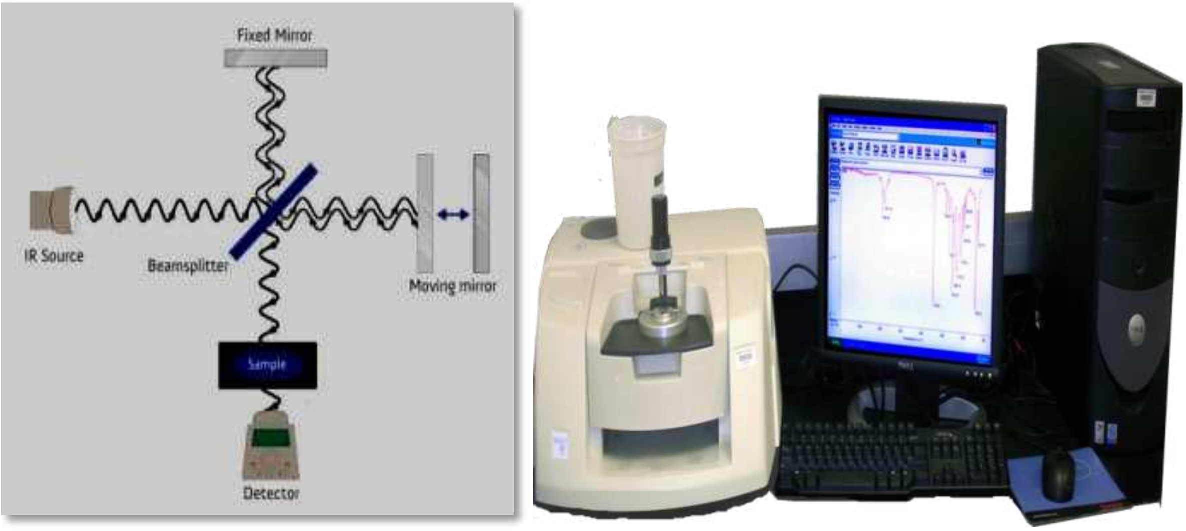


Fig 4.3 Instrumentation of FTIR

4.3.2 APPLICATION OF FTIR:

- FTIR spectrometers do require an aperture to restrict the convergence of the collimated beam in the interferometer. This is because convergent rays are modulated at different frequencies as the path difference is varied.
- For a given resolution and wavelength this circular aperture allows more light through than a slit, resulting in a higher signal-to-noise ratio.

4.3.3 ADVANTAGES OF FTIR:

- FTIR also aids in the detection and identification of diamond treatments such as irradiation.
- FTIR is the detection of fillers used for clarity enhancement such as oils and polymers in emeralds, jade, and other gemstones.

- FTIR spectroscopy has been the most common technique to identify various filler substances from organic oils to polymer resins.

4.3.4 DISADVANTAGES OF FTIR:

- The sampling chamber of an FTIR can present some limitations due to its relatively small size.
- Mounted pieces can obstruct the IR beam. Usually, only small items as rings can be tested.
- Several materials completely absorb Infrared radiation; consequently, it may be impossible to get a reliable result.[42]

4.4 X-RAY DIFFRACTION:

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample . The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law:

$$\mathbf{n\lambda = 2d\sin\theta}$$

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction, and u is the diffraction angle. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed, and counted.[43]

Fig 4.4 Instrumentation of XRD

4.4.1 APPLICATION OF XRD:

- XRD is a nondestructive technique
- To identify crystalline phases and orientation.
- To measure thickness of thin films and multi-layers
- To determine atomic arrangement.[44]

4.4.2 ADVANTAGES OF XRD:

- X-ray is the cheapest,the most convenient and widely used method.
- X-ray are not absorbed very much by air,so the specimen need not be in an evacuated chamber.

4.4.3 DISADVANTAGES OF XRD:

- They do not interact very strongly with lighter elements.
- To determine structural properties: Lattice parameters (10-4Å), strain, grain size, expitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion.
- To measure thickness of thin films and multi-layers.[45]

CHAPTER V

RESULT AND DISCUSSION

5.1 UV Analysis:

The UV –Visible spectra observed for the PPy-TiO_2 Sample is in the range 200-800nm. The nanocomposites of PPy-TiO_2 also have consistent peak at ~250nm & ~ 490nm.The Wavelength ~ 490nm at which is characteristic of π-π* transition of neutral PPy-TiO_2[16]. This result clearly indicates presence of structural change upon increase in dopant percentage of TiO_2 in PPy.

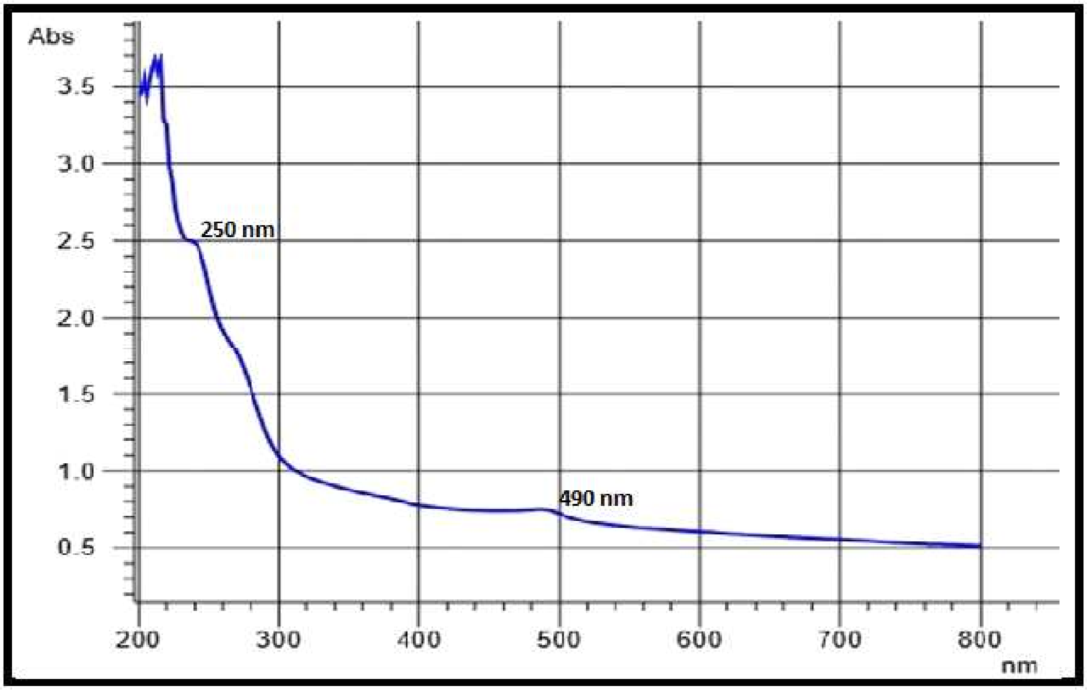


Fig 5.1 UV-Visible spectra Absorbance vs Wavelength of PPy-TiO_2 Nanocomposite

5.2 FT-IR studies:

The formation of PPy was verified with Fourier transform infrared (FTIR) analysis.The stretching peaks of N-H were detected at 3412.04 cm^{-1}.The band at 2924.40 cm^{-1} is related to Counter anion - CH_2 .The stretching peaks of C=C is detected at 1562.68 cm^{-1}.The absorption peak at 1040.17 cm^{-1} is corresponded to C-H and N-H deformations. All these peaks are the main characteristic of PPy.

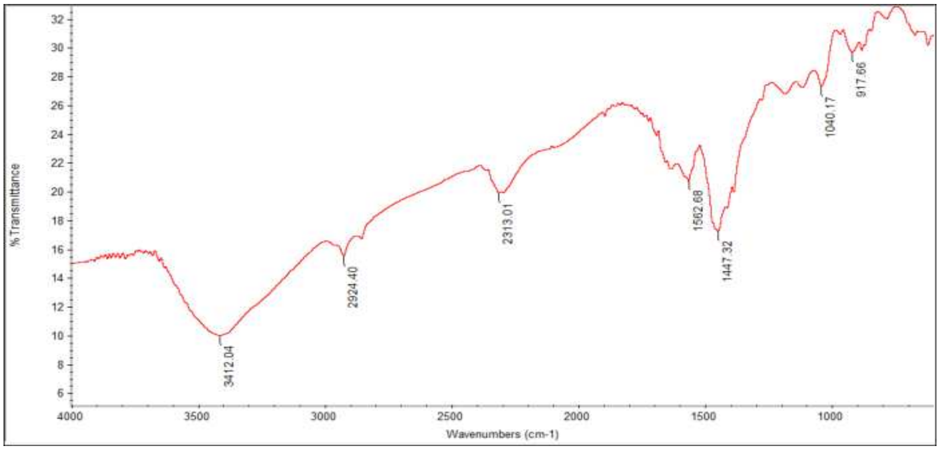


Fig 5.2(a) The spectrum of FTIR of the Ppy sample

Table 5.2(a) FTIR data of the sample for PPy

Vibrations	**Wavenumber(cm^{-1})**
N-H stretching	3412.04
C=C stretching	1562.68
C-N Stretching	1447.32
C-C & N-H in plane deformation	1040.17

The Polypyrrole and TiO_2 Nanocomposite samples were characterized by FTIR.The peaks at 3426.30 cm^{-1} indicate O-H stretching vibration.The band at 1563.25 cm^{-1} is related to C-C stretching vibration.The stretching peaks of C-N is corresponded to 1448.33cm^{-1}.The absorption peak at 1040.02cm^{-1} is related to C-H deformation.

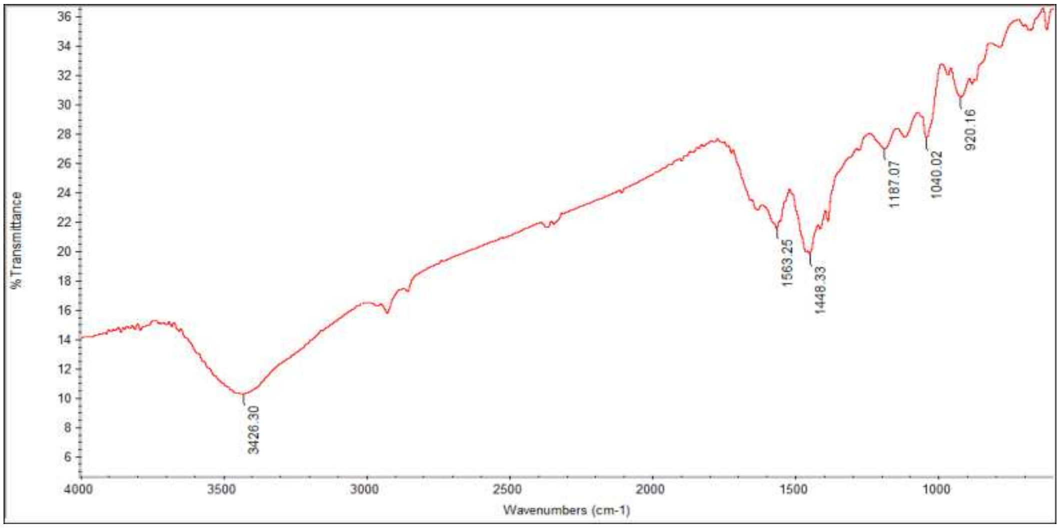


Fig 5.2(b) The FTIR spectrum of the Ppy-TiO_2 Sample

Table 5.2(b) FTIR data of the Ppy-TiO_2 sample

Vibration	**Wavelength(cm^{-1})**
O-H stretching	3426.30
C-C stretching	1563.25
C-N stretching	1448.33
C-H deformation	1040.02

5.3 FE-SEM characterization:

The morphology and size distribution of the synthesized Polypyrrole and Polypyrrole with TiO_2 nanocomposite was be measured by FE-SEM.The average grain size range is 100µm.

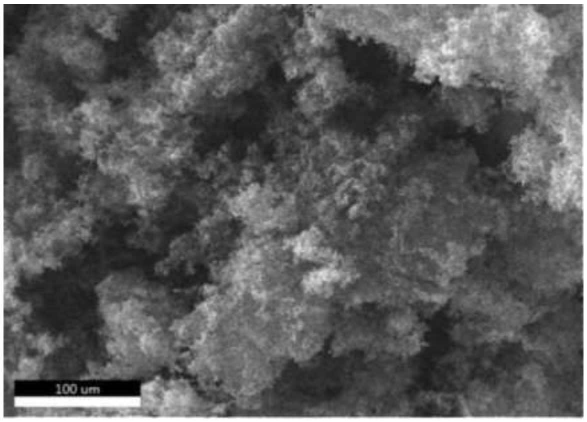


Fig 5.3(a)SEM image of Polypyrrole

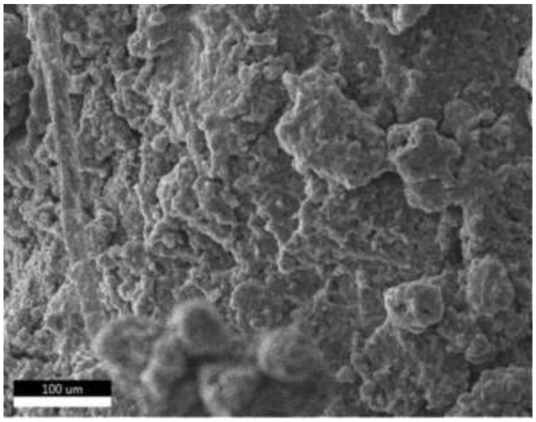


Fig 5.3(b) SEM image of PPY-TiO_2

5.4 EDAX Analysis:

The purity and composition of the prepared PPy and PPy -TiO_2 samples were determined by EDAX analysis.The result indicate the presence of the element indicate that the atomic ratio of **S** is **72.26%** & **Ti** is **81.17%**

Fig 5.4(a) Dispersion of Sulfate

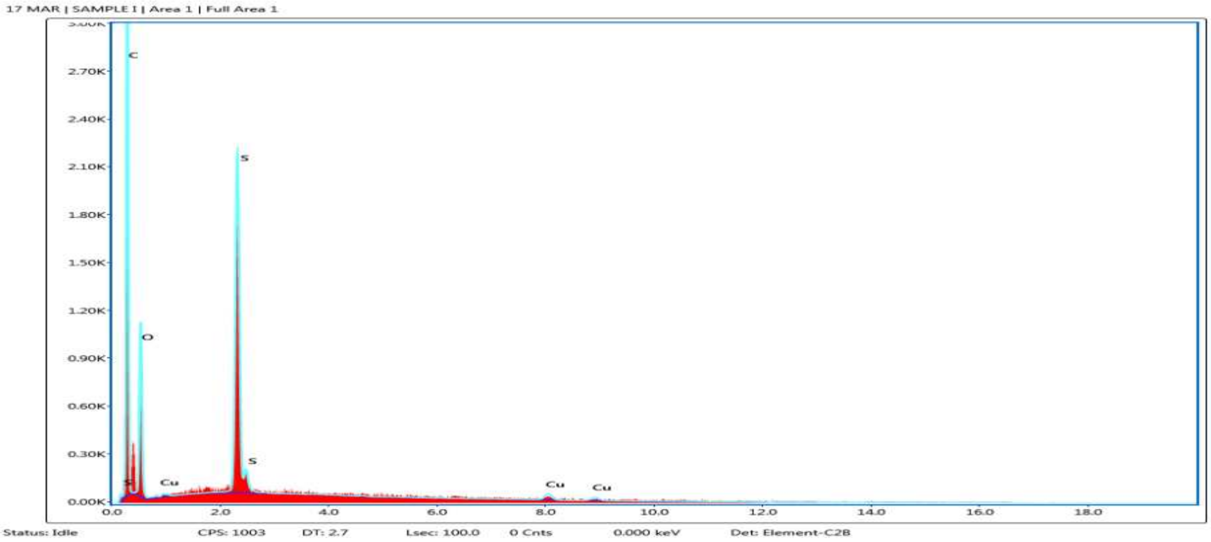


Fig 5.4(b) EDAX Spectrum of PPy sample

Element	Weight(%)	Atomic(%)	Error(%)
C K	28.92	24.66	11.58
O K	7.04	2.99	1.95
S K	63.61	72.26	8.01
Cu K	0.43	0.09	18.04

Table 5.4(a) EDAX data of the PPy sample

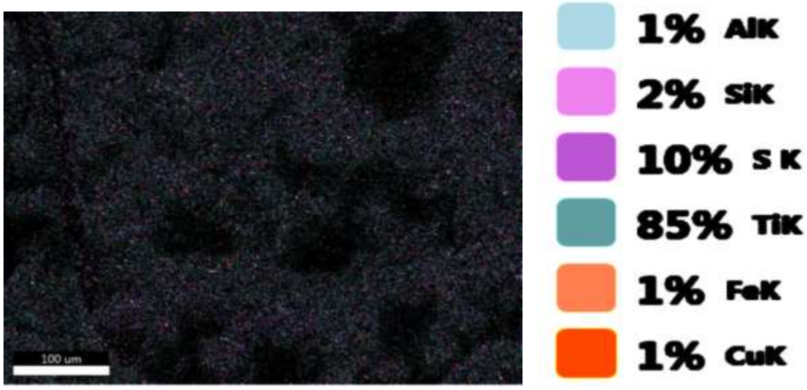


Fig 5.4(c) Dispersion of Titanium

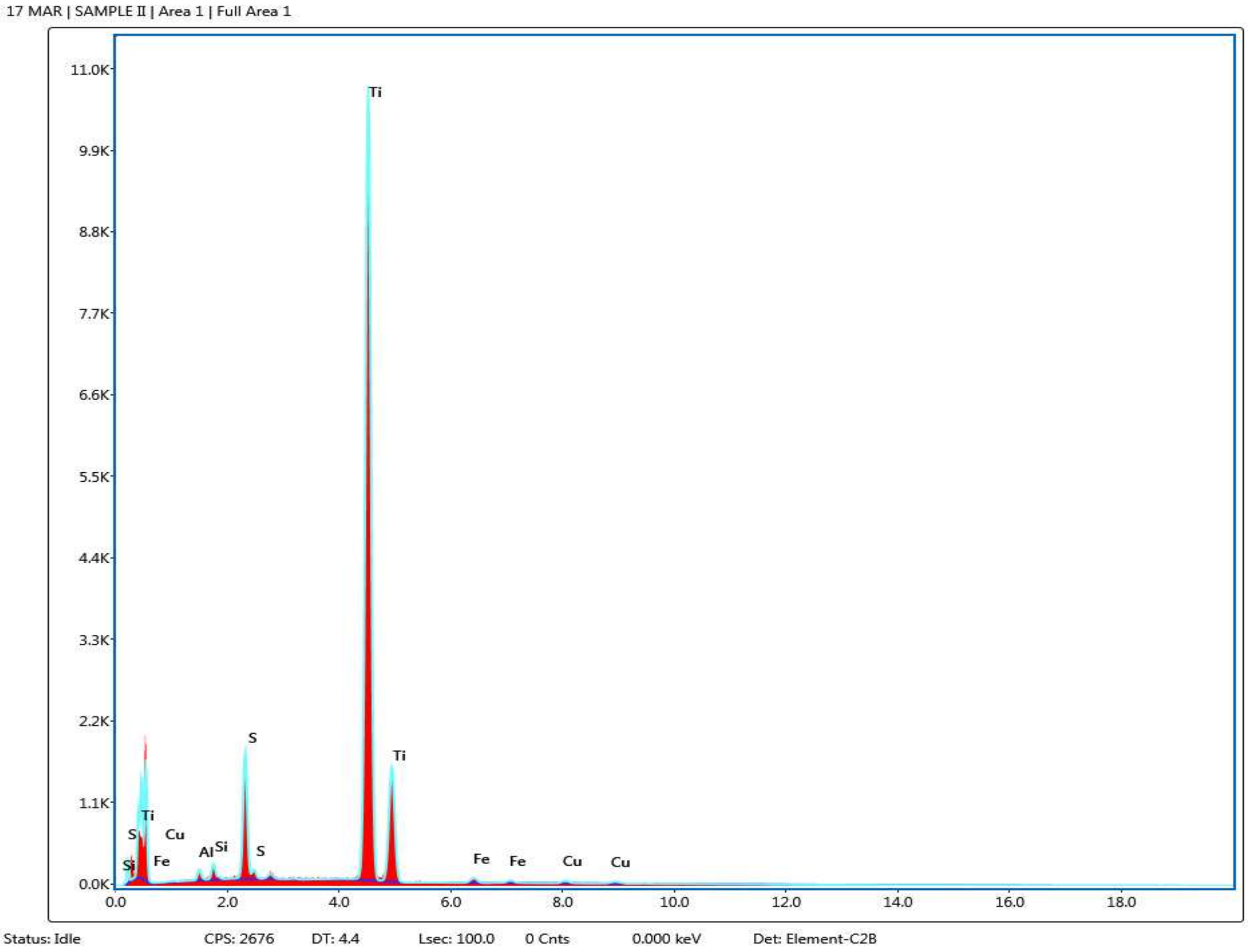


Fig 5.4(d) EDAX Spectrum of PPy-TiO_2

Table 5.4(b) EDAX data of the Sample

Element	**Weight(%)**	**Atomic(%)**	**Error(%)**
Al K	1.25	2.08	15.29
Si K	1.31	2.10	11.31
S K	9.47	13.31	4.87
Ti K	86.24	81.17	1.39
Fe K	1.08	0.87	15.66
Cu K	0.67	0.47	28.46

5.5 XRD Calculations:

The average crystallite size (D) was calculated using the well known Scherer's formula. $\mathbf{D = k\lambda / \beta \cos\theta}$

Where **D** is the average crystalline diameter in nanometer(nm),

K is the Scherer constant equal to 0.94,

β is the full width at half maxima(FWHM)intensity of the diffraction peak

$$\beta = (\pi / 180)\, 2\theta \text{ (radian)}$$

θ is the Bragg's angle,

λ is the wavelength of X-rays (1.5406 Å).

The average crystallite size (D) of synthesized nanoparticles was found to be

19.9621nm.

Table 5.5(a)To calculate average crystallite size(D) for PPy

2θ(deg)	**θ(deg)**	**Cos θ(deg)**	**β(radians)**	**D(nm)**
29.2434	14.6217	0.9676	0.5101	29.3447
38.4001	19.2000	0.9443	0.6698	23.4422
44.5795	22.2897	0.9252	0.7776	20.3258
64.6968	32.3484	0.8448	1.1285	14.4083
77.6275	38.8137	0.7791	1.3542	12.2896

Average = 19.9621nm

Table 5.5(b) To identify the lowest common quotient **K** for PPy

2θ(deg)	**θ(deg)**	**$\text{Sin}^2\theta$(deg)**	**$\frac{\text{Sin}^2\theta(\text{deg})}{2}$**	**$\frac{\text{Sin}^2\theta(\text{deg})}{3}$**
29.2434	14.6217	0.0637	**0.0318**	0.0213
38.4001	19.2000	0.1081	0.0540	**0.0318**
44.5795	22.2897	0.1438	0.0719	0.0479
64.6968	32.3484	0.2862	0.1431	0.0954
77.6275	38.8137	0.3928	0.1964	0.1309

K = 0.0318

The appearance of peaks at values 2θ of 29.24,38.40,44.57,64.69 and 77.62 are as (100),(111),(200),(221),and (222) respectively.

Table 5.5 (c) To select appropriate pattern of $h^2+l^2+k^2$ values and to identify the bravais lattice for PPy

2θ(deg)	**$\mathrm{Sin}^2\theta$(deg)**	**$\frac{\mathrm{Sin}^2\theta(\mathrm{deg})}{K}$**	**$h^2+l^2+k^2$**	**hkl**
29.2434	0.0637	2.0031	2	100
38.4001	0.1081	3.3994	3	111
44.5795	0.1438	4.5220	4	200
64.6968	0.2862	9	9	221
77.6275	0.3928	12.352	12	222

The lattice value $\mathbf{a = \lambda / 2\sqrt{k}}$ **(Å)**

$= 1.5406 / 2\sqrt{0.0318}$

$=$ 4.3202Å

The lattice value **a** for the synthesized Polypyrrole was found to be **4.3202 Å**

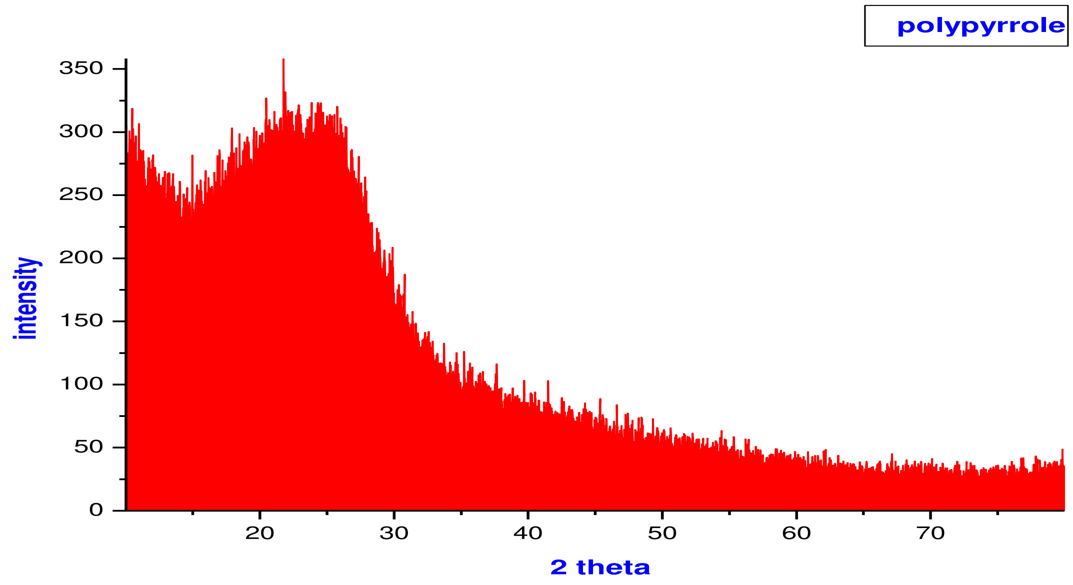


Fig 5.5(a) XRD pattern of the PPy

The average crystallite size (D) of PPy-TiO_2 nanocomposite was found to be

21.3751nm.

Table 5.5(d)To calculate average crystallite size(D) for PPy-TiO_2

2θ(deg)	**θ(deg)**	**Cosθ(deg)**	**β (radians)**	**D(nm)**
28.1737	14.0868	0.9699	0.4915	30.3789
36.8265	18.4132	0.9488	0.6424	23.7598
41.9470	20.9735	0.9337	0.7317	21.1967
55.0082	27.5041	0.8869	0.9596	17.0165
69.6173	34.8086	0.8211	1.2144	14.5231

Average =21.3751nm

Table 5.5(e) To identify the lowest common quotient **K** for PPy-TiO_2

2θ(deg)	**θ(deg)**	**$Sin^2θ$(deg)**	**$\frac{Sin^2θ(deg)}{2}$**	**$\frac{Sin^2θ(deg)}{3}$**
28.1737	14.0868	0.0592	0.0296	0.0199
36.8265	18.4132	0.0997	**0.0498**	0.0333
41.9470	20.9735	0.1281	0.0640	**0.0498**
55.0082	27.5041	0.2133	0.1066	0.0711
69.6173	34.8086	0.3258	0.1629	0.1086

K = 0.0498

The appearance of peaks at values 2θ of 29.17,36.82,41.94,55.00 and 69.61 are as (100),(110),(111),(200),and (211) respectively. The plane (110)indicate the tetragonal specimen line of TiO_2

Table 5.5 (f) To select appropriate pattern of $h^2+l^2+k^2$ values and to identify the bravais lattice for PPy-TiO₂

2θ(deg)	**$Sin^2θ$(deg)**	**$\frac{Sin^2θ(deg)}{K}$**	**$h^2+l^2+k^2$**	**hkl**
28.1737	0.0592	1.1887	1	100
36.8265	0.0997	2.0020	2	110
41.9470	0.1281	2.5722	3	111
55.0082	0.2133	4.2831	4	200
69.6173	0.3258	6.5422	6	211

The lattice value $\mathbf{a = \lambda / 2\sqrt{k}}$ **(Å)**

$= 1.5406 / 2\sqrt{0.0498}$

$= 3.4519$Å

The lattice value **a** for the PPy –TiO₂ nanocomposites was found to be **3.4519Å** the XRD result.

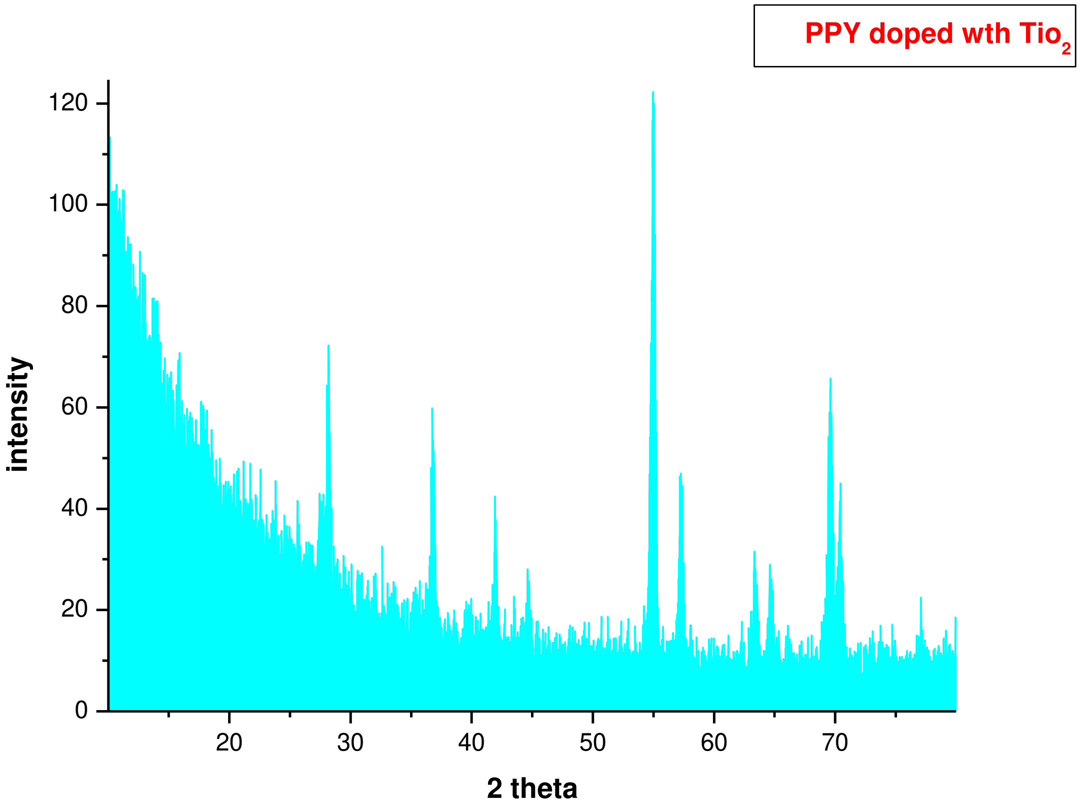


Fig 5.5(b)XRD patterns of the PPy-TiO$_2$ composites

CONCLUSION

Results UV Spectra show that the nanocomposites of PPy-TiO_2 also have consistent peak at ~250nm & ~ 490nm.The Wavelength~ 490nm at which is characteristic of π-π* transition of neutral PPy-TiO_2.

The properties of polypyrrole highly depend on the synthesis conditions. Lower monomer/oxidant ratio influences the formation of shorter polymer chains, and the Polypyrrole and TiO_2 Nanocomposite samples were proved by FTIR spectroscopy. The Stretching peaks (~3412.04 cm^{-1} to ~1040.17 cm^{-1}) of FTIR spectrum confirmed the formation polypyrrole.The Stretching peaks (~3426.30 $cm^{-1}$to 1040.02cm^{-1}) all these peaks are the main characteristic of PPy-TiO_2 nanocomposites.

The morphology and size distribution of the synthesized Polypyrrole and Polypyrrole with TiO_2 nanocomposite was be measured by FE-SEM.The average grain size range is 100µm.The quantitative analysis result indicates that the atomic ratio of S is 72.26% & Ti is 81.17%.

From XRD studies for PPy exhibited diffraction peaks at 2θ=29.24°,38.40°,44.57°,64.69°,77.62° corresponds to (100),(111),(200),(221) planes (222).PPy-TiO_2 2θ =29.17°,36.82°,41.94°,55.00° and 69.61°are correspond as (100),(110),(111),(200),(211) planes.The plane (110)indicate the tetragonal specimen line of TiO_2[17].

REFERENCE

1. Kerstin Muller et al., " Review on the Processing and Properties of Polymer Nanocomposites and Nanocoatings and Their Applications in the Packaging, Automotive and Solar Energy Fields", Published: 31 March 2017.

2. International Journals of Nanoscience,https://emm.nano.org

3. International Journals of Nanotechnology,https://emm.nano.org

4.Cowie, J. M. G. (John McKenzie Grant) (1991). Polymers: chemistry and physics of modern materials. Glasgow, Blackie.

5. Hall, Christopher (1989). Polymer materials , London; New York: Macmillan.
Rudin, Alfred (1982). The elements of polymer science and engineering. Academic Press.

6. http://www.meerutcollege.org/mcm_admin/upload/1587184940.pdf

7. https://en.wikipedia.org/wiki/pyrrole

8. Alan R. Katritzky," Handbook of Heterocyclic Chemistry" (Third Edition), 2010

9. Gordon W, "Pyrrole and Application" ,Gribble Dartmouth College, Hanover, NH, USA

10.https://en.wikipedia.org/wiki/Ammonium_persulfate

11. Jon Varteresian,"Ammonium per sulfate", Fabricating Printed Circuit Boards, 2002

12.https://www.vedantu.com/chemistry/ammonium-persulfate

13.https://www.chemeo.com/cid/51-726-9/Ammoniumpersulfate

14. Marc Hirsch ,"Titanium Dioxide: An Introduction"

Posted on September 23, 2016

15.https://byjus.com/chemistry/titanium-dioxide/

16. Manik A. Chougule et al.," Synthesis and Characterization of Polypyrrole (PPy) Thin Films" Materials Research Laboratory, Mumbai,India, Published Online January 2011

17. S. Deivanayaki, et al., "The structure and properties of polypyrrole/ titanium dioxide nanospheres of various dopant percentages by chemical oxidation method" Sri Ramakrishna mission Vidyalaya College of arts and Science, Coimbatore 20, India , 31 August 2012.

18. Vanja Gilja, et al.,"Synthesis and characterization of polypyrrole/TiO2 composites as a photocatalyst ", Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia

19. Trong Tung Nguyen, et al., "Effect of TiO2 Rutile Additive on Electrical Properties of PPy/TiO2 Nanocomposite", College of Television Vietnam, Vietnam

20.M.q.he, et al.," Synthesis of molecularly imprinted polypyrrole/titanium dioxide nanocomposites and its selective photocatalytic degradation of rhodamine B under visible light irradiation ", School of Chemistry and Chemical Engineering, Jiangsu University, China, 13 June 2014

21.Sobhan Bahraeian, et al., “Study on Synthesis of Polypyrrole via Chemical Polymerization Method”, Article in Advanced Materials Research , September 2013

22.Wei Shi , et al., “Synthesis of Polypyrrole/V2O5 Composite Film on the Surface of Magnesium Using a Mild Vapor Phase Polymerization (VPP) Method for Corrosion Resistance”, College of Materials, Xiamen University Published: 18 April 2020

23**.**Chepuri R.K.Rao, et al., “ Synthesis and properties of polypyrrole obtained from a new Fe(III) complex as oxidizing agent”, Article in Indian Journal of Chemistry , July 2013

24.Mostafizur Rahaman, et al**.,”S**ynthesis of Antibacterial Conductive Polypyrrole/Titanium Dioxide Core–Shell Nanocomposites”,15 may 2020

25.Ayaz Mahmood Dar,et al.,” Simple and Multi-Component Synthesis of Pyrrole Heterocycles” , Govt. Degree College Kulgam, University of Kashmir, India , Published: December 07, 2017

26.Abdirahman Yussuf ,et al., “Synthesis and Characterization of Conductive Polypyrrole: The Influence of the Oxidants and Monomer on the Electrical, Thermal, and Morphological Properties”, Petroleum Research Center, Kuwait,Published 18 July 2018

27.Reza ansari, et al., “Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies” , Faculty of Science, Guilan University, Rasht, Iran,1 June 2006.

28.Behzad Rezaei,et al., “Applications of Titanium Dioxdie Nanocoating”, Isfahan University of Technology, Isfahan, Iran ,1February 2006

29.Andrea Leon, et al., “FTIR and Raman Characterization of TiO2 Nanoparticles Coated with Polyethylene Glycol as Carrier for 2-Methoxyestradiol”, Published: 4 January 2017

30.Ziyang Li, et al., “ Preparation of Nanocomposites of Polypyrrole-metal (or Metal Oxide) on the Surface of V2 O5 Coated Cathode through a One-step Method” ,To cite this article: Mater. Sci. Eng. 611 012037

31. J.Y.Lee, et al., “Synthesis of Conducting Polypyrrole-Titanium Oxide Nanocomposite: Study of Structural, Optical and Electrical Properties”, 12 September 2017

32. Nazih K,” Chemical oxidation”, Graduate Environmental Engineering Program Lenox Institute of Water Technology, Lenox

33. http://www.ijirset.com/upload/2014/june/110_Synthesis.pdf

34. Kestur Gundappa Satyanarayana, “Nanocomposites: Synthesis, Structure, Properties”, Universidade Federal do Parana, Jardim das Americas, 81531-990 Curitiba - PR, Brazil Received: November 24, 2008; Revised: February 10, 2009

35. https://www.sciencedirect.com/topics/chemistry/field-emission-scanning-electron-microscopy

36. A.Alyamani,”FESEM characterization of some Nanomaterial”,

Published: March 9th 2012

37. Ranvijay Pratap Singh,” UV & VISIBLE SPECTROSCOPY”,Faculty of Engineering & Technology University of Lucknow

38. http://blamp.sites.truman.edu/files/2012/03/322-UV-Vis-Instrumentation.pdf

39. http://www.chemguide.co.uk/analysis/uvvisiblemenu.html#top

40.https://en.wikipedia.org/wiki/Fourier-transform_infrared_spectroscopy

41.https://www.findlight.net/blog/2019/03/27/ftir-principles-applications/

42.https://www.innovatechlabs.com/newsroom/672/stuff-works-ftir-analysis/

43.http://web.pdx.edu/~pmoeck/phy381/Topic5a-XRD.pdf

44.https://www.slideshare.net/hephz/ppppppptttttt-x-ray

45. https://www.slideshare.net/shivadheeraj/x-ray-diffraction

STRUCTURAL CHARACTERIZATION OF ZnS THIN FILMS SYNTHESIZED BY SILAR METHOD

A project report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'SCOLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI.

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

V. MARISELVI

Reg.No:19SPPH07

Under the guidance of

DR. A.NIRMALA SHIRLEY M.Sc., B.Ed., M.Phil.,Ph.D.,

DEPARTMENT OF PHYSICS
ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' grade by NAAC)

2020-2021

CERTIFICATE

This is to verify that this project report work entitled **"STRUCTURAL CHARACTERIZATION OF ZnS THIN FILMS SYNTHESIZED BY SILAR METHOD"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI**, In partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and record of workdone during the academic year 2020-2021 by

V. MARISELVI **Register No: 19SPPH07**

A. Nirmala Shirley
Signature of the Staff–in-charge

Padmavathy S
Signature of the Coordinator

Joyce
Signature the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose
Signature of the principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Padmavathy S
13/4/21
Signature of the Examiner

ACKNOWLEDGEMENT

First of all, I thank lord Almighty for his blessing and grace to complete this report work.

I am deeply indebted to our Principal **Dr. Sr.A.S.J.LUCIA ROSE M.Sc, PGDCA, M.Phil, Ph.D.,** for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC,**Dr**. **Sr. F.MARY JOYCE BABY M.A.,M.Phil., Ph.D.,**for her support in my work.

I would like to express my special gratitude to **Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil.,Ph.d,** Head of The Department of physiscs, for her inspirational words to complete this report work.

I would convey my heart felt thanks to**Mrs. P. PADMAVATHI M.Sc., M.Phil.,** SSC Co-ordinator, Department to Physics for her and encouragement in successful completion of this project.

I wish to record my sincere thanks to **Dr. A.NIRMALA SHIRLEY M.Sc., B.Ed.,M.Phil., Ph.D.,** Assistant professor, Department of Physics for her enthusiastic guidance and support for completion of this project.

CONTENT

CHAPTER I **PAGE NO**

CHAPTER II

CHAPTER III

CHAPTER IV

CHAPTER V

LIST OF TABLES AND FIGURES.

CHAPTER- I

1.1 INTRODUCTION

In recent years increasing attention is being paid to thin films of metals, semiconductors, mostly due to their importance in industry as well as in research. These are being widely used in preparation of reflectors, fluorescent screens, interference filters, multiple beam interferometry integrated circuits and in man microelectronic devices. Their useful application is diverse fields invite more detailed studies of these films.

The term “thin film” has often been loosely used in literature to impel not only a layer of a solid material but also of a liquid or a gaseous phase However, there is neither any well-defined limit of its thickness to imply the end of the thin film stage nor can one indicate its transition to the thicker film region. So a “thin film” may arbitrarily be defined as a solid layer having a thickness varying form a few A^0 to about 10μm or so Since the thickness limitation is rather arbitrary, even somewhat thicker films may also come within the scope of this definition.

Thin Film technology(TFT)has a world-wide reputation in the field of thin film deposition process. This thin film deposition is an enabling technology for man large area electronics applications, such as thin film solar (O)LED lighting and (O)LED displays, thermal camera application etc. Thin film is very important material for technology because this type materials show different properties from its own bulk materials and this properties provides lots of benefits There is lots of thin film production methods.

Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films,and scientific curiosity about the behaviour of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are passed on phenomena uniquely characteristic of the thickness, geometry and structure of film.

When we consider a very thin film of some substance, we has situation in which the two surfaces are so close to each other that they can have a decisive influence on the internal physical properties and processes of the substance, which differ, therefore, in a profound way from those of a bulk material. The decrease in distance between the surfaces and their mutual interaction can result in the rise of completely new phenomena. Here the one dimension of the material is reduced to an order of several atomic layers which creates an intermediate system between macro system and molecular systems, thus it provides us a method of investigation of the microphysical nature of various processes. Thin films are especially appropriate for application in microelectronics and integrated optics. However the physical properties of the films like electrical resitivity do not substantially differ from the properties of the bulk material For a thin film the limit of thickness is considered between tenths of manometer and several micrometers.

Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices The properties of material significantly differ when analysed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optic properties or wear residence. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and devices, magnetic thin films in recording devices, magnetic sensors. A.R.coating, photoconductors, IR detectors filters, solar cells, polarizer's temperature controller in satellite, superconducting films, anticorrosive and decorative coatings. Thin film has become an essential aspect of human life, so that hardly can we find any field of activity where they are not present.

Each material surface is exposed to various environmental influences. The surface of a solid body is subjected to corrosion and wear interacts with light and electromagnetic fields. From the technological point of view the miniaturization of mechanic, electronic, optical and optoelectronic components permanently increases the surface to volume ratio of the involved materials In modern material science specific surface properties therefore gain increasing importance.

Thin films can also be found in optoelectronic, electronic and magnetic thin films which may deviate significantly from those of the bulk material A prominent example foe (GMR) which only operate due to the special properties of a combination of magnetic and insulating thin films.

The beginning of "thin film science" can possibly by traced to the observation of grove who noted that metal films were formed by sputtering of cathodes with high energy positive ions .since then it has come a long way and today it is no longer a subject of some casual academic interest but has become a full fledged discipline.

1.2 THIN FILM

A thin film is a larger of material ranging from fractions of a nanometer to several micrometers in thickness. A stack of thin films is called multilayer. In addition to their applied interest, thin film play an important role in the development and study of materials with new and unique property

1.3 DEPOSITION

1.3.1 PHYSICAL DEPOSITION

Evaporation techniques

- Vacuum thermal evaporation.
- Electron beam evaporation.
- Laser beam evaporation.
- Arc evaporation.
- Molecular beam epitaxy.
- Ion plating evaporation.

1.3.2 CHEMICAL DEPOSITION

Sol-gel technique

Chemical bath deposition

Spray pyrolysis technique

1. **Plating**
    1. Electroplating technique.
    2. Electroless deposition.
2. **Chemical vapor deposition (CVD)**

1. Low pressure (LPCVD)
2. Plasma enhanced (PECVD)
3. Atomic layer deposition (ALD)

1.4 SILAR METHOD:

The successive ionic layer adsorption and reaction (SILAR) method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution. The collection of a substance on the surface of another substance is known as adsorption, which is the fundamental building block of the SILAR method. The term adsorption can be defined as the interfacial layer between two phases of a system. Adsorption may be expected when two heterogeneous phases are brought into contact with each other. Hence,gas–solid, liquid–solid and gas–liquid are three possible adsorption systems. In SILAR method, we are only concerned with adsorption in liquid–solid system. Adsorption is an exothermic process. The adsorption is a surface phenomenon between ions and surface of substrate and is possible due to attraction force between ions in the solution and surface of the substrate. These forces may be cohesive forces or Van-der Waals forces or chemical attractive forces. Atoms or molecules of substrate surface eare not surrounded by atoms or molecules of their kind on all sides. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, adatoms can be holding on the surface of the substrate. The factors like temperature of solution, pressure, nature of the substrate, concentration of the solution, area of the substrate etc affect the adsorption process. The reaction in pre-adsorbed (cations) and newly adsorbed (anions)forms the thin films of desired material.

1.4.1 BASICS OF SILAR

The SILAR is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR process is intended to grow thin films of water insoluble ionic or ion covalent compounds of the type KpAa by heterogeneous chemical reaction at the solid solution interface basis of SILAR growth. It consists of atleast four different steps: adsorption, rinsing (I), reaction and rinsing (II).Adsorption: In this first step of SILAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: the inner (positively charged) and outer (negatively charged)layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

Rinsing (I): In this step, excess adsorbed ions, pK a^{+} and aAp-, are rinsed away from the diffusion layer. This results into saturated electrical double layer. Reaction: In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to thelow stability of the material, KpAa, a solid substance is formed on the interface. This process involves the reaction of pKa^{+} surface species with the anionic precursor aAp^{-}

Rinsing (II): In last step of a SILAR cycle, the excess and un reacted species ap^{-} X, Y, and the reaction by product from the diffusion layer are removed.By repeating these cycles, a thin layer of material, KpAa, can be grown. Following the above-mentioned steps the maximum increase in film thickness per one reaction cycle is theoretically one monolayer. This results into a solid layer of the compound KpAa. Dividing the measured overall film thickness by number of reaction cycles, growth rate can be determined. This gives a numerical value forgrowth rate under the given conditions. If the measuredgrowth rate exceeds the lattice constant of the material, ahomogeneous precipitation in the solution could havetaken place. In practice, however, the thickness increaseis typically less than or greater than a monolayer. Thus, the process involves an alternate immersion of the substrate in a solution containing a soluble salt of the cation of the compound to be grown. The substrate supportingthe growing film is rinsed in highly purified deionized water after each immersion. The facts affecting the growth phenomena are the quality of the precursor solutions, their pH values, concentrations, counter ions, individual rinsing and dipping times.In addition, complexing agent and pretreatment of the substrate have been shown to affect the SILAR growth.

1.4.2 MECHANISM OF SILAR METHOD

The growth mechanism involves three most important steps: (i) specific adsorption of the most strongly adsorbed ions of the compound to be grown, by the substrate immersion in a solution of one of its cationic precursor,(ii) water rinsing of the excess solution still adhering to the substrate, and (iii) chemical reaction between the moststrongly specific adsorbed cations and the less strongly adsorbed anions by the subsequent substrate immersion in the solution.

The critical operations for the deposition of thin films bysuccessive ionic layer adsorption and reaction (SILAR) method, are adsorption of the cations, rinsing with deionized water, reaction of pre-adsorbed cations with newly adsorbed anions and again rinsing with deionized water. Generally, manual, electropneumatic and computer based systems have been used to perform these operations inSILAR method. These methods are discussed in brief in the following sections.

1.4.3 MANUALLY OPERATED

This system does not require any power supply for operations, hence it is economical. In this system, four or more glass beakers of typically 50 ml capacity containing precursor solutions and de ionized water are placed separately in the tray. The beakers containing precursor solutions and de ionized water are alternately placed as shown . The beaker containing de ionized water is placed in between the beakers containing cationic and anionic precursor solutions. The immersion and rinsing of substrates are done manually. The SILAR deposition of sufficiently thick film requires many hours and therefore manual deposition of certain materials is not possible fora single person.

1.4.4 COMPUTER BASED

The schematic diagram of computer-based operating system (Nicolau 1985; Jim’enez-Gonz’ailez and Nair 1995). The equipment consists of two beakers of 50 ml each containing the precursor solution andtwo rinsing vessels, lying in a circle on the circular tray.Each rinsing vessel being placed in between beakers containing cationic and anionic precursor solutions. The substrates are attached vertically by means of four arms. The arms are set out in line or a right angle and supported on the spindle. The spindle can turn and slide tightly in a bearing.

1.5 MATERIALS STUDIED

1.5.1 ZINC SULFHIDE

Zinc sulfide (or zinc sulphide) is an inorganic compound with the chemical formula of ZnS. This is the main form of zinc found in nature, where it mainly occurs as the mineral sphalerite. Although this mineral is usually black because of various impurities, the pure material is white, and it is widely used as a pigment. In its dense synthetic form, zinc sulfide can be transparent, and it is used as a window for visible optics and infrared optics.

1.5.1.2. STRUCTURE OF ZINC SULFHIDE

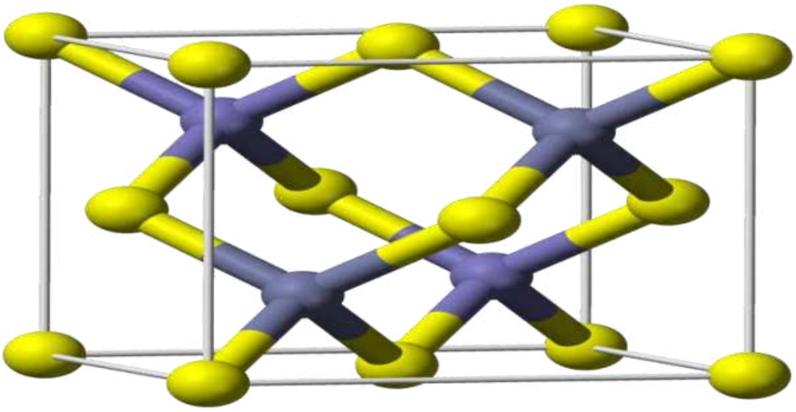


Fig.1.1 structure of zinc sulfide

1.5.1.3 PROPERTIES OF ZINC SULPHIDE

Chemical formula	Zns
Molar mass	97.474 g/mol
Density	4.090 g/cm^3
Melting point	1,850 °C (3,360 °F; 2,120 K) (sublime)
Solubility in water	Negligible
Band gap	3.54 eV (cubic, 300 K) 3.91 eV (hexagonal, 300 K)
Refractive index(np)	2.3677

Table 1.1 properties of zinc sulfide

1.5.1.3 APPLICATIONS OF ZINC SULPHIDE:

It is commonly used as a white pigment.Detector of alpha-rays, which render it luminescent.Infrared optics.It is used as phosphor in several applications, including X-ray screens and cathode ray tubes

1.5.2 ZINC CHLORIDE

Zinc chloride is the name of chemical compound with the formula $ZnCl_2$and its hydrates. Zinc chloride, of which nine crystalline forms are known, are colorless or white, and are highly soluble in water.$ZnCl_2$ itself is hygroscopic and even deliquescent. Samples should therefore be protected from sources of moisture including the water vapour present in ambient air. Zinc chloride finds wide application in textile processing, metallurgical fluxes, and chemical synthesies. No mineral with this chemical composition is known aside from the very rare mineral simonkolleite.

Fig1.2 structure of Zinc Chloride

1.5.2.1 PROPERTIES OF ZINC CHLORIDE

Chemical formula	$ZnCl_2$
Molar mass	136.315g/mol
Appearance	White crystalline solid hygroscopic And very deliquescent
Odour	Odourless
Density	2.907g/cm^3
Melting point	290°c(554°F,563 K)
Boling point	732°c (1,350°F , 1,005K)
Solubility in water	432.0g/100g (25°C)
Solubility	Soluble in ethanol, glycerol and acetone
Solubility in alcohol	430.0g/100ml

Tab 1.2 Properties of Zinc Chloride

1.5.2.1.1 PHYSICAL PROPERTIES

Zinc chloride is solid at room temperature and has a white crystalline appearance. It is odourless.The solubility of this compound in water corresponds to 432g/100g. It is also soluble in acetone, ethanol, and glycerol..The four polymorphs of $ZnCl_2$feature a tetrahedral coordinate geometry between the Zn^{2+} ions and the Cl^{-}Molten zinc chloride is highly viscous and has a relatively low electrical conductivity value.

1.5.2.1.2 CHEMICAL PROPERTIES

When $ZnCl_2$ is dissolved in water, the resulting solution is acidic in nature. The pH of an aqueous solution of zinc chloride with a concentration of 6M is 1.This compound reacts with ammonia to form complexes. Examples include $Zn(NH_3)_4Cl_2$and $ZnCl_2(NH_3)_2$.When heated, the hydrated form of zinc chloride loses water and small quantities of ZnCl(OH) are obtained.

1.5.2.2 APPLICATIONS OF ZINC CHLORIDE:

1.5.2.2 .1 METALLURGICAL FLUX

Zinc chloride reacts with metal oxides (MO) to give derivatives of the idealized formula $MZnOCl_2$.[*additiona citation(s) needed.*This reaction is relevant to the utility of $ZnCl_2$solution as a flux for soldering it dissolves passivating oxides, exposing the clean metal surface. Fluxes with $ZnCl_2$ as an active ingredient are sometimes called "tinner's fluid".

1.5.2.2.2 IN TEXTILE AND PAPER PROCESSING

Concentrated aqueous solutions of zinc chloride (more than 64% weight/weight zinc chloride in water) have dissolving starch, silk, and cellulose. Relevant to its affinity for these materials, $ZnCl_2$ is used as a fireproofing agent and in fabric "refresheners" such as Febreze. Vulcanized fibre is made by soaking paper in concentrated zinc chloride.

1.5.2.2.3 SMOKE GRENADES

The zinc chloride smoke mixture("HC") used in smoke grenades contains zinc oxide, hexachloroethane and granular aluminium powder, which, when ignited, react to form zinc chloride, carbon and aluminiumoxidesmoke, an effective smoke screen

1.5.2.2.4 FINGERPRINT DETECTION

Ninhydrin reacts with amino acids and aminesto form a colored compound "Ruhemann's purple" (RP). Spraying with a zinc chloride solution forms a 1:1 complex RP:$ZnCl(H_2O)_2$, which is more readily detected as it fluoresces more intensely than RP.

1.5.2.2.5 DISINFECTANT AND WOOD PRESERVATIVE

Dilute aqueous zinc chloride was used as a disinfectant under the name "Burnett's Disinfecting Fluid". From 1839 Sir William Burnett promoted its use as a disinfectant as well as a wood preservative. The Royal Navy conducted trials into its use as a disinfectant in the late 1840s, including during the cholera epidemic of 1849; and at the same time experiments were conducted into its preservative properties as applicable to the shipbuilding and railway industries. Burnett had some commercial success with his eponymous fluid. Following his death however, its use was largely superseded by that of carbolicacid and other proprietary products.

1.5.2.2.6 SKIN CANCER TREATMENT

Zinc chloride has been used in alternative medicine to cause eschars, scabs of dead tissue, in an attempt to cure skin cancers.Various products, such as Cansema or "black salve", containing zinc chloride and sold as cancer cures have been listed by the a (FDA) as fake with warning letters being sent to suppliers.Scarring and skin damage are associated with escharotic substances

1.5.3 THIOUREA

Thiourea is an organosulfur compound with the formula $SC(NH_2)_2$.It is structurally similar to urea, expect that the oxygen atom is replaced by sulphur atom, but the properties of urea and thiourea differ significantly. Thiourea is a reagent in organic synthesis. "Thioureas" refers to a broad class of compounds with the general structure $(R^1R^2N)(R^3R^4N)C=S$. Thioureas are related to thioamides.e.g . $RC(S)NR_2$,where R is methyl, ethyl etc.,

1.5.3.1 STRUCTURE OF THIOUREA

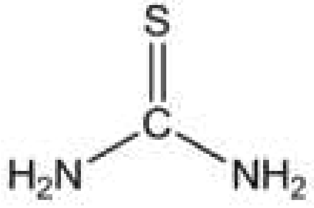


Fig 1.3 Structure of Thiourea

1.5.3.2 PROPERTIES OF THIOUREA

Chemical formula	CH_4N_2S
Molecular weight	76.12
Boiling point	150-160°c
Melting point	182°c (360°F , 455K)
Appearance	White solid
Density	1.405 g/ml
Solubility in water	142 g/l (25°C)
Magnetic susceptibility	$-4.24*10^{-5}$ cm^3mol

Table 1.3 Properties of Thiourea

1.5.3.3 APPLICATIONS OF THIOUREA

1.5.3.3.1 THIOX PRECURSOR

Thiourea has few applications. It is mainly consumed as a precursor to thiourea dioxide which is a common reducing agent in textile processin

1.5.3.3.2 FERTILISER

Recently thiourea has been investigated for its multiple desirable properties as a fertiliser especially under conditions of environmental stress.It may be applied in various capacities, such as a seed pretreatment (for priming), foliar spray or medium supplementation.

1.5.3.3.3 OTHER USES

Other industrial uses of thiourea include production of flame retardant resins, an vulcanisation accelerators. Thiourea is used as an auxiliary agent in diazo paper, light-sensitive photocopy paper and almost all other types of copy paper. It is also used to tone silver-gelatin photographic prints. Thiourea is used in the Clifton-Phillips and Beaver bright and semi-bright electroplating processes. It is also used in a solution with tin(II) chloride as an electroless tin plating solution for printed circuit boards.

1.5.4 DISTILLED WATER:

Distilled water is water that has been boiled into vapor and condensed back into liquid in a separate container. Impurities in the original water that do not boil below or near the boiling point of water remain in the original container. Therefore, distilled water is one type of purified water.

CHAPTER II

2.1 LITERATURE SURVEY:

Samir G Pandya reported that, Chemical method was utilized to fabricate Zinc Sulphide (ZnS) Nanocrystalline thin films. These films were prepared by changing the [S]/[Zn] ratio in the solution. All the films were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), UV-VISIBLE Spectroscopy, Hot probe, four probe and Hall Effect technique. The XRD Patterns of the synthesized film show the preferred orientation of (111), (220) and (311) planes, confirming the Cubic structure of ZnS. Surface morphology of thin film were studied using SEM. The optical properties of the prepared film were characterized by UV-VIS spectrometry and show the presence of direct transition with band gap energy about 3.14 eV. The conductivity, carrier concentration and mobility were measured.

Anuar Kassim reported that, The structure and morphology of ZnS thin films were investigated. ZnS thin films have been grown on an indium tin oxide glass substrate by electro deposition method using zinc chloride and sodium thiosulfate solutions at room temperature. The X-ray diffraction patterns confirm the presence of ZnS thin films. From the AFM images, grain size decreases as the cathodic potential becomes more negative (from −1.1 to −1.3V) at various deposition periods. Comparison between all the samples reveals that the intensity of the peaks increased, indicating better crystalline phase for the films deposited at −1.1V. These films show homogeneous and uniform distribution according to AFM images. On the other hand, XRD analysis shows that the number of ZnS peaks increased as deposition time was increased from 15 to 30min at −1.1V. The AFM images show thicker films to be formed at −1.1V indicating more favourable condition for the formation of ZnS thin films.

P.Mitra reported that,Polycrystalline zinc sulphide (ZnS) thin film was synthesized using chemical bath deposition(CBD) technique. The films are phase pure and polycrystalline with crystallite size approximately 12nm. The crystallite size was measured using X-ray line broadening method. The electrical characterization was carried out using conventional DC two-probe technique. An activation energy barrier value of 0.60 eV was observed, which can be associated with deep acceptor levels due to excess zinc atoms.

A U Ubale reported that, Zinc sulfide thin films have been deposited onto glass substrates by chemical bath deposition. The various deposition parameters such as volume of sulfide ion source, pH of bath, deposition time, temperature are optimized. Thin films of ZnS with different thicknesses of 76–332 nm were prepared by changing the deposition time from 6–20 h at 30°C temperature. The effect of film thickness on structural and electrical properties was studied. The electrical resistivity was decreased from 1·83 × 105 Ω-cm to 0·363 × 105 Ω-cm as film thickness decreased from 332 nm to 76 nm. The structural and activation energy studies support this decrease in the resistivity due to improvement in crystallinity of the films which would increase the charge carrier mobility and decrease in defect levels with increase in the thickness

Alexander Axelevitch reported that ,Zinc sulfide (ZnS) is a wide-bandgap compound semiconductor that is broadly used for various micro- and opto-electronic applications. ZnS is also applied as an emitter layer in thin-film photovoltaic devices. The preparation of thin-film photovoltaic devices requires suitable methods for doping semiconductor layers up to the desired level. For this purpose, in the present work, an ion assisted deposition system was developed and evaluated. We used a combination of simple thermal vacuum evaporation coupled with plasma discharge in the reactive

Abdullah Goktas reported that, Zinc sulfide (ZnS) thin films of different thickness were coated on glass substrates by the sol–gel dip-coating technique. Thickness dependent structural and optical properties of the films were studied in detail. X-ray diffraction (XRD) analysis indicated that the films had mixture of cubic (β) and hexagonal (α) phases with cubic (β) phase being predominant. Scanning electron microscope (SEM) showed that the film surfaces were smooth and crack free. Energy dispersive X-ray (EDX) measurement showed no impurity in the ZnS compound with elemental concentration of Zn/S being 50.38/49.62. Optical measurements showed that optical transmittance of the films were decreased in the visible range as the film thickness increased and band gap of the thin films were estimated to be about 3.61, 3.56, and 3.39 eV for the films with thickness of 100, 220, and 360 nm, respectively. Reactive indices and extinction coefficients of the films were measured by Spectroscopic Ellipsometer. Both the refractive index (n) and extinction coefficient (k) of the films were increased as the film thickness decreased. Electrical measurements showed that the resistivity of the films were decreased as the substrate temperature and film thickness increased.

Fei long reported that, ZnS thin films were prepared by an improved chemical bath deposition method, which the substrates were preheated before being mounted in the reaction solution. X-ray diffraction (XRD) and energy dispersive spectrometer (EDS) reveals that thin film ZnS has a cubic structure and the typical composition ratio of Zn/S is 52:48. Scanning electron microscopy (SEM) characterization shows that the surface of the sample is compact and uniform. The transmission spectrum indicates a good transmission characteristic with an average transmittance of 82.2

Seyed Mostafa Mosavi reported that, un- and Cd-doped ZnS nanostructures were synthesized using an electrodeposition method. The electrolyte contained 20 mM $ZnCl_2$, 20 mM $Na_2S_2O_3$ and the various amounts of $CdCl_2$ solution. The X-ray diffraction (XRD) patterns of the as-deposited samples exhibited that Cd doping leads to decrease the crystallite size (D) of ZnS meanwhile the lattice strain, lattice stress, dislocation density (γ), and stacking fault energy (SF) were increased. Field emission scanning electron microscopy (FESEM) images depicted very fine …

HMMN Hennayaka reported that, ZnS thin films were grown on indium–tin-oxide coated glass substrates using pulsed electrodeposition and the effect of the deposition temperature on the structural and optical properties of the ZnS films was investigated. Polycrystalline cubic ZnS films were obtained at all the deposition temperatures. At temperatures below 70 °C, less dense films were obtained and particle agglomeration was visible. On the other hand, at temperatures above 70 °C, more dense films with well-defined grains were obtained. With increasing deposition temperatures …

Nada M Sadeep reported that, Zinc Sulfide (ZnS) is important II-VI semiconductors material for the development of various modern technologies and photovoltaic applications. ZnS thin film was prepared by using chemical spray pyrolysis technique. The spray solutions contains ZnCl2 and SC (NH2) 2 with molar concentration 0.1 M/L. ZnS thin films was growth onto hot glass substrates at substrates temperature 400oC. The Structure of the prepared film was studied from X-ray diffraction pattern, the results shows that the film was polycrystalline with hexagonal structure, the grain size of ZnS film was calculated, it was 139 Å at the high peak. The optical properties of the film were studied using measurement from UV–VIS spectrophotometer; the results appear that a good optical transparency of about 65% was observed in the visible region. The optical constants were studied as a function of the photon energy within the wavelength in the range (300-900) nm. The refractive index was calculated in the visible region, it was 2.45 at 500 nm. The optical band gaps for the direct and indirect transition were estimate too and it was 3.2–3.1 eV respectively.

CHAPTER III

3.1 METHODOLOGY

Various methods were used for the preparation of thin film.They can be classified into many types.

A deposition technique is considered as the integral key for the creation of thin film new materials to meet the ever-increasing demand from industries for versatile and multi-dynamics materials. The deposition techniques determine virtually all the properties of the thin film and can also be used to modify the existing properties. Proper consideration needs to be given to the deposition techniques depending on the area of application because not all the deposition techniques result into the identical properties such as microstructure, surface morphology, tribological, electrical, biocompatibility, optical, corrosion and hardness A single material can be used for different application and tailored to the properties to meet the optimum requirements by using different deposition techniques. Combination of different techniques can also be used to form a hybrid deposition process with each contributing to the outcome of the thin film. Most deposition techniques follow these three major sequences:

1. Synthesis of the deposition species,
2. Conveyance from source to substrate,
3. Deposition and adhesion of the source onto the substrate and subsequent film growth.

There are several types of deposition techniques, but since the focal point of this review is on thin films deposition for forming layers below one micron, priority will be given to the two major deposition techniques used for thin films. The prominent subsets of deposition techniques are physical vapour deposition (PVD) and chemical vapour deposition (CVD). The distinguishing feature between PVD and CVD is in the vapour. In PVD, the vapour is made up of atoms and molecules that simply condense on the substrate, and for CVD, the vapour undergoes a chemical reaction on the substrate which resulted into a thin film depicts the types of thin film deposition which are purely in the gaseous state, solution state, and molten or semi-molten state.

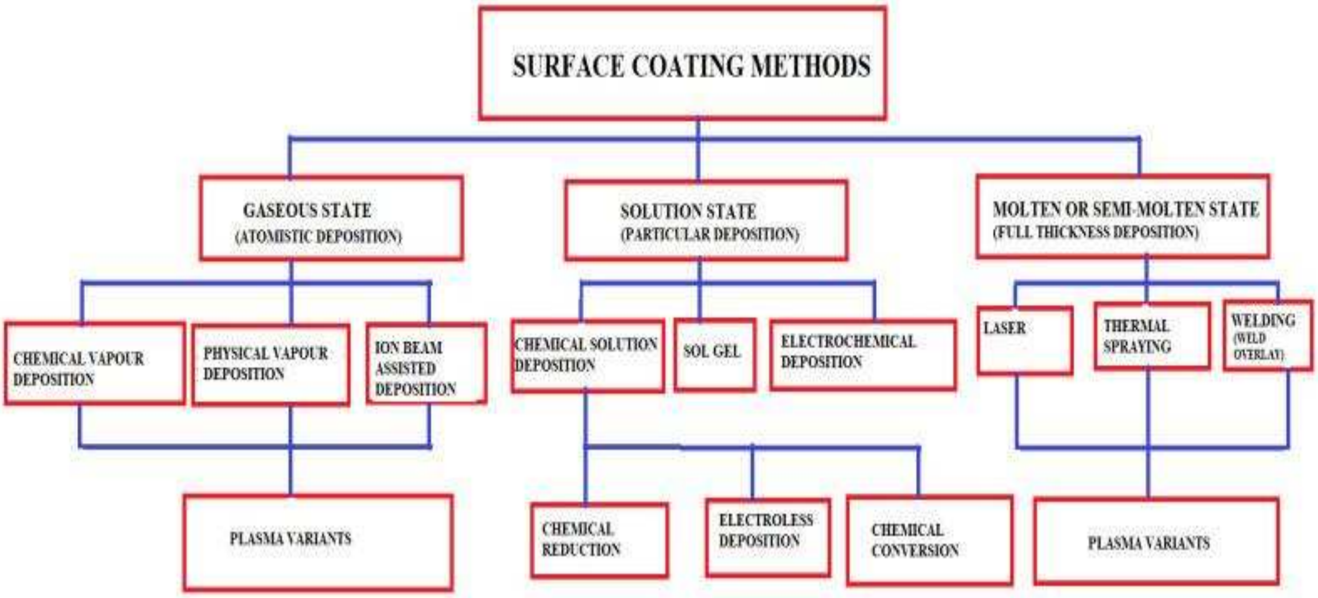


Figure 3.1. Variants of thin film deposition techniques.

3.2 PHYSICAL VAPOUR DEPOSITION (PVD)

Physical apour deposition (PVD) is a generic term used to quantify thin film deposition processes that require condensation of the vaporized solid material on top of the surface of the solid material under a partial vacuum condition . PVD is an atomistic deposition process in which there is a physical discharge of atoms or molecules and condensation and nucleation of these atoms onto a substrate through a vacuum or low pressure gaseous or plasma environment. Plasma or ions are usually the constituents of the vapour phase. Sometimes, the reactive gas can be introduced to the vapour during the deposition process and this is called reactive deposition. The atoms or molecules are conveyed in the form of a vapour via a vacuum or low pressure gaseous or plasma environment to the surface of the substrate for condensation to take place. Commonly, PVD processes are used to deposit thin films with thickness in the range of a few nanometres to a thousandth of nanometres. They can also be applied for multilayer deposition coating, graded composition deposits, very thick deposits, free-standing structure and in hybrid form with other deposition techniques .

Every PVD process can be attributed to three basic step which they all\obeyed .Creation of vapor-phase species. This requires conversion of materials to be deposited from a solid state to a vapour phase by evaporation, sputtering or ion bombardment. Movement or transportation from source to the substrate. The ejected atoms or molecules from the target will be transported through molecular flow conditions and thermal scattering processes. Also, if the partial pressure of the metal vapour or gas species in the vapour state is high enough for some of these species to be ionized, there will be a large number of collisions in the vapour phase during movement to the substrate. Film growth on the surface. The transported atom or molecule will start to nucleate around the substrate and grow by a number of processes. The incipient growth of the film determines the types of interface formation between the substrate and the atom or molecule. The composition and microstructure of the thin film can be altered by bombardment of the growing film by ions from the vapour phase, resulting in sputtering, re-condensation, and nucleation of the film atoms and enhanced surface movement of the atoms around the surface of the film.

The major variants of PVD are listed in below, but the three basic processes of PVD are vacuum or thermal evaporation, ion plating and sputtering.

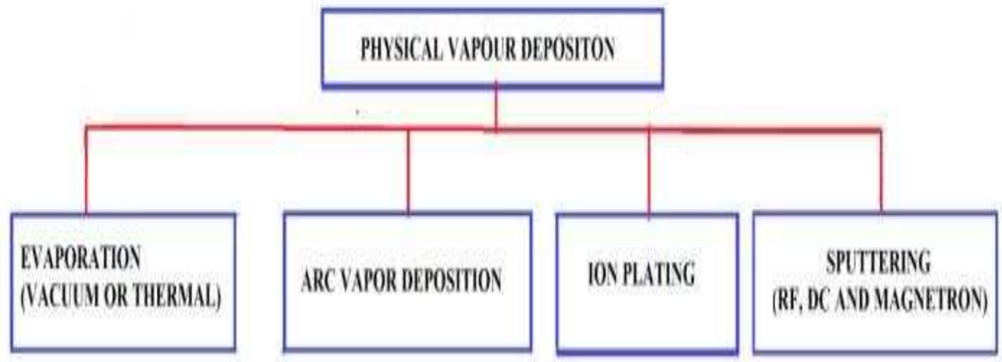


Figure 3.2. Variants of Physical Vapour Deposition. .

3.2.1 THERMAL (OR VACUUM) EVAPORATION

Thermal (or vacuum) evaporation is an old deposition process used for the formation and growth of the thin film on the surface of solid materials. The process is still beneficial in a contemporary environment and extensively applicable in the laboratory and industries for deposition of the thin film. The basic sequential steps for thermal or vacuum evaporation are given below:

The vapour is created from subjecting the target material to very high temperature by subliming or boiling, The ejected vapour from the target material is transported to the substrate through a vacuum, Condensation of the vapour takes place to form a solid thin film on the surface of the substrate, and further repeatability of the deposition cycles result in thin film growth and nucleation.

During the thermal evaporation process, the target material vaporized from the thermal process sources gets to the substrate material with minimal interference. The process is often carried out at a high vacuum pressure (HV), and the trajectory of the movement of the target material to the substrate is a straight path trajectory termed line of sight. Vapour flux is created by heating the surface of source material to a sufficiently elevated temperature in a vacuum. The flux can then condense to the surface of the substrate material to form a thin film. The vacuum environment creates a safe zone to reduce gaseous contaminants in the deposition process to an acceptable and minimal level and allows the evaporated atoms to undergo essentially collisionless transport from the source onto the substrate. The gas pressure range is usually between 0.0013 Pa to 1.3×10^{-9} Pa depending on the degree of the contamination in the deposition system, with the mean free path (MFP, the average distance between collisions occurring between species) no smaller than 5 mm. The thermal vaporization rate might be very high compared to other PVD processes . Tungsten wire coils are commonly used as the source of the thermal heat or by using high energy electron beam for heating the target material to an elevated temperature.

Evaporation process has been reported to be performed using different configurations. These are Molecular beam epitaxy, reactive evaporation and activate reactive evaporation. Molecular beam epitaxy (MBE) was discovered by J.R Arthur and Alfred Y. Cho at Bell telephone laboratories around 1960. MBE is used for growing epitaxy through the active interaction of distinct or numerous atomic or molecular beams on the surface of a heated crystalline substrate material. The evaporation occurs at an ultra-high vacuum for deposition of the controlled composition of uniform thickness of the thin film from specific deposition rate. This process has been applied in the manufacturing of semiconductor devices like cellular phone, transistor conductors and Wi-Fi . Reactive Evaporation involves the evaporation of atoms of metal from a target material in a chamber with the presence of reactive gas at a partial pressure. During the evaporation process, the atoms react with the gas chemically to form a compound thin film on the surface of the substrate. Reactive evaporation can form stoichiometric oxides, alloys . Another variant of evaporation technique is Activated Reactive Evaporation (ARE). ARE takes place by evaporation of atom from the surface of the target material in the presence of plasma and react this with the reactive gas within the chamber to form compounds with faster deposition rate and improved adhesion property. The plasma improves the rate of reaction between the target and the substrate, ionization of both coatings of metals and gas atom in the vapour phase and higher conversion of the neutral atoms into ions or energetic neutrals thus enhancing reaction probabilities and rates to deposit refractory compounds. If ARE process substrate is held at a negative bias voltage, it becomes biased activated reactive evaporation

3.2.2. SPUTTERING

Sputtering is a vital and prominent procedure among the PVD processes. It's a non-thermal vaporization process whereby individual atom escapes from the target surface due to atomic collision cascades by suitable high energy ion bombardment. Unlike evaporation, the source is no longer created by thermal but by ion impact on the target. Also, the target to substrate distance is shorter and, in many cases, it has outperformed other PVD processes with more functionality and performance like improved adhesion and thicker film. During the sputtering process, atoms are removed from the surface of the target material by transfer of sustainable momentum from an atomic-sized energetic bombarding particle usually gaseous ion accelerated from a plasma. Sputtering deposition can be achieved in a vacuum at low pressure plasma of < 0.67 Pa where the sputtered particles is in line of sight and can also be done at higher plasma pressure of 0.67 to 4 Pa, where energetic particles sputtered or reflected from the sputtering target are thermalized by gas phase collision before they reach the substrate surface. Sputtering is also being used as an etchant for cleaning the surface of solid materials and for pattern delineation because of its potential to eject atoms from an electrode surface.

The sputtering deposition has become a generic name for a variety of sputtering processes. These processes are named based on their source and the orientation of the process. Variants of sputtering are diode sputtering (cathode or radio frequency), reactive sputtering, bias sputtering, magnetron sputtering and ion-beam sputtering.

Sputtering deposition technique employs various sources for power, and the working pressure varies depending on the power configuration. DC sputtering is made up of a pair of planar electrodes (referred to as the cold cathode and anode). The target material to be deposited is placed on the cathode, and the substrate is positioned at the anode. The working gas inside the deposition chamber is usually argon gas due to the larger mass compared to neon and helium because higher mass correlates to more energetic collision with the target material and lower cost when compared to xenon and krypton. DC voltage is supplied between the cathode (target material) and anode (substrate) to sustain the glow discharge. The gaseous ions resulted from the sustained glow discharges are accelerated towards the target material, and sputtering takes place resulting in deposition of a thin film on the surface of the substrate material. In the DC sputtering system, the target is composed of conducting material usually metal since the glow discharge (current flow) is maintained between the metallic electrodes

Radio Frequency (RF) Sputtering is another variant of sputtering which involves alternating the electrical potential of the current in the vacuum environment at radio frequencies to avoid charge building up on certain types of sputtering target materials. In RF sputtering, the cathode (the target) which is to become the thin film coating and an anode is connected in series with a blocking capacitor in between. The capacitor is part of an impedance-matching network that provides the power transfer from the RF source to the plasma discharge. The cathode is bombarded by high voltage in a vacuum chamber leading to high energy ions sputtering off atoms as a thin film covering the substrate to be coated at a fixed frequency of 13.56 MHz. The essence of the capacitor is to develop DC self-bias and increase the optimization of power transfer for the target material to the plasma generated. RF sputtering offers numerous advantages like possibility of deposition on insulating materials, ability to sustain plasma at low pressure of 0.13 to 2 Pa, diffusion of RF plasma throughout the entire chamber, reduction of the creation of race track erosion on the surface of the target and ability to clean up the target materials after each cycle from building up charge to reduce arcing effect.

During sputtering process, secondary electrons are usually emitted from the target surface as a result of ion bombardment and magnetron sputtering makes use of the magnetic field to restrict the movement of the secondary electron to the vicinity of the target material. The configuration and strength of the magnetic field array determine the rate of the ionization efficiency current delivers to the target material resulting in higher deposition rate at the substrate. The increased ionization efficiency noticed during magnetron sputtering allows running of the sputtering process at a lower pressure of 100 Pa and lower voltage of -500 V compare to 10 Pa and -2 kV to 3 kV for the conventional sputtering process. The two major configurations for magnetron sputtering are conventional (balanced) and unbalanced magnetron sputtering. In balanced configuration, the plasma is confined to the target region while for unbalanced configuration, not all the magnetic field lines are closed but some are directed towards the substrate while some follow the closed field path. Further reading on this can be found in . Conductive materials can be deposited using a direct

current (DC) power supply and insulators can be deposited by using a radio frequency (RF) power supply. Magnetic arrays in magnetron sputtering configuration can be varied in situ without tempering with the electromagnet.

Reactive Sputter Deposition is used for creating the compound thin film. During sputtering, a reactive gas such as nitrogen or oxygen is introduced to the deposition chamber and gas react with the target material to form a compound thin film on the surface of the substrate. This process is referred to as reactive sputtering. An increase in reactive gas causes the topmost layer of the target material to transform from single phase to compound phase, which often results in changes in the properties such as the conductivity, e.g., conductive surfaces become non-conductive, and vice versa. The inert gas usually used for this process is Argon and its possible to combine the inert gas with ionized non-inert gas (reactive gas) or introduced the ionized non-inert gas (reactive gas) alone in the chamber. The percentage of reactive gas added to the chamber is controllable to produce a specific stoichiometric ratio of the compound. Argon is in most cases the main gas and the amount of a reactive gas introduced into a process chamber is controlled to either achieve a certain amount of doping or produce a fully reacted compound. The resulting deposited thin film is different from the target.Of recent, another variant of magnetron sputtering was invented called Pulsed Magnetron Sputtering PMS regarded as an emerging technology. The technique provides a solution to the challenging problems with other magnetron techniques like low deposition rate experience with RF magnetron sputtering and target poisoning and arc event associated with reactive magnetron sputtering. PMS concept is based on short or intermittent pulsing the medium frequency range between 10–200 kHz of the magnetron discharge for tens of microseconds at a low duty circle. The two modes for operating PMS are unipolar PMs where the voltage of the target material is pulsed between the ground and standard operating voltage and bipolar pulsed sputtering where the voltage of the target material is being reversed and turns to positive during the pulse-off duration. The pulsing process leads to the creation of super-dense plasma with exquisite properties which result in the creation of more uniform thin film and the possibility of achieving a smooth surface coating with complex and irregular shaped substrate materials .

3.2.3. ION PLATING

Mattox was the first to report Ion plating technique in 1960. It uses continuous or intermittent bombardment in an inert gas discharge system for the deposition of a film by atomic sized energetic particles to amend and regulate the properties of the depositing film. The plasma is created in a hollow cathode discharge source. The substrate material is subjected to bombardment by a high energy flux ions adequate to cause substantial sputtering on the surface of the substrate before and during thin film growth . The deposition material may be vaporized by other physical vapor deposition techniques like evaporation, sputtering, arc erosion or by decomposition of a chemical vapour precursor but the evaporated atoms pass through the gaseous glow discharge on their way to the substrate which causes some of the vaporized atoms to be ionized. The ions bombardment during film growth helps to create denser films with the densities closer to that of the bulk material and thus make it suitable for depositing a hard-thin film on compound materials. The gas pressure for ion plating process is between the ranges of 1 to 0.1 Pa. This pressure is enough to sustain glow discharge as well as scatter the vapour particles in all direction through numerous collisions to improve the overall coating of the substrate during film growth. A reactive gas can be added to form a compound surface coating, and the process is known as reactive ion plating.

3.2.4. ARC VAPOUR DEPOSITION

Arc vapour deposition is a deposition process that uses electric arc at high current and low voltage to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The substrate is usually biased so as to fast-track the film ions to the surface and also, the vaporized material are highly ionized. Flux is generated by creating an arc that travels across the surface of the target. The arc strikes lead to ejection of atoms from the target materials and condense on the substrate as a thin film coating. A substantial proportion of the metal atoms become ionized and makes it distinguished from vacuum or thermal evaporation. This substantial proportion of ionized atom makes it reliable for the formation of a thick coating and can be used for hard decorative surface-coating operations.

3.3 CHEMICAL VAPOUR DEPOSITION(CVD)

CVD is a generic term for deposition of the thin film via series chemical reaction. The process of material synthesis occurs when the constituent of the target in the vapour phase reacts via a chemical process near the surface or onto the surface of the substrate, leading to the growth of the thin film. Note that the mechanisms behind CVD differ drastically from the PVD process. In PVD, thin film formation is caused by condensation of atoms or molecules on the surface of the substrate due to evaporation, ion bombardment, or sputtering . On the other hand, CVD is a thermodynamically complex process involving chemical reactions under specific conditions such as temperature, pressure, reaction rates, and momentum, mass, and energy transport. Several process factors and chemical reaction between the reactant and substrate are responsible for the quality of films produced during CVD and the quality of the film can be controlled and modified by using the appropriate combination of process parameter like flow rates, pressure, temperature, concentration of chemical species, reactor geometry, etc. The main characteristics unique features of chemical vapour deposition are its resourcefulness for producing both simple and complex compounds with relative ease at generally low temperature, excellent throwing power and production of a coating of uniform thickness. CVD coating growth rate is high with ease of growth epitaxial film and offers good reproducibly of coating with same or almost similar mechanical, optical, chemical and physical properties. In addition, CVD has the ability to deposit materials which are problematic to evaporate with low porosity property on a substrate of complicated shapes which are difficult to produce by other deposition techniques. During CVD, the chemical composition of the reaction and physical structure can be tailored by monitoring and regulating the chemical reaction and deposition process parameters such as temperature, input concentration, pressure, gas flow rates, and reactor geometry CVD essential principles comprise of an interdisciplinary range of gas phase reaction chemistry, thermodynamics, kinetic and transport mechanisms, film nucleation phenomena, and reactor engineering. It should be noted that not all types of chemical reactions are desired in all kinds of CVD processes. There are various types of chemical reaction possible during CVD. The CVD reaction types possible are pyrolysis, reduction, oxidation, compound formation, disproportionation, and reversible transfer. The chemical reaction taking place depends on the reactant (precursor) gas and the by-products. In addition, the reaction has to be thermodynamically predicted, i.e., there is a need for availability of adequate energy for the reaction to take place and the Gibbs free energy (total available energy) has to decrease in order to allow the temperature and pressure of the reaction to be altered. This process involves the reaction of one or more volatile precursor transported via the vapour phase to produce a non-volatile solid that deposits atomistically on a suitably placed substrate within the confinement of a reaction chamber. The fundamental sequential steps that occur in every CVD process are stated below :

Convection or diffusion movement of reactant in a gas phase to the reaction chamber, Chemical and gas phase reactions leading to the formation of reactive species and by-products, Transport of the reactants through the boundary layer to the substrate surface, Chemical and physical adsorption of the reactants on the substrate surface,Heterogenous surface reactions leading to the formation of a solid film,Desorption of the volatile by-product to the main gas stream by diffusion through the boundary layer, Removal of gaseous by-products out of the reactor via convection and diffusion process.

CVD process usually characterized by volatile reaction of by-products and unused precursor species. Many CVD reactions by-products are very hazardous volatile by-products such as H_2, Cl_2, HCl, HF or water vapour. Proper safety precaution is needed when using CVD. Venting, scrubbing of by-products and unreacted compounds are essential in CVD processes. CVD can be grouped based on energy used to drive the chemical reaction. Sources of energy can either be a photon, laser or temperature(thermal) illustrates the variants of the CVD process

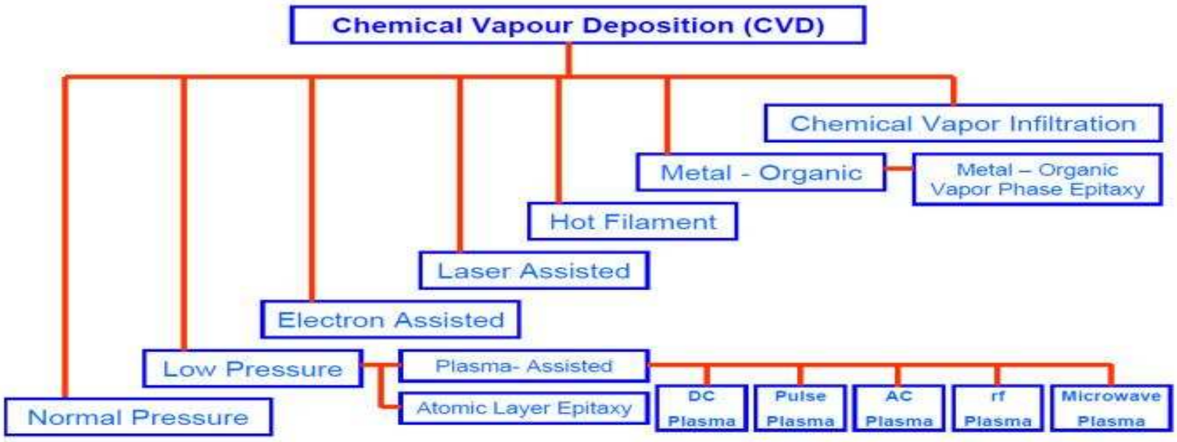


Figure 3.3 Variants of Chemical Vapour Deposition.

3.3.1 THERMAL CVD

Thermal CVD is a CVD process for depositing a thin film on various materials. This process uses heating lamps or other methods to heat the substrate rapidly and activate the energy needed for the reaction to take place. The growing film surface is exposed to thermal energy from either the condensing atoms or substrate heater to create the thin film. This thermal surface energy is responsible for mobilizing the atoms which lead to the creation of thin film with uniform thickness and good surface coverage and finishing. Since the thermal surface energy is dependent on the working temperature, an increase in temperature also resulted in a better thin film distribution on the surface of the substrate. The surface chemistry and surface atom mobility are aided by the substrate temperature alone.

4.2. LASER CVD (LCVD)

LCVD is also a variant of CVD process. It involves exposing a focused laser beam to locally heat the substrate of one or more volatile precursors which react on the surface to produce thin film deposition. The laser which occurs because thermal energy produces a coherent, monochromatic high-energy beam of photons can be used effectively to drive CVD reactor for deposition of the thin film .

3.3.3 PHOTON CVD

Photon CVD is another type of CVD. The chemical reaction is driven by the photon usually ultraviolet (UV) radiation which has the necessary energy to break the chemical bonds among the reactant molecules for deposition of the thin film .

3.3.4 PLASMA-ENHANCED CVD (PECVD)

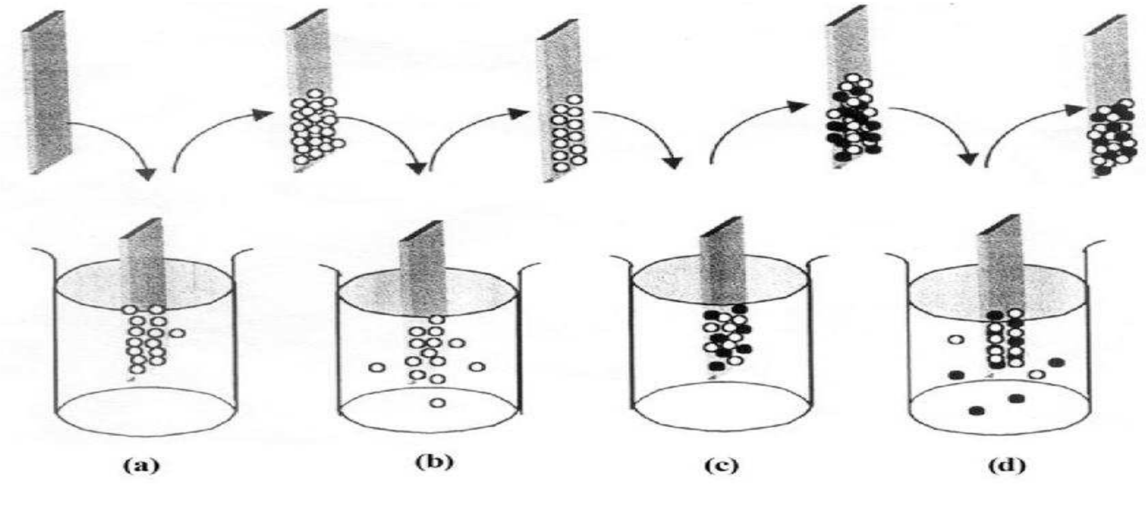
PECVD is a variant of CVD that is used to deposit a thin film from gaseous state to a solid state on the substrate. The chemical reaction takes place after the creation of a plasma in the reactor chamber and subsequently leads to deposition of a thin film on the surface of the substrate. PECVD uses an electrical source of energy to generate plasma and sustain the reaction process rather than thermal energy for the majority of the CVD processes. The electrical energy is used to initiate homogeneous reactions for the creation of chemically active ions and radicals that can partake in heterogeneous reactions, which, in turn, lead to layer formation on the substrate. The main benefit of PECVD over thermal CVD processes is the possibility of deposition to take place at a very low temperature close to the ambient temperature and permits materials sensitive to temperature change to be worked on . The use of plasma to activate the gas phase chemistry opens up several new reaction paths for deposition at a significantly lower temperature

3.3.5 PULSED CVD

Pulsed CVD also was known as atomic layer deposition (ALD) or atomic layer epitaxy (ALE). Its origins can be traced back to two different places. ALD was first developed as a promising coating technology on inorganic materials by Aleskovskii during the 1960s in Russia and was referred to as molecular layering . It became a major innovation when Suntola in the 1970s developed the atomic layer epitaxy technique to deposit ZnS for electroluminescent displays. ALD is based on self-limiting reactions between two gaseous precursors and allows the deposition of thin films in a layer-by-layer fashion. The ability to deposit conformal films on high aspect ratio structures, with high uniformity over large areas, at (relatively) low temperatures and moderate pressure, as well as exquisite thickness control are well beyond the reach of other thin film technologies such as physical vapor deposition and chemical vapor deposition and has made ALD a technique of choice for the preparation of ultrathin films. It uses only surface chemical reactions to build up ultrathin films with the ability to achieve a very precise control of thin film thickness down to atomic level . ALD allows a wide range of deposition and also viewed as an alternative method for exploring more surface growth mechanisms to form new hybrid nanostructures. It has been extensively used for the nanofabrication processes for microelectronic applications. ALD became commercially important in the early 2000s when the semiconductor industry started to adopt ALD for manufacturing high-performance complementary metal–oxide–semiconductor (CMOS) transistors. Both Intel and IBM have utilized ALD to fabricate high-k dielectric layers in CMOS since 2007. Recently, Intel stated that the use of ALD was a key factor for the successful development of the high-k metal gate transistors that allowed further downscaling of the size of integrated circuit chips . Nowadays, ALD has already percolated into the multitudinous application domain such as magnetic recording heads, optics, demanding protective coatings, and micro-electromechanical systems. Some more detailed information on ALD application has been summarized by Octavio , Hong and Bo Yan .Other notable mention deposition techniques that use CVD reaction principle of operation are metal organic vapour phase epitaxy, metal organic CVD, pyrolysis, reduction, oxidation, compound formation, disproportionation, and reversible transfer. Some CVD processes can also be carried out in atmospheric pressure known as Atmospheric pressure CVD or APCVD. APCVD are commonly used to form SnO_2 on hot glass using $SnCl_4$ or monobutyltntrichloride and dopants to make the coating on the surface

3.4 SILAR METHOD

ZnS thin films were prepared by SILAR method using glass substrates. Before deposition substrates were cleaned in dilute hydrochloric acid, and then in acetone. Later they were rinsed with double distilled water. For this deposition, cationic precursor used as zinc chloride and anionic precursor as thiourea Well cleaned glass substrates were dipped into aqueous solution of zinc chloride. The surface of the substrate was absorbed by zinc ions. Then substrate was rinsed by double distilled water to expulsion of loosely bound Zn2+ ions. Next to this, the substrates were dipped into aqueous solution of thiourea .The sulphide ions reacted with adsorbed zinc ions. Finally, to avoid precipitation the substrates were rinsed with distilled water. This is the growth cycle of SILAR method. To obtain desired thickness of the films, these growth cycles have been replicated.



3.4 Schematic representation of SILAR method

CHAPTER IV

4.1 INTRODUCTION

The synthesized thin films can be characterized using different techniques. In the present study ZnS thin films were subjected to XRD, SEM andAFM.

4.2 X-RAY DIFFRACTION(XRD)

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material

A primary use of XRD analysis is the identification of materials based on their diffraction pattern. As well as phase identification, XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects

The Bragg equation ,$n\lambda=2d\sin\theta$ is one of the keystones in understanding X-ray diffraction .

$n \rightarrow$ is an integer

$\lambda \rightarrow$ is character wavelength of the X-ray impinging on the crystallize sample

$d \rightarrow$is the interplaner spacing between rows of atoms

$\theta \rightarrow$ is the angle of the X-ray beam with respect to these planes when this equation is satisfied X-ray scattered by the atoms in the plane of a periodic structure are in phase and diffraction occurs in the direction defined by the angle θ. In the simplest instance , an X-ray diffraction experiment consists of a set of diffracted intensities and the angles can be thought of a chemical fingerprint and chemical identification can be performed by comparing this diffraction pattern to a data base of known patterns

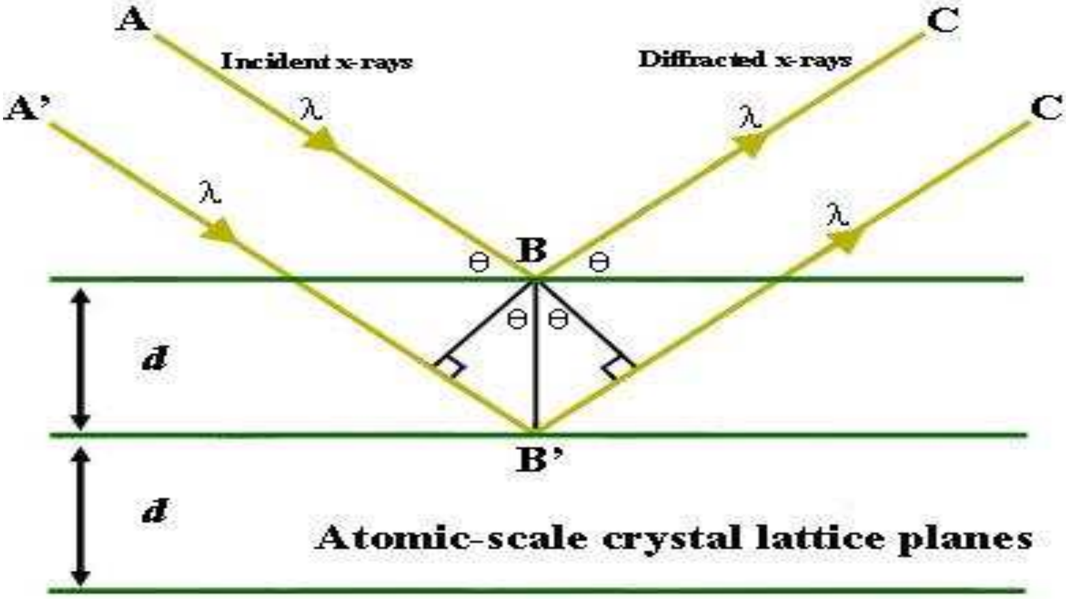


Fig 4.1 X-Ray Diffraction patteren

4.3 XRD PATTEREN OF ZnS PREPARED BY SILAR METHOD

To study structural properties of the deposited ZnS thin films. X-ray diffraction (XRD) study was carried.The XRD pattern for the ZnS thin film with the high density peaks absorbed at $2\theta = 30.610$ along the (102)hkl plane , $2\theta= 26.972$ along the (100) hkl plane presented in the Fig 4.3. All diffraction peaks of the ZnS thin film correspond to the characteristic wurzite structure of ZnS thin film.

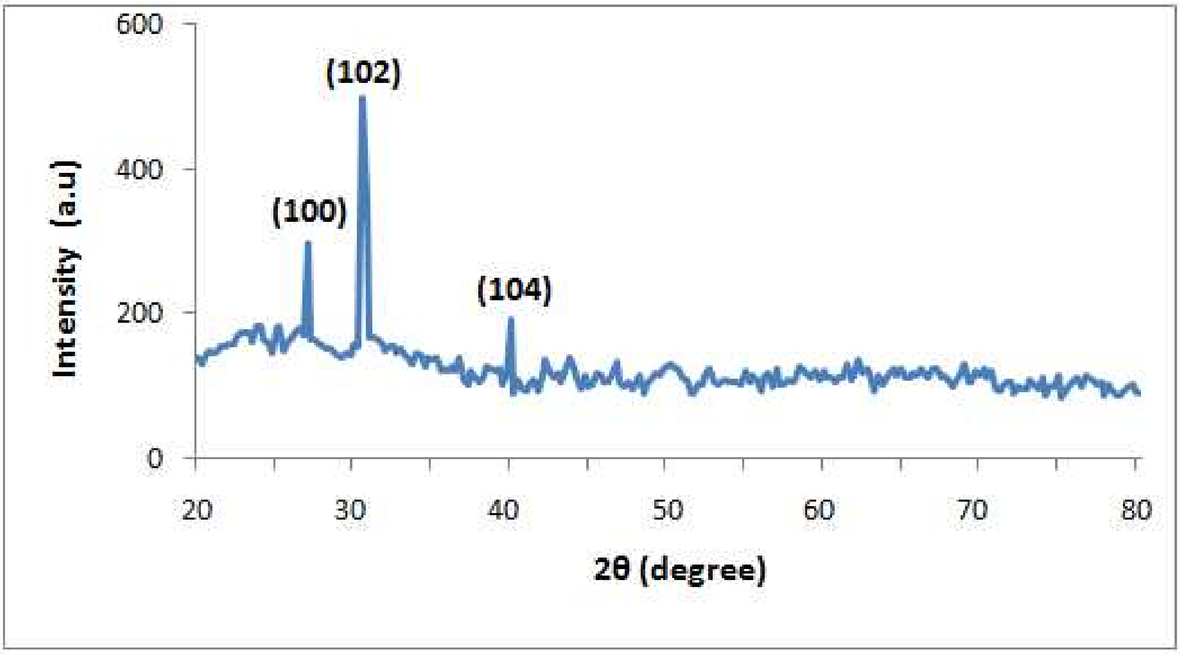


Fig 4.2 XRD Pattern of ZnS thin film

The crystal structure describes the atomic arrangement of a material. diffraction peaks in an X-ray scatteringpattern. Interatomic distances determine the positions of the diffraction peaks. The atom types and positions determine the diffraction peak intensities.The crystal structure describes the atomic arrangement of a material.

The observed ‘d’ values are compared with standard ‘d’ values using Joint Committee on Powder Diffraction Standards (JCPDS) diffraction file or American Society for Testing Materials (ASTM) data card for the same material synthesized by standard chemical methods.

Using Fig4.2 to investigate structural properties of the deposited film, further analysis of XRD studies have been done. The crystallite size of thin film was calculated from XRD patterns by using Scherrer's formula given below

$$D= \frac{k\lambda}{\beta cos\theta}$$

Where

D= Crystallite size

β=Corrected FWHM of the most intense peak

θ = Bragg's angle

K = constant

Using these formula grain size can be dertermined . The grain size for (100) values was found to be 3.0306. and the grain size for(102) value was obtained to be 2.6925.and the grain size for (104) value was obtained to be 2.1269.

The grain size and dislocation density and microstrain and lattice spacing of ZnS thin film have been given below

The dislocation density has been calculated using crystallite size, by the equation

$$\text{Dislocation} = 1/D^2$$

The microstrain has been calculated by the given formula,

$$\text{Microstrain} = \frac{\beta \cos\theta}{4}$$

The lattice constant has been calculated by the gien formula

$$\text{lattice constant} = [4/3\left(h^2 + k^2 + \mathrm{hk}\right) l^2(\left(\frac{a}{c}\right)^2]1/a^2$$

Hkl	2θ (Degree)	Grain size (D)nm	Dislocation density (lines/m^2)	Microstrain	Lattice spacing
100	26.972	3.0306	0. 1088	0.1143	0.0339
102	30.610	2.6925	0.1379	0.1287	0.1356
104	39.743	2.1269	02210	0.1629	0.4674

Table 4.3 Structural parameters of ZnS thin fim

4.4 AFM (ATOMIC FORCE MICROSCOPY)

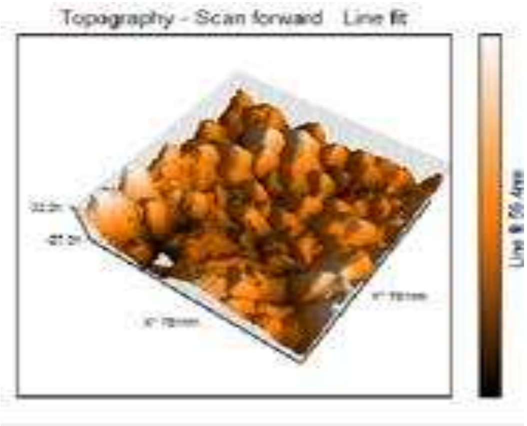


Fig 4.4 atomic force microscope image of ZnS thin film

Atomic force microscopy is one of the most popular techniques for metrology measurements such as surface roughness due to its ability to quantitatively measure the x, y, and z direction with nanoscale resolution.

AFM is one of the few tools that is able to quantitatively measure all 3 dimensions of a surface: lateral (x and y) and height (z). Unlike other high resolution microscopic characterization methods that rely on interactions of electrons with a material, in AFM there is a mechanical contact between a tip and sample enabling an accurate measurement of sample topography and surface texture. With a resolution of 5-10nm laterally and sub-nanometer vertically, AFM is a powerful measurement instrument for quantitative measurements of a surface. This powerful quantitative measurement is coupled with flexibility in sample surface: there are no requirements on a sample to be able to be measured by AFM except that it fits into the instrument. Quantitative measurements of sample topography enable important metrological measurements such as roughness profile, finding irregularities on the surface, as well as more advanced measurements such as skewness

4.5 SEM (SCANNING ELECTRON MICROSCOPE)

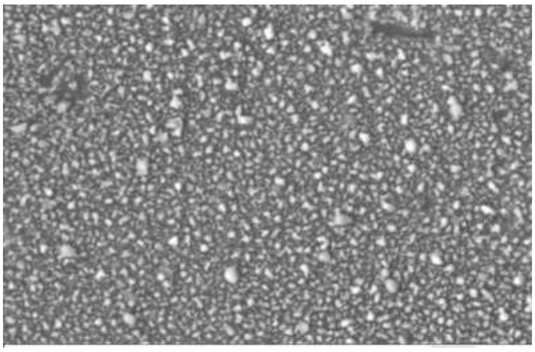


Fig 4.5 SEM image for ZnS thin film

(SEM) scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition.

The scanning electron microscopy technique is familiar for the study of surface morphology of metal chalcogenides in the thin film form.The ZnS film prepared with optimized parameters is used for SEM observation.Fig.shows the SEM micrograph of ZnS thin film. The film is homogeneous, well adherent and covers glass substrate without cracks and pin hole. The film compactness is high, the grain size is generally small and they are agglomerated in some places.

CHAPTER V

5.1 RESULT AND CONCLUSION

In this project ZnS thin films were prepare by SILAR method and was characterised by various studies such as XRD , AFM and SEM.

The synthesised films were characterised by XRD. The grain size of ZnS was calculated by Debye-scherrer's formula which proves that ZnS thin film is a hexagonal structure . The average grain size of the thin film is about 2.6166nm. The miller indices values well agree with the JCPDS files.

The surface roughness is measured is by atomic force microscope. SEM studies reveal information about the surface topography and composition.

In future, ZnS thin films will be characterised by further studies such as optical and electrical studies for solar cell applications.

REFERENCES

[1] Mayer H ,structures and properties of thin films,(willey, New York)1959,225

[2] Goswami, A.and Ojha, S.M. thin solid films (1973).

[3]Milton ohering, material science of thin films(2002).

[4]S.Datta roy and P.Mitra"Preparation of ZnS thin film by SILAR method" Material Science Research India (2008)

[5]Alexandar axelevitch,Boris Apter, " preparation and study of doped ZnS thin films", microelctronic engineering(2007).

[6]Nada M Sadeed,structural and optical properties of ZnS thin films prepared by spray pyroysis technique.(2011)

[7]Samir G Pandya, "synthesis and characteriszation of zinc sulphide thin film deposited by chemical method"(2006/

[8]Anuar kassim, "XRD and AFM studies of ZnS thin films produced by electrodeposistion method".(2010)

[9]A U Ubale and D K Kukarni"Chemical bath deposition of ZnS thin films".(2004).

[10]Abdullah Goktas, " preparation and characterisation of thickness dependent nano-structured ZnS thin films by sol-gel technique".(2002).

[11]Martin PM(2009) " hand book of deposition technologies for film and goatings".

[12]Mattox DM(2010) “ hand book of physica vapour deposition (PVD) processing”.

[13]H M Pathan and C D Lokhande(2003), “Deposition of metal chalcogenide thin films by SILAR method.

[14]V K Gowrish Rao K (2018), “ structural and optical properties of ZnS thin films by silar technique.”

[15]A Djelloul, “structural and optical study of ZnS thin films prepared by SILAR method (2006)”.

[16]www.wikipedia.distilled water.

[17]Dler adil jameel“Thin film deposition processes.(2015).

[18] Masatsugu sei Suzuki and itsuko S. Suzuki (2006) “Lecture note on solid state physics X-ray diffraction”.

[19] M. Balachander , M. Saroja, M.Venkatalachalam , S. Shankar “Preparation and Characterization of Zinc Sulfide thin film deposited by Dip Coating Method” International Journal of Innovative Science, Engineering & Technology, Vol. 2 (2015)

[20] A,H,Eid, S,M.Salim, M.B.Sedik, H.Omar “Preparation and characterization of ZnS thin films”Journal of Applied Science Research vol.6 (2010).

[21]Vidit pandey“Thin fim synthesis and applications”.(2020).

[22]K.L Chopra.et.al“ thin film device application”,(1983)

[23] Ayan Mukherjee , Patha Mitra " Characterization of Sn doped ZnS thin film synthesized by CBD" .Material Science vol.20,(2017)

[24] S,Patra , S.Mondal , and P.Mitra " Preparation of ZnS and SnS nano powder by modified SILAR method" Journals of Physical Science vol.13,(2009)

[25]www.wikipedia.zinc sulphide.

[26]www.wikipedia.thiourea

[27] V. D. Patake and C. D. Lokhande, Appl. Surf. Sci. 254 (2008) 2820.

[28] R. R. Salunkhe, D. S. Dhawale, T. P. Gujar, C. D. Lokhande, Mater. Res. Bull. 44 (2009) 364.

[29] M. Ristov, G. J. Sinadinovskia, I. Grozdanov, Thin Solid Films 123

[30]Fei-peng,surfaceand structura morphology.(2014).

VOLUMETRIC INVESTIGATIONS IN CURCUMIN WITH BENZYL PROPIONATE

project report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI.

In partial fulfillment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

R. REDEEMA FERNANDO

Reg. No: 19SPPH08

Under the supervision and guidance of

Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this project work entitled **"VOLUMETRIC INVESTIGATIONS IN CURCUMIN WITH BENZYL PROPIONATE"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** in partial fulfillment of requirements for the award of MASTER **OF SCIENCE IN PHYSICS** and is a record of work done during the year 2020-2021 by

R. REDEEMA FERNANDO **Register No: 19SPPH08**

Padmavathi P
Signature of the Guide

Padmavathi P
Signature of the SSC Coordinator

Joyce
Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose
Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

A. Nirmala Shirley
Signature of the Examiner

DECLARATION

I hereby state that the project entitled, **“VOLUMETRIC INVESTIGATIONS IN CURCUMIN WITH BENZYL PROPIONATE**” submitted to **ST. MARY’S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY TIRUNELVELI,** for the award of the Degree of Master of Science in Physics is my unique work and no part of this project has been submitted for any Degree, Diploma or other similar titles.

Station: Thoothukudi **R. REDEEMA FERNNADO**

Date: **Signature of the student**

ACKNOWLEDGEMENT

"GIVE THANKS TO THE LORD FOR HE IS GOOD "

First of all, I thank the Lord Almighty for his blessing and grace to complete this comprehension work.

I am deeply indebted to our Principal **Rev. Dr. Sr. A. S. J. LUCIA ROSE M. Sc., PGDCA., M. Phil., Ph. D.,** for the encouragement she bestowed upon us.

I wish to express my sincere thanks to our Director of SSC, **Rev. Sr. F. MARY JOYCE BABY M.A., M.Phil.,** for her support in my work.

I would like to express my special thanks of gratitude to **Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D.,** Head of the Department, for her inspirational words and encouragement to complete this project.

I am thankful to **Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,** SSC Coordinator, who guided and helped me to make this work complete.

I would like to express my sincere gratitude to my guide **Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,** Assistant Professor, Department of Physics (SSC) for the continuous support, patience, motivation, and immense knowledge. Her guidance had encouraged me to do this project successfully.

I am grateful to my parents who have provided me through moral and emotional support to complete my work.

An endeavor over a long period can be successful only with the advice and supports of many well-wishers. I take this opportunity to express my gratitude and appreciations to all these people.

Abstract:

Ultrasonic technique has been found very fruitful in finding physic-chemical behaviour of binary/ ternary liquid mixtures. In this present study, the thermo-acoustical parameters of curcumin with benzyl propionate have been found using ultrasonic velocity (u), density(ρ), and viscosity(η) at a room temperature of 308K. Benzyl propionate is a liquid with a sweet, fruity odour, which is used in perfumery for floral, fruity notes and in fruit flavour compositions. Curcumin, a primary bioactive substance present in turmeric, helps in the administration of oxidative and incendiary conditions, metabolic disorder, joint inflammation and nervousness. Derived parameters like adiabatic compressibility (β_a), Intermolecular freelength (L_f), relaxation time (τ), acoustic impedance (Z) , Gibb's energy (ΔG) and their excess values have been calculated from the measured values of ultrasonic velocity (u), density(ρ), and viscosity(η). The type of interaction has been reported using these values.

LIST OF CONTENTS

List of tables

List of figures

Symbols, Abbreviations & Nomenclature	**Meanings**
U	Velocity
K	Wave number
K_s	Adiabatic bulk modulus
ρ	Density
ρ_0	Ambient hydrostatic pressure
ρ_{mix}	Density of binary mixtures
P	Acoustic pressure
α	Cubical expansion coefficient
β^{a}	Adiabatic compressibility
γ	Ration of specific heats
ω	Angular frequency
ξ	Particle displacement
ξ_0	Peak value of the particle displacement
m	Molecular weight
U_T	Isothermal sound velocity
R	Gas constant

Symbols, Abbreviations & Nomenclature	**Meanings**
T	Temperature
N_A	Avogadro number
R_m	Molar refraction
Z_i	No. of atoms in the i^{th} molecules
A_i	Additive volume
W	Sound velocity
T_c	Critical Temperature
T_0	Melting point
V_0	Volume per mole
V_f	Free volume
V_a	Available volume
V_{OA}, V_{OB}	Molar volume of the components A, B
L_f	Free length
L_{mix}	Free length in binary mixtures

CHAPTER-1

THE LIQUID STATE

1.1 INTRODUCTION

While it is often said that a liquid is intermediate in its properties between a solid and a gas, this statement should not be understood to mean that every property of a liquid is intermediate in value between those of the other two states. If the actual figures are compared, it is found that in the great majority of cases the value of any property of a liquid is approximately equal either to that of the solid or to that of the gas. The intermediateness, then, is a statistical one-a liquid has some of the properties of a solid, and some of the properties of gas. The most obvious resemblance between liquids and gases is their lack of rigidity neither offers permanent resistance to a shearing stress. The immediate consequence of this is that neither a liquid nor a gas possesses shape of its own, but always offer a resistance to shearing stress.

Between liquids and solids, the most prominent resemblance is that both possess cohesion, which enables each to maintain a free surface, whereas a gas will always completely fill any container. A second, and hardly less fundamental, property common to liquids and solids, is their relative incompressibility compared to gases. While the compressibility of solids are usually of the order or of10^{-6} atm^{-1}, those of liquids are only slightly larger (about10^{-5} atm^{-1}).

The compressibility of a gas, on the other hand, is roughly equal to the reciprocal of the pressure, or, at a pressure of one atmosphere, about 10^5 times as great as that of liquid. Closely allied to the second similarity between liquids and solids is the third: their similarity in density. The density change which takes place when a solid melt is usually of the order of 10 to 50 percent, but on vapourization the density decreases by a factor of 100 or 1,000.

From these simple facts considerable information can be obtained about the nature of the molecular arrangement in liquids. From the density, for example, the mean distance between molecules can be calculated. Taking Argon as a typical example, the molar volumes of the solid, liquid and gas at the boiling point are respectively 24.3 cc, 28.1 cc and 7.050 cc. As a first molecules of the liquid and gas are arranged like those of the solids in a face centered cubic lattice. To obtain the correct densities it is then necessary to assume that the distance between nearest neighbors is 3.84 $\overset{\circ}{A}$ in the solid 4.03 $\overset{\circ}{A}$ in the liquid 25.4 $\overset{\circ}{A}$ in the gas. In the solid, the molecules are in contact. In the liquid, there is a little space (about 5 percent of the molecular diameter) between molecules is about six times the molecular diameter.

Since the forces between molecules are short range forces, and act through a distance of only two or three times the molecular diameter, it is immediately obvious that in the gas these forces are of little importance. Any such regular arrangement of molecules as that we have assumed will therefore be destroyed by the thermal motions of the molecules, and the usual assumption that the molecules of a gas are arranged in space and are randomly distributed.

In the solid, on the other hand, the close-packed arrangement of the molecules prevents any molecule moving from moving far from its original position, which results in turn in the rigidity of the crystal. At the same time the low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must be accomplished by reducing the size of the molecule.

themselves. If the liquid maintains the arrangement we have assumed, it is difficult to see how to explain its fluidity. The molecules are packed so closely together that no interior molecule can change its position by much more than can the molecule of the solid. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane molecule. Such a motion, however, would require the simultaneous lengthening of a great number of intermolecular distances and hence a large energy of activation for the flow process. To avoid this difficulty, it is obviously necessary to assume that a few molecules move at a time, but this in turn implies that it must be relatively easy for molecules to become displaced from the regular lattice.

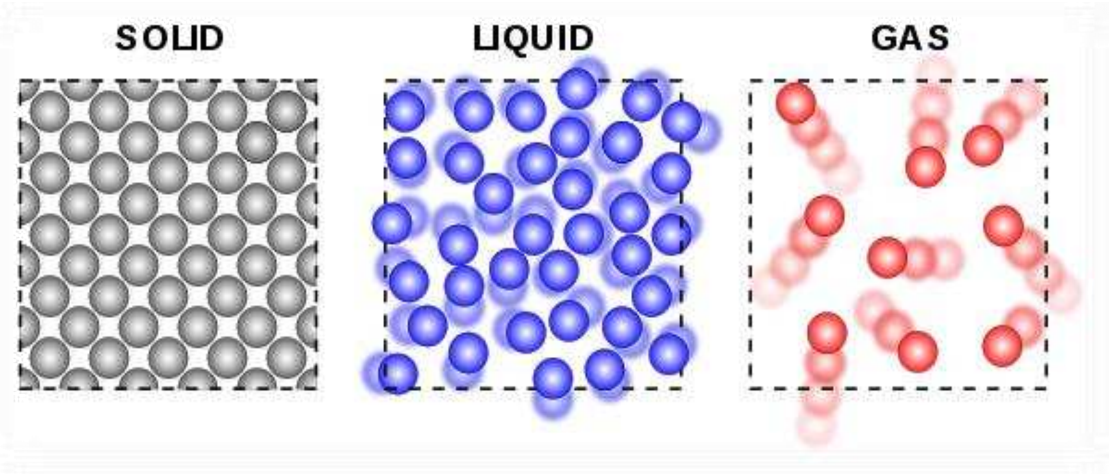


Fig1.1Relative spacing of molecules in solid, liquid and Gaseous Phases

On the other hand, the problem of packing so many spheres into a given volume does not permit any great variation from the regular closed packed structure. In fact, the only reasonable modifications which can be made are two in number. First, there may be local irregularities caused by groups of molecules coming closer together, leaving wider spaces elsewhere in the structure. Second, there may be gradual distortion of the structure as we go from molecule to molecule, so that although the pattern in the immediate neighborhood of a given molecule be quite regular, the pattern is irregular at a distance.

1.2 SHORT AND LONG RANGE ORDER

The tendency of a liquid molecule to surround itself with a more or less definite number of neighboring molecules at a near a definite distance shows that if we consider a region in the liquid so small that it contain only a few molecules, - say about 20 – these molecules must be arranged very nearly in as regular fashion as in the corresponding crystal. On the other hand, if the size of the region is enlarged, the irregularities mount up, and the positions of the molecule no longer can be related to a lattice of the type occupied by the molecules in the crystal. The regularity exhibited by the crystal is now generally referred to as long range order, since the positions of molecules many diameters away from a central molecule can be predicted from a knowledge of the position of the central molecule and the molecules immediately surrounding it.

In the liquid, on the other hand, this long range order has disappeared. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite, we can say that the liquid still possesses short range order. The crystal, of course, has short range order as well as long range order, but in the gas phase even the short range order has disappeared.

We can, therefore, state as an experimental fact that the melting of a crystal is accompanied by the disappearance of long range order, and the evaporation of a liquid is accompanied by the disappearance of short range order.

1.3 THE LOOSE PACKING OF RIGID SPHERES

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied a minimum, them a regular crystal-like lattice-either hexagonal or cubic is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of the structure will disappear. This has been demonstrated in two dimensions by a number of experimenters[1] who have studied the distribution of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by Morrell and Hildebrand[2] by suspending hard gelatin spheres in a solution of the same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

It would appear from this experimental evidence that the principal factor in the determination of the radial distribution function in a liquid is the volume occupied by the molecules themselves, that is to say, the repulsive forces between the molecules rather that their attraction.

1.4 THEORIES OF LIQUID STATE

The readiness with which liquids flow and diffuse suggests a random molecular structure analogous to the gas. On the other hand, the cohesion and compactness exhibited by liquids indicate a structure resembling that of a solid. The similarities between a liquid and a solid make one to consider the two states of matter collectively as a “condensed matter” while the properties of fluidity shared by liquid and gas connect them collectively as “fluids”. Hence liquid state theories are broadly of two types.

1. Considering it as a condensed gas so that the interaction between the neighboring molecules may be calculated through “pair potential functions” and
2. Considering it as a disordered solid lattice.

1.5 MOLECULAR INTERACTION IN LIQUIDS

There are two kinds of interaction

1. Dispersion interaction and
2. Dipole-dipole interaction in liquids.

In the case of non-polar molecules, the average dipole moment averaged over all phases of electronic motions is zero while the instantaneous dipole moment is never zero.

If two non-polar molecules are placed near each other, the instantaneous dipole moment will interact and will produce some potential energy, which may be positive (or) negative. Such interaction between the molecules is termed as dispersion interaction and is present in all the aggregates of molecules irrespective of the nature of the atoms and molecules.

The second category of interaction is specific. It requires a Hydrogen atom attached to a fairly high electronegative atom and an atom at an optimum distance with non-bonded electrons (ion-pairs). This results in the formation of complexes between molecules while the dispersion interaction leads to positive contributions to excess thermodynamic quantities, the latter category makes negative contribution.

The determination of sound velocity, density, viscosity etc., leads to an understanding of the nature and type of molecular interactions especially in binary mixtures of liquids through the excess thermodynamic quantities. Normal liquids obey certain empirical rules such as Trouton's rule, The heat of vaporization at the boiling point is nearly equal to $85 \pm 10\, JK^{-1} mole^{-1}$, the associated liquids (having hydroxyl group), do not obey these empirical rules. The deviation is due to association of molecules found in the vapor to form larger molecules in liquids. In the case of alcohols and acids, the links between the individuals are provided by hydrogen bonds.

The protic dipolar liquids are ordinarily intermolecular hydrogen bonded. This class of liquids has been extensively studied, the best example being water. Aliphatic and aromatic alcohols and amines, carboxylic acids and amides are typical representatives of this class of liquids. The liquids of this class possess an entropy of vaporization which is 30% higher than for normal non-associated liquids. A notable exception is the carboxylic acids.

The alcohols show regularly changing liquid properties as the aliphatic chain length is increased (or) as the number of hydroxyl groups is increased. For example, the di-electric constant drops as the chain length increases, but increases with the increase in number of hydroxyl groups.

When two liquids are mixed, the solution is said to be ideal if there is no volume change (or) enthalpy change on mixing. But in practice, solutions of liquids are never ideal. The deviation from ideality is much more marked in the case of associated solutions. The thermal energy is less than the interaction energy. The thermal perturbation cannot disturb the association very much. In a binary system of associated liquids, a distortion occurs depending on the concentration. The distortion in the structure of the associated molecules leads to large changes in the physical properties such a dielectric constant, viscosity, free volume,etc.Considerable dissociation must occur when alcohols are mixed with diluents, the hydrogen bonds are broken and this explains the positive heats of reactions.

Self associations in alcohols are shown on fig 1.2. The earliest model of self association in alcohols is that of Oster and Kirkwood[5], which assumed long chain association with free rotations of the O.H. around the H-bond in such a situation,

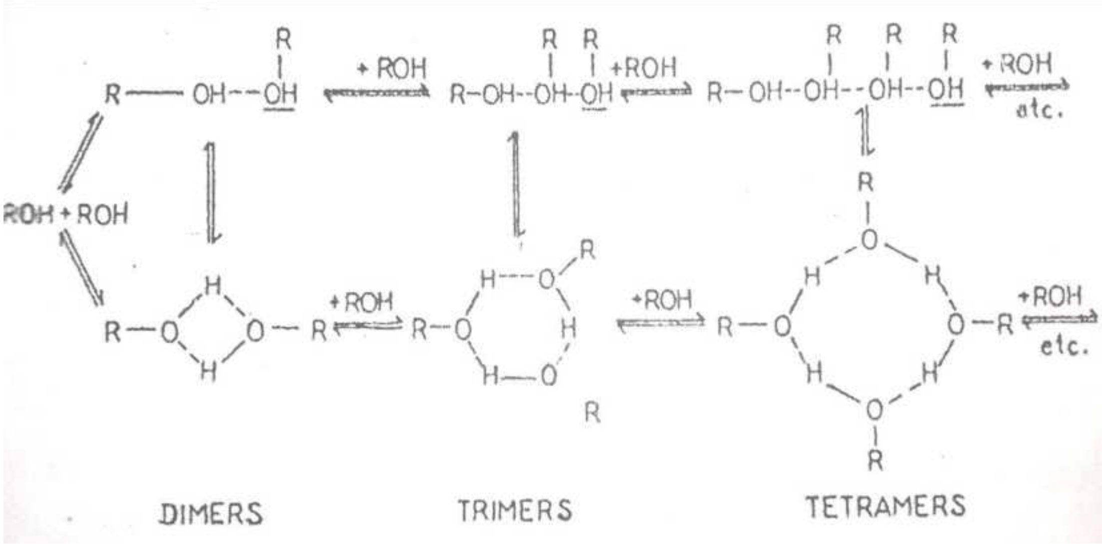


Fig: 1.2 POSSIBLE EQUILIBRIA IN THE SELF-ASSOCIATION OF ALCOHOLS

Dipole moment of the alcohol solution should be greater than that of its monomer unit, which is not the case always[6, 7]. In the most alcohols, dilution with non-polar solvents resulted in a dip in dipole moment at a definite concentration[8], which means qualitatively that dilution leads to the formation of cyclic multimers of lesser dipole moment. Bellamy and Pace[9] and Coburn Oxrunwald[10] were of the view that such cyclic structures must be multimers and not dimmers because of unfavorable bonding angles in dimers. Since the cyclic form possesses one additional H-bond compared to the open (or) linear form, the change in enthalpy AH^o for cyclic form should be greater than that corresponding to the open structure. Hence it is possible to look for specific information from the experimental studies of enthalpy and entropy. Such studies[11, 12] also do not provide sufficient data to permit a decision in favour of or against a particular model. Bordewijk[13], from his dielectric studies showed in mono alcohols, the large multimers are cyclic, probably tetramers, without of plane Oxygen and Hydrogen atoms.

Though there are plenty of data available on the ultrasonic behavior of mono alcohols[14-19] and in mixtures with inert solvents, they do not provide enough information on the model of mono alcohols.

Since the ultrasonic velocity is very sensitive to change in the free volume, it is desirable to look at the data on ultrasonic compressibility's of liquids from the thermo-dynamic point of view. The change in free volume results in a large change in the internal pressure of the liquids and hence the enthalpy of the system. The ease with which one can distort the fluid structure is determined by the energy holding the lattice together. In H-bonded liquids, it is reasonable to assume that this internal energy is related directly to the number of H-bonds per unit volume. The ultrasonic wave propagation in such liquids should result on the distortion of the fluids structures. Based on this concept, Sabesan et.al[20] studied the internal pressure and excess of mixing (H^E) for several alcohols including cyclo hexanol, amyl alcohol, Isoamyl alcohol, Isopropanol, n-butonol, 2-butonol, Isobutanol and tert-butanol in dioxin at different concentrations at 303, 308 and 313K. The positive values of H^E for the systems reported was explained as arising due to the stronger, self-associations that was broken, rather strongly by dioxin compared to n-heptane (or) n-hexane. Among that the isomer alcohols, the n-compounds were found to have less H^E at a given concentration and temperature, than the corresponding isomer.

The role of free volume in systems involving propylene, glycol in several interacting systems was analyzed by Varadarajan and Bharathi[21]. The length of the side chain of hexanols was found to have a definite influence on the excess enthalpy values, on mixing with the interacting solvents [22].

1.6 VELOCITIES OF ULTRASONIC WAVES IN LIQUIDS

The first extensive measurements of ultrasonic velocity in organic liquids were done by Parthasarathy. He arrived at the assumptions that the aromatic compounds usually have higher velocities than the corresponding aliphatic compounds, although their densities are higher velocity in liquids of high density is low, but not in proportion, the increase in density being to some extent set off by an accompanying decrease in compressibility, polar molecules favour high velocities, long molecules give rise to higher velocity, a double bond of unsaturation tends to lower velocity and in similar derivatives changes from a light to a heavy atom lowers velocity. The results in many organic liquids indicate that as a rule an increase in density is to some extent balanced by an accompanying increase in β_0[23]. Nevertheless, since a number of inconsistencies developed from some of these rules, no quantitative derivations were possible[24]. However, Schaaffs had contradicted Parthasarathy's rule arguing that the aromatic substances have generally higher velocities than aliphatics. Increasing density through a homologous series ought to decrease u, but, in fact does not. In halogen compounds the abnormal in molecular weight accounts for the observed fall in U through a series. Increase in molecular volume and the density go hand in hand. These are the factors, which cause the increase of U when heavier atoms are substituted and not increased in molecular weight per sec. There is real evidence that dipole moment is of important in this connection[25].

The velocity of ultrasonic waves in liquids varies from about 900 to 2000ms^{-1}. The value of U also depends on the temperature and pressure. For most pure liquids at temperatures far from the critical values the value of U decreases as the temperature increases. Water is an exception to this general rule and in this case U increases by about 2 ms^{-1} for each Kelvin rise in temperature and reaches a maximum at 346 mK, above this temperature, U decreases as the temperature rises further. As far as pressure changes are concerned, the velocity U increases in an approximately linear way with pressure for all liquids. This is simply as consequence of the fact that the bulk modulus increases as the molecules are squeezed closer together. For water U increases by about 0.2 ms^{-1} for every increases of one atmosphere[26].

In ultrasonic work, it is convenient to work with plane waves of small amplitude. When an ultrasonic waves passes through a liquid, the pressure and density of an element of liquid vary periodically with time. The variations in P and ρ may be assumed reversible and adiabatic. An ultrasonic wave is propagated as a longitudinal wave in a liquid because the particles of the liquid oscillate in the same direction in which the wave is moving. This is because the liquid possesses only one elastic modulus, the bulk modulus K. The propagation velocity, U, of the wave depends on this modulus and on the density ρ_0 of the liquid according to the equation,

$$U = \sqrt{\frac{Ks}{\rho_0}} \qquad (1.1)$$

where K_s is the adiabatic bulk modulus. The above equation holds for small excess pressure amplitudes for which ρ_0 can be considered to remain a constant. This excess or acoustic pressure P is equal to the difference between the instantaneous pressure P and the ambient hydrostatic pressure ρ_0 i.e.,

$$P = P - \rho_0 \tag{1.2}$$

Let us consider a plane wave traveling in a liquid in the x-direction. Its propagation is given by the well known equation,

$$\frac{\partial^2 p}{\partial t^2} = U^2 \frac{\partial^2 p}{\partial X^2} \tag{1.3}$$

As the wave proceeds, each particle of the liquids sutlers a certain displacement from its mean position, we denote this particle displacement we denote this particle displacement by 'ξ'. The corresponding particle velocity v in the medium is given by v =$\frac{\partial \xi}{\partial t}$ and the particle acceleration by

$$a = \frac{\partial v}{\partial t} = \frac{\partial^2 \xi}{\partial t^2} \tag{1.4}$$

In equation (1.3), the propagation of sound wave has been described in terms of the acoustic pressure, p. This equation is also satisfied by other quantities such as velocity potential cp, particle displacement ~ and particle acceleration

$$\frac{\partial^2 \xi}{\partial t^2} = U^2 \frac{\partial^2 \xi}{\partial X^2} \tag{1.5}$$

We consider the typical solution

$$\xi = \xi_0 . \exp j\ (\omega t - kx) \tag{1.6}$$

In this equation ξ_0 represents the peak value of the particle displacement, $\omega =$ f is the angular frequency and k =$\frac{\omega}{U} = 2\frac{\pi}{\lambda}$ is the wave number[27, 28].

CHAPTER-2

LITERATURE SURVEY

2.1 REVIEW

Dash Ashok Kumar et al.,(2014)[29] proposed that the ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of binary mixture of dimethyl acetamide (DAMC) and diethyl ether at temperature 308K have been measured at different frequencies (2MHZ, 4MHz 6MHZ and 8MHZ). Adiabatic compressibility (K_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and their respective excess values have been computed for entire range of concentration and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time (τ), excess enthalpy (H^E) and absorption coefficient (α/f2) have been calculated and discussed. On the basis of the experimental values of density, ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixture, it is concluded that there exists dipole-dipole, dipole-induced dipole and dispersion interactions in the binary liquid mixture of DMAC diethyl ether.

D. Ubagaramary et al., (2018)[30] discovered that the functions of ultrasonic velocity, density and viscosity for ternary liquid mixtures of 1-proponol, 1- butanol and 1-pentanol with tetra hydro furan are determined by 303.15 K-313.15 K. This data is used to calculate various parameters like the excess free volume, excess internal pressure and Gibb's free energy, which is used to discuss molecular interactions in the ternary liquid mixtures.

Nabaparna Chakraborty et al., (2020)[31] revealed that the Velocity of sound and density of binary liquid mixture of Dichloromethane with Ethanolamine have been calculated at different range of temperatures for various concentrations. Liquid-liquid interaction is confirmed by obtaining experimental values of fundamental parameters; ultrasonic velocity and density. Then these parameters are used to determine various other dependent parameters such as acoustic impedance (Z), intermolecular free length (Lf), adiabatic compressibility (β), Rao's constant (R), Wada's constant (W), Vander Waal's constant (b), effective molecular weight and Relative strength. Graphs are plotted for all parameters versus mole fraction. The linear variation of most of the acoustical parameters shows the absence of complex formation in the mixture. The decrease in ultrasonic velocity indicates that there is weak interaction between the molecules of the mixture. The solution tested, consisting of Dichloromethane and Ethanolamine, was selected in order to obtain data on the molecular interaction between their constituent particles.

R. K. Kolhe et al.,(2020)[32] proposed that the viscosity (η), density (ρ) and ultrasonic velocity (U) of dimethylsulphoxide with 1-Octanol have been measured at different concentrations and temperatures from 303.15K to 318.15K. Above measured data is used to calculate the parameters like adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), free volume (V_f), and available molar volume (Vα). These calculated parameters are helpful to explain the strength of interaction among the molecules of liquid binary mixture under investigation. From observed values of ultrasonic speed, viscosity and density of mixture, other parameters such as adiabatic compressibility, acoustic impedance, free length, free volume and available volume for binary mixtures of dimethylsulphoxide with 1-Octanol at various temperatures, it is found that, molecular association is present among the molecules of liquid combinations.

Nabil M. Abdel Jabbar et al.,(2017)[33] proposed that the ultrasonic velocities have been measured for different binary mixtures of common choline chloride-based deep eutectic solvents (DESs), namely, reline, glyceline and ethaline with water, in the range of temperature: 303.15–353.15 K. The experimental data measurements with different mole fractions of DES–water solutions were utilised in fitting four different models for speed of sound. These models correlate the speed of sound with some physical properties such as molar volumes, molar components sound velocity, densities, molecular weights, collision factors etc. A close match was obtained with these models with an average relative error of less than 4% for all data points used. It was observed that the ultrasonic velocity increases with the concentration of DES solvent and decreases with temperature. Moreover, this study roughly indicated that the intermolecular interactions in reline and ethaline aqueous mixtures exist in the form of disruption of dipole–dipole interactions (that varies considerably as a function of DES mixture composition and solution temperature). On the other hand, the interactions on the molecular level in glyceline aqueous solution are mainly due to dipole–dipole intermolecular forces. The speed of sound and density data of different aqueous solutions of three common choline chloride-based DESs were measured as a function of temperature within the range 323.15–353.15 K.

K. P. Singh et al.,(2018)[34] the work presented in this paper deals with the study of thermodynamic properties of new working fluids for absorption machines, mainly for characterization of absorbent–refrigerant pairs that could improve the cycle performance. The study of atomic motion in liquids plays an important role in understanding the solid-like behaviour of liquids. The accurate measurement of the energy changes due to scattering can be used to study the dynamical behaviour of liquids. Measurements of the ultrasonic velocity (u), density (ρ) and viscosity (η) for binary mixtures of polyethylene glycol 250 dimethyl ether with 1-propanol and 1-butanol have been made at three temperatures (T = 293, 303 and 313 K) over the entire composition range in order to investigate the nature of intermolecular interactions between the components of these liquid mixtures. Non-linear variation of derived quantities with the mole fraction supports the molecular interaction occurring between component molecules. From above studies, it is concluded that presence of strong interaction through hydrogen bonding between unlike molecules is characterized by non-linear behaviour of excess values of Gibbs's free energy of activation for viscous flow (ΔG^{*E}) and internal pressure (π_i^E).

N. P. Mohabansi et al.,(2020)[35] discovered that the Density(ρ), Viscosity(η), Ultrasonic Velocity(U) and Surface Tension(γ) of an aqueous-consolute, Na2SO4 solution of [2-(dimethylamino)-1-(4-methoxyphenyl) ethyl] cyclohexan-1-ol (Venlafaxine) 0.0201,0.0402,0.0804,0.1608 mol/kg were measured at 293.15, 303.15 and 313.15K. The resulting data were used to calculate various acoustical parameters, acoustic impedance (Z), adiabatic compressibility (β), Intermolecular free length (L_f), Wada's Constant (W), Rao's Constant (R), free volume (V_f), Relative Association (RA) were calculated which provides valuable information regarding drug-electrolyte (Na2SO4) interaction. The excess parameters viz. partial molar volume and excess adiabatic compressibility (β^E), excess inter molecular free length (L_f^E), excess free volume (V_f^E) were also calculated. These calculations help in predicting the intermolecular interactions. In an aqueous 2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]cyclohexan-1-ol and co-solute Na2SO4 solution, ultra-sonic velocity, density, viscosity and surface tension are measured at 293.15, 303.15 and 313.15K.

S. R. Dandwate et al.,(2018)[36] in the present studyattempt has been made to determine acoustic and thermodynamic parameters for binary liquid mixture of DMSO with methanol at 295.15 K, 300.15 K, 305.15 K, 310.15 K and 315.15 K temperatures. The excess values of isentropic compressibility, acoustic impedance, and internal pressure have been calculated using experimental data of ultrasonic velocity, density and viscosity. Molecular interactions in mixture form have been discussed depending upon deviations in excess values. Experimental data have been validated using Redlich-Kister polynomial equation. The values of excess isentropic compressibility have been found negative over entire concentration range at all temperatures.

P. S. Syed Ibrahim et al.,(2019)[37] deal the values of ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary liquid mixtures containing meta methoxy phenol and 1-propanol in n-hexane at different temperature 303 K,308 K and 313 K at a fixed frequency of 2MHz., experimentally. Using the experimental data of velocity, density and viscosity, various acoustical and thermodynamical parameters like Gibb's free energy, entropy, molecular interaction parameter, stability constant and excess property like solvation number are either calculated or computed. All these parameters have been discussed to throw light on intermolecular interactions between the component of ternary mixtures. The dependence of excess property in particular solvation number of the ternary mixture is compared and discussed in the context of intermolecular interaction and other factors. The result is interpreted in terms of molecular interactions under the influence of ultrasonic sound. From this present study it is concluded that the values of solvation number support the molecular reactions rather than the ionic reactions and henceforth interaction will be allowed due to dipole-dipole interactions and dipole – induced dipole interactions and nature of the hydrogen bonding and some extent due to steric effect of the substituent present in the benzene ring between MMP and 1- propanol in n hexane and these facts are substantiated by the values of thermodynamic properties such as ΔG^0 & ΔS.

V. Vanathi et al.,(2019)[38] proposed that the ultrasonic velocity (U), density (ρ), viscosity (η) for the ternary mixture of benzene þ chloroform þ cyclohexane in the whole range of composition has been carried out at various temperatures 303.15, 308.15 and 313.15K. From the measured parameters U, ρ and η, some derived parameters β, Lf, Vf, πi, Z, R,W with molar enthalpy (Hm) and apparent molar volume (ϕv) are also estimated. The decreasing trend of η, R,W, Hm, and ϕv with concentrations and other parameters are in increasing trend were observed. The trend of acoustical and physico-chemical parameters confirm the dynamics of molecules at higher temperature and the magnitude of intermolecular interactions among the constituents of the mixtures always reflects the nature of substance. The role of enthalpy and apparent molar volume has been used to determine their thermal response. The sign and magnitude of these properties are evident for the nature of interactions between component molecules. In summary, the ultrasonic velocity, density and viscosity measurements on ternary organic mixtures at various temperatures are carried out.

Sudhir P. Dange et al.,(2020)[39] reported that the Ultrasonic velocity (u), density (ρ) and viscosity (η) at 2 MHz in the binary mixtures of Riboflavin with methanol in the concentration range (0 to 0.1 M) and at temperature of 298K using ultrasonic interferometer technique. The experimental parameters, ultrasonic velocity, density and viscosity were used to calculate various acoustic and thermodynamic parameters. The obtained results support the nature and strength of molecular interaction, Physico-chemical behaviour in the binary liquid mixture of Riboflavin and Methanol. The Non-linear variation of thermo-acoustical parameters with molar concentration reveals that, there exist intermolecular forces in the binary liquid mixture of Riboflavin and methanol.

Pallavi B. Nalle et al.,(2019)[40] discovered that the ultrasonic velocity, density and viscosity of drug *Piperine* with MgCl2 have been measured as a function of number of moles n = (0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) at 323.15 K, 328.15 K and 333.15 K. The experimentally collected data have been used to calculate various acoustical, thermodynamic and excess

parameters such as excess values of adiabatic compressibility, excess intermolecular free length, excess specific acoustic impedance, excess relaxation amplitude and excess relaxation time have been calculated. Above excess

parameters are fitted to the Redlich-Kister equation. The results of acoustical, thermodynamic and excess properties reveal the existence of strong molecular interaction in the mixtures. The drug works as a structure breaker (it breaks the structure of MgCl2) and there is ion formation in the system. Acoustic, thermodynamic and excess parameter of mixture reflects the structural deformation in terms of intermolecular interaction. As the isentropic compressibility goes on increasing in a negative manner, the prepared solvent mixture maleic acid and methanol (60/40) can be used for the bleaching purpose of coconut coir fibres.

T Karunakar et al.,(2013)[41] revealed that the ultrasonic velocity and density measurements for binary mixtures of aniline + 1-butanol at T= (303.15 – 318.15) K, are conducted at atmospheric pressure. Some thermo acoustical parameters like adiabatic compressibility (β), molar volume (V_m), inter molecular free length (L_f) and acoustic impedance (Z) have been calculated from experimental measurements. The results have been used qualitatively to explain the molecular interaction between the components of these mixtures. Further, the results are further supported by FT-IR spectra. From the data of ultrasonic velocity and density various acoustical parameters of the mixtures of aniline with 1-butanol at 303.15, 308.15, 313.15 and 318.15 K were calculated.

R. C. Verma et al.,(2014)[42] proposed that Density, Ultrasound velocity and viscosities of Ethyl propionate with butanol-1 and pentanol-1 have been measured over entire range of composition at 308 K and atmospheric pressure. The computed acoustic and thermodynamic properties of Ethyl propionate in higher alcohols will give the excess values of issentropic compressibility, molar volume and viscosity. The excess value will decided the nature and extent of molecular interaction of Ethyl propionate in butanol-1 and pentanol-1.

L. Palaniappan et al.,(2020)[43] proposed that the ultrasonic velocity, density and viscosity measurements carried out for the binary mixtures of toluene, m-xylene with some butanols at 303 K. Various theoretical models have been applied to these binary systems; evaluate the sound velocity values and compared with the experimental values. The validity of Nomoto theory (NT), Van Deal-

Vangeal (IMR) and Free length theory (FLT) is checked and a comparative study of the above models is made. The non-ideal behaviour of the system is explained in terms of molecular interactions of the constituents of the mixture. The interactions further, evident with percentage deviation, molecular interaction parameter and goodness fit test. Among the three theories taken up for the prediction of sound velocity, Namoto Relation is found to yield excellent comparison with the experimental value for the systems investigated.

Sk. Md Nayeem et al.,(2015)[44] proposed that the ultrasonic velocities, u, and densities, q, of binary liquid mixtures of dimethyl sulphoxide (DMSO) with ketones such as acetophenone (AP), cyclohexanone (CH), and 3-pentanone (3P), including pure liquids, over the entire composition range have been measured at 308.15 K. Using the experimental data, deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess molar volume, V_m^E, excess intermolecular free length, L_f^E and excess acoustic impedance, Z^E, partial molar volumes, $V_{m,1}$, $V_{m,2}$, and excess partial molar volumes, $V^E_{m,1}$, $V^E_{m,2}$, have been calculated. Molecular interactions in the systems have been studied in the light of variation of excess/deviation values of calculated properties and these properties have been fitted to Redlich–Kister type polynomial equation. The observed positive values of V_m^E, Δk_s, L_f^E and negative values of Δu, Z^E for all the binary liquid mixtures studied clearly indicate the presence of the dominance of weak physical interactions between the components of molecules. Further, FTIR spectra support the conclusions drawn from deviation/excess properties. Moreover, theoretical values of ultrasonic velocity in the mixtures have been evaluated using various theories and such values were compared with experimental velocities to verify the applicable of such theories to the systems investigated.

Subhraraj Panda(2020)[45] proposed that the measurement of ultrasonic velocity is helpful to interpret solute-solute, solute-solvent interaction in aqueous medium. The ultrasonic speed (U), density (ρ) and viscosity (η) at 313 K have been determined using ultrasonic interferometer at four different frequencies *i.e.* 1MHz, 5MHz, 9MHz and 12 MHz, pycnometer and Ostwald's viscometer of dextran in aqueous medium respectively. All the three measurements were carried out in a water bath of constant temperature with an uncertainty of ±0.1 0C. The derived acoustical parameters such as free volume (Vf,), internal pressure (πi), absorption coefficient (α), molar sound velocity (R) and molar sound compressibility (W) have been determined from experimental data. The outcomes are described in terms of molecular interaction between the solution components. Ultrasonic speed, density and viscosity have been measured for aqueous dextran solution at different frequencies in constant temperature.

R. Chithra Devi et al., (2019)[46] proposed that the density (ρ), viscosity and ultrasonic velocity (u) in ternary liquid mixture of acrylonitrile (AN) with benzene in N-N-di methyl aniline have been measured at (303,308 and 313)K respectively, over the entire composition range by using an ultrasonic interferometer for measuring velocity at 2MHz frequency. From the experimental data various acoustical and thermodynamical parameters such as; adiabatic compressibility(β), Intermolecular free length (Lf), Specific acoustic Impedance (Z), relative association(RA) and molar sound velocity have been computed using the standard relations. The results have been analysed on the basis of variation in thermodynamic parameters. These parameters are found to be very sensitive in exploring the interaction between the component molecules, which enable to have better understanding of the liquid mixtures. Since the system show similar trends for evaluated parameter so the constituent ternary mixture at different temperatures. The results have been interpreted in terms of dipole induced dipole interaction. The results obtained for the present study indicates that the molecular interaction is present in the liquid mixtures.

Chapter 3

Materials and Methods

3.1 Introduction:

Ultrasonic, thermo-physical and thermodynamic properties of liquid mixtures are of great significance in obtaining an in depth knowledge of inter and intra-molecular interactions, structural and physiochemical behavior and also in verifying various liquid state theories which attempt in estimating the properties of liquid mixtures. Systematic study of thermodynamic properties of solutions with a new type of multi-frequency ultrasonic interferometer is done for precise measurement of the velocity of sound in liquids. The path length in the cell is varied by motion of a reflector, at the electrical reaction of the cell upon the oscillator is used to fix standing wave position at a standard frequency, and their locations are determined with a suitable cathetometer.

An investigation in the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been found to be an excellent quantitative way to elicit information about molecular structure and intermolecular forces in liquid mixtures. This has given impetus to the theoretical and experimental investigation of excess thermodynamic properties of liquid mixtures. Measurement of physiochemical properties such as density and ultrasonic velocity of pure components and their binary mixtures are being increasable used as tools for investigations of the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures. The significance reasons for the study of thermo-physical and thermodynamic properties of multi-component liquid mixtures are as follows:

- They provide way for studying the physical forces acting between molecules of different species.
- The study of liquid mixtures provides appearance of new phenomena, which are absent in pure liquids. The most interesting of these are the new types of phase equilibria, which are introduced by the variation in the promotion of the pure components.
- Liquid mixtures are the most direct source for studying the various parameters. The study of thermo-physical and thermodynamic properties of liquid mixtures helps in obtaining in depth knowledge about molecular interactions.

3.2. Theory:

Ultrasonic interferometer is a simple and direct device which yields accurate and consistent data, from which one can determine the velocity of ultrasonic sound in a liquid medium with a high degree of accuracy. A crystal-controlled interferometer (model M-83S) supplied by Mittal Enterprises, New Delhi, operating frequency 2 MHz has been used to measure the ultrasonic velocity.

3.3. Ultrasonic:

Ultrasonic sound refers to sound pressure with a frequency greater than the human available range (20 Hz to 20 KHz). When an ultrasonic wave propagates through a medium, the molecules in that medium vibrate over short distance in a direction parallel to the longitudinal wave. During this vibration, momentum is transferred among molecule. This causes the wave to pass through the medium.

3.4. Ultrasonic Interferometer:

An Ultrasonic Interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy.

Fig 1: Experimental setup for ultrasonic interferometer.

The salient features of ultrasonic interferometer are given below:

- It is a simple in design, rugged and gives very accurate and reproducible results.
- Experiments may be performed over a wide range of temperature from -30 ^{0} C to +80 ^{0} C on all liquids except those which reacts with the plating of cell and crystal.
- Nearly 10 ml of experimental liquid is required.
- There is no danger of any change such as depolymerisation, due to ultrasonic effect since a very small ultrasonic energy is required.

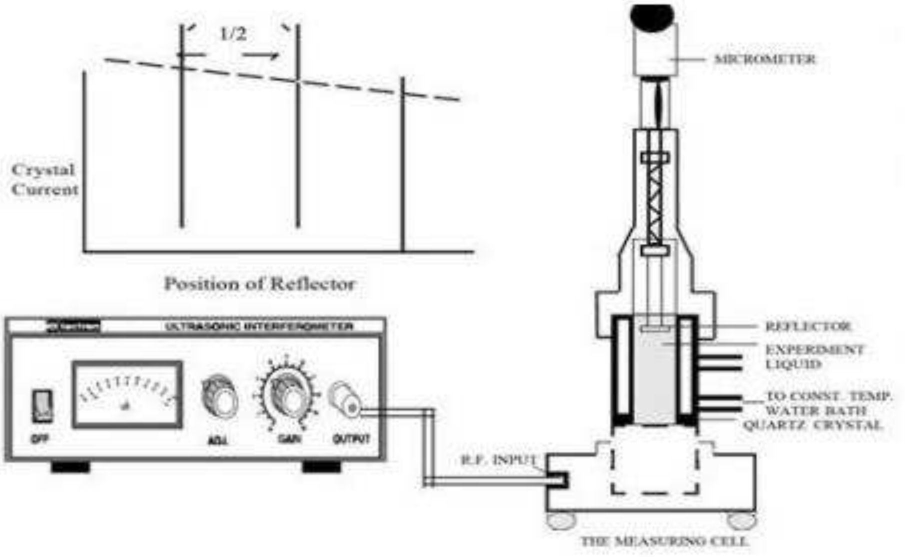


Fig 2: Cross section of the liquid cell and graph plotted position of reflector versus crystal current.

In an ultrasonic interferometer, the ultrasonic waves are produced by the piezoelectric methods. At a fixed frequency variable path interferometer, the wavelength of the sound in an experimental liquid medium is measured, and from this one can calculate its velocity through that medium. The ultrasonic cell consists of a double walled brass cell with chromium plated surfaces having a capacity of 10 ml. The double wall allows water circulation around the experimental liquid to maintain it at a known constant temperature. The micrometer scale is marked in units of 0.01 mm and has an overall length of 25 mm. Ultrasonic waves of known frequency are produced by a quartz crystal which is fixed at the bottom of the cell. There is a movable metallic plate parallel to the quartz plate, which reflects the waves. The waves interfere with their reflections, and if the separation between the plates is exactly an integer multiple of half wave length of sound, standing waves are produced in the liquid medium. Under these circumstances, acoustic resonance occurs. The resonant waves are a maximum in amplitude, causing a corresponding maximum in the anode current of the piezoelectric generator. The ultrasonic interferometer consists of the following mainly two parts:

3.4.1. The high frequency generator.

3.4.2. The measuring cell.

3.4.1. The high frequency generator

The high frequency generator is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the “measuring cell”. A micrometer to observe the changes in current two controls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the high frequency generator.

3.4.2. The measuring cell

The measuring cell is specially designed for maintaining the temperature of the liquid constant during the experiment. A fine digital micrometer screw (LC 0.001 mm) has been provided at the top, which can lower or raise the reflector plate in the liquid within the cell through a known distance. It has a quartz crystal fixed at its bottom.

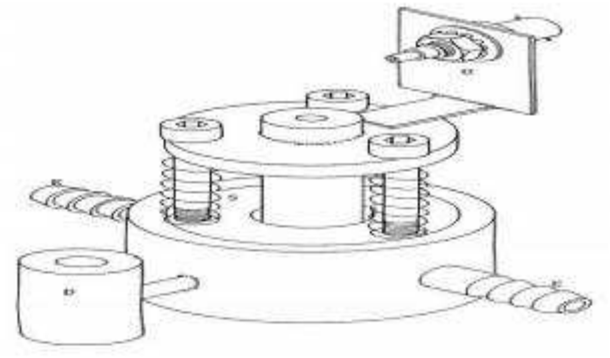


Fig 3: Ultrasonic interferometer cell liquid mixtures.

3.5: Working principle

The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator become a maximum. If the distance is now increased or decreased and the variation is exactly one-half wavelengths($\lambda/2$) or multiple of it, anode current become maximum from the knowledge of wavelength (λ) the velocity (U) can be obtained by the relation:

Velocity = Wavelength × Frequency $U = \lambda \times f$ (1)

3.6: Adjustment of ultrasonic interferometer

For initial adjustment two knobs are provided on high frequency generator, one is marked with "ADJ" to adjust the position of the needle on the ammeter and the knob marked “GAIN” is used to increase the sensitivity of the instrument for greater deflection, if desired. The ammeter is used to notice the number of maximum deflection while micrometer is moved up or down in liquid.

3.7. Procedure

- Unscrew the knurled cap of cell and lift it away from double walled construction of the cell. In the middle position of it pour experimental liquid and screw the knurled cap. Wipe out excess liquid overflowing from the cell.
- Insert the cell in the heavy base socket and clamp it with the help of a screw provided on its side. 7.3 Connect the high frequency generator with cell by coaxial cable provided with the instrument. In ultrasonic interferometer frequency selector knob should be positioned at desired frequency (same frequency as that of liquid cell chosen).
- Move the micrometer slowly in either clockwise or anticlockwise direction till the anode current on the ammeter on the high frequency generator shows a maximum or minimum.
- Note the reading of micrometer corresponding to the maximum or minimum (which is sharper) in micrometer. Take about 50 reading of consecutive maximum or minimum and tabulate them. 7.6 Take average of all differences ($\lambda/2$).
- Once the wavelength (λ) is known the velocity (U) in the liquid can be calculated with the help of the relation.

3.8. Sample calculations Sample:

water Average ($\lambda/2$): 0.375mm.

Ultrasonic velocity in sample: $U = \lambda \times f = 1480$ m/sec.

Density of the liquid = 996.458 Kg/m3

Adiabatic compressibility (ʉad) = 1/ρv2 = 1/996.458 ×(1480)2

ad = 4.58×10-10 N/m^2

3.9. Measurement of the density:

The density (ρ)of the liquid mixture was determined by a specific gravity bottle with the liquid mixture was immersed in a temperature controlled water bath. The density was determined using the relation:

$$\rho_2 = \left(\frac{W_2}{W_1}\right)\rho_1$$

Where W_1, W_2, ρ_1 and ρ_2 are masses of distilled water, mass of liquid mixture ,density of distilled water, and density of liquid mixture, respectively.

Measurement of viscosity

The viscosity measurements were done through Ostwald's viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. The water in the viscometer is allowed for some time to attain the experimental temperature. Using a suitable arrangement, the water is sucked above the marked level and then it is allowed to flow freely. The time taken for the flow of water is noted. The water is replaced with a mixture; whose viscosity is to be determined. Using the same procedure, the time taken for flow of liquid mixture at the experimental temperature was determined. Using the time taken for the distilled water and mixture, the viscosity of unknown liquid mixture is determined:

ꝗs / ηw = ρs/ ρw × ts/ tw (2)

Where ηw, ρw and tw are the viscosity, density and time flow of water respectively and ੧s, ρs and ts are the viscosity, density and time flow of unknown liquid mixture respectively. Viscosity is an important transport property for process design in petroleum, petrochemical, chemical and other chemical industries involving fluid transportation, mixing agitation, heat exchange and concentration. The estimation of the viscosity of a mixture is more difficult than of the pure compound. The prediction of the viscosity of liquid mixtures is a goal of long standing with both experimental and theoretical importance. Many industrial, chemical processes or laboratory works need experimental data of viscosity at any given temperature and composition for the liquid mixtures.

3.9 Theoretical methods for the estimation of acoustical thermodynamic parameters of liquid and liquid mixtures

3.9.1 Adiabatic compressibility (βad)

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation;[47]

$$\beta ad = \frac{1}{v}[\partial v / \partial p] \qquad (3)$$

It can also be calculated from the speed of sound (U) and the density of the medium (ρ) using the equation of Newton Laplace as;

$$\beta ad = 1/u\rho^2 \ Kg^{-1}ms^2 \qquad (4)$$

3.9.2 Intermolecular free length (L_f)

The intermolecular free length is the distance covered by sound wave between the surfaces of the neighboring molecules. It is measure of intermolecular attractions between the components in binary mixture. The increase or decrease in free length indicates weakling and strengthen of intermolecular attraction. As the ultrasonic velocity increase due to the increases in concentration, the interaction free length has to decrease and vice-versa. It is related to ultrasonic velocity and density as; [48]

$L_f = K/\rho U)^{1/2} m$ (5)

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighboring molecules and is given by the relation,[49]

$L_f = K_T \beta^{1/2}$ (6)

Where, $K_T = (93.875+0.345T) \times 10^{-8}$.

3.9.3 Relaxation time (τ)

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of the ultrasonic velocity in binary mixture reveals information about the Characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation; [50]

$$\tau = \frac{4}{3}\beta\eta \qquad (7)$$

3.9.4 Gibb's free energy (ΔG)

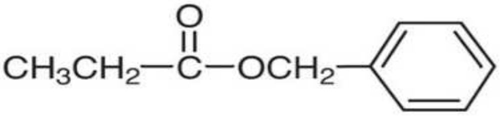
The relaxation time (τ) is related to the activation free energy for a given transition. The variation of τ with temperature can be expressed in the form of Eyring salt process theory and the rearranged equation is given as;[51]

$\Delta G = -KT \log [h/KT\ \tau]$ (8)

Where K is the Boltzmann constant and h is the plank's constant

BENZYL PROPIONATE

Structure



Molecular Formula: $C_{10}H_{12}O_2$

Molecular Weight: 164.2 g/mole

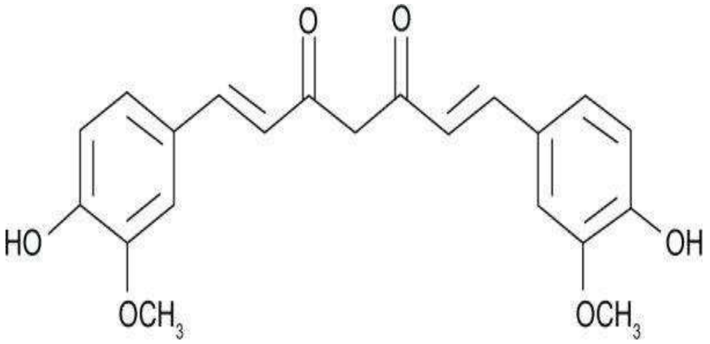
Density : 1.03g/ml

Uses:

- Benzyl propionate is a clear colourless liquid with a sweet, fruity odor which is used in perfumery for floral, fruity notes and in fruit flavour composition.
- It is soluble in most fixed oils and alcohols, slightly soluble in propylene glycol, and insoluble in glycerine.
- Air care products
- Cleaning and furnishing care products
- Laundry and dishwashing products
- Non-TSCA products
- Personal care products.

CURCUMIN

Structure:



Molecular Formula: $C_{21}H_{20}O_6$

Molecular Weight: 368.38 g/mole

Density **:**1.3 ±0.1 g/cm^3

Uses:

- Curcumin is mostly used as a flavouring agent in food as it tastes like turmeric.
- It is obtained from turmeric and is used in food, cosmetics and pharmaceuticals industries.
- Curcumin contains a yellow-coloured chemical, it is an antioxidant.
- Used in textiles and dye-sensitized PV technology.

CHAPTER – 4

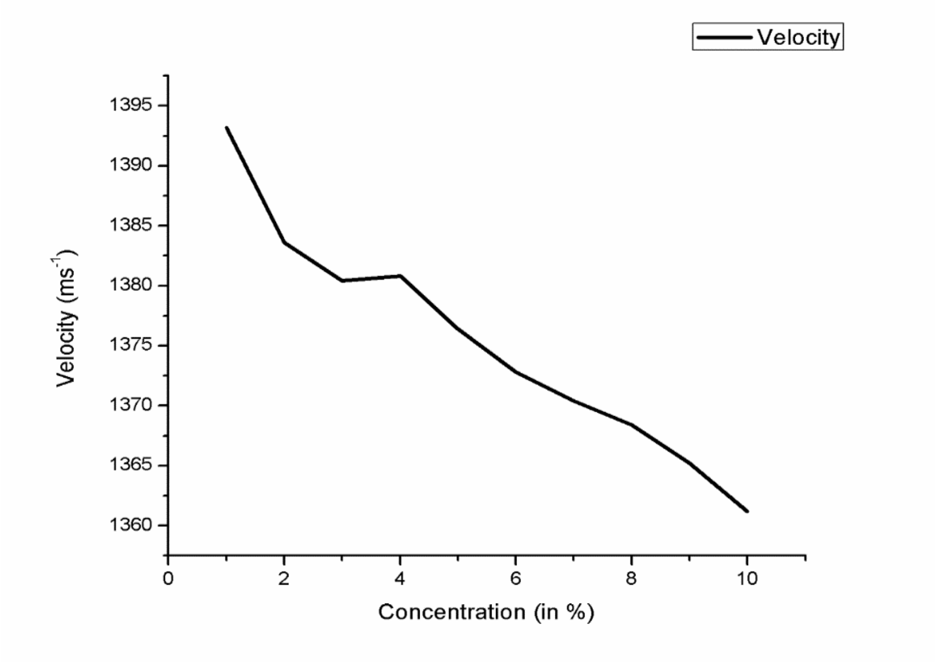
RESULT AND DISCUSSION

Table 4.1: The experimental values of ultrasonic velocity (U), density (ρ) and viscosity (η) at temperature 308K for the binary mixture of benzyl propionate with curcumin .

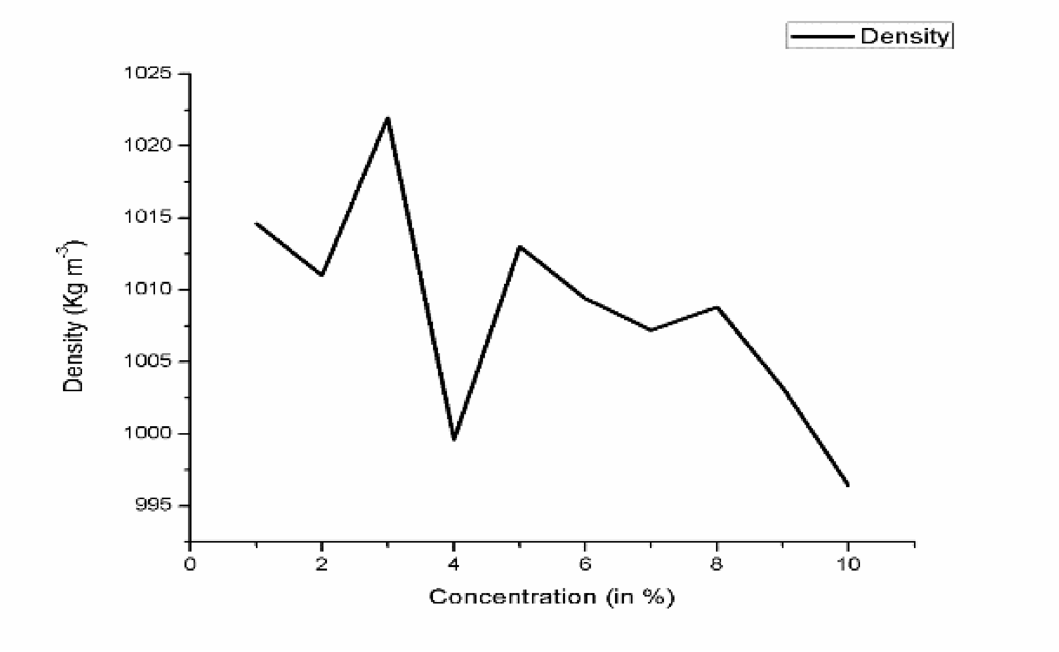
Concentration in %	Ultrasonic velocity ms^{-1}	Density Kg m^{-3}	Viscosity x10^{-3} Nsm^{-2}
1%	1393.2	1014.6	1.596
2%	1383.6	1011	1.484
3%	1380.4	1022	1.535
4%	1380.8	999.6	1.477
5%	1376.4	1013	1.503
6%	1372.8	1009.4	1.478
7%	1370.4	1007.2	1.440
8%	1368.4	1008.8	1.453
9%	1365.2	1003.2	1.432
10%	1361.2	996.4	1.375

Table 4.2: The calculated valves of Adiabatic compressibility (βa), Free Length (Lf), Relaxation time(τ) and Gibbs Free energy (G) for different concentration.

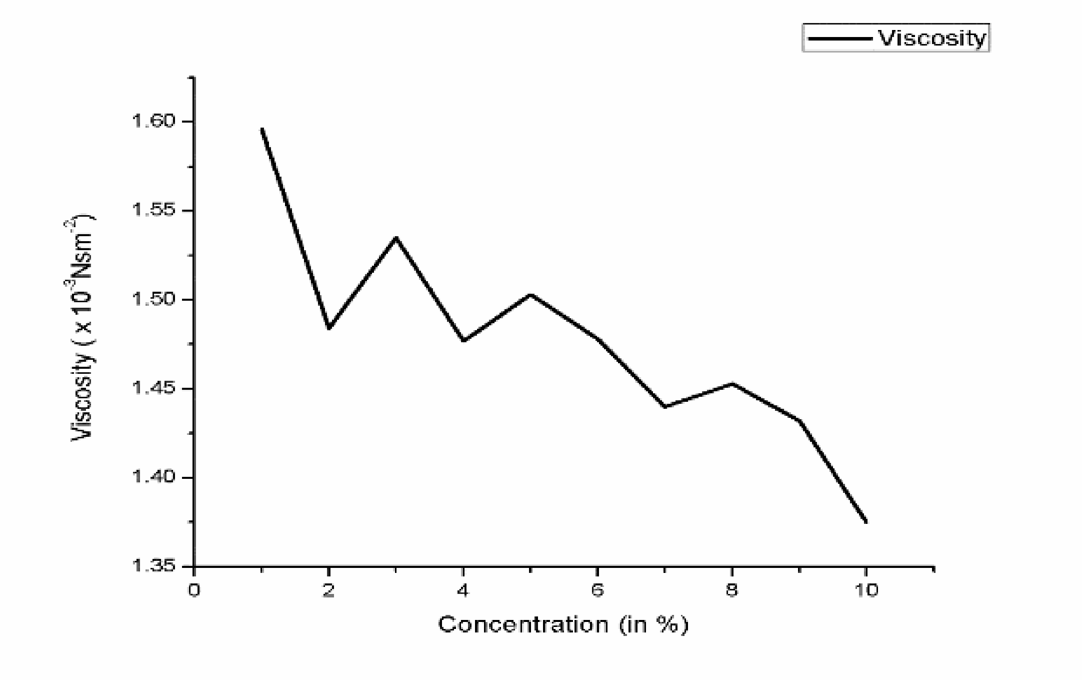
Concentration in %	Adiabatic compressibility x10^{-10} m^2N^{-1}	Free length x 10^{-11} m	Relaxation time x 10^{-12} s	Gibbs Free energy x10^{-21} J/mole
1%	5.077	4.718	1.080	8.229
2%	5.166	4.759	1.022	7.996
3%	5.134	4.744	1.051	8.112
4%	5.247	4.796	1.033	8.042
5%	5.210	4.779	1.044	8.087
6%	5.256	4.800	1.036	8.050
7%	5.286	4.814	1.015	7.965
8%	5.293	4.817	1.025	8.008
9%	5.348	4.842	1.021	7.990
10%	5.416	4.872	0.993	7.872



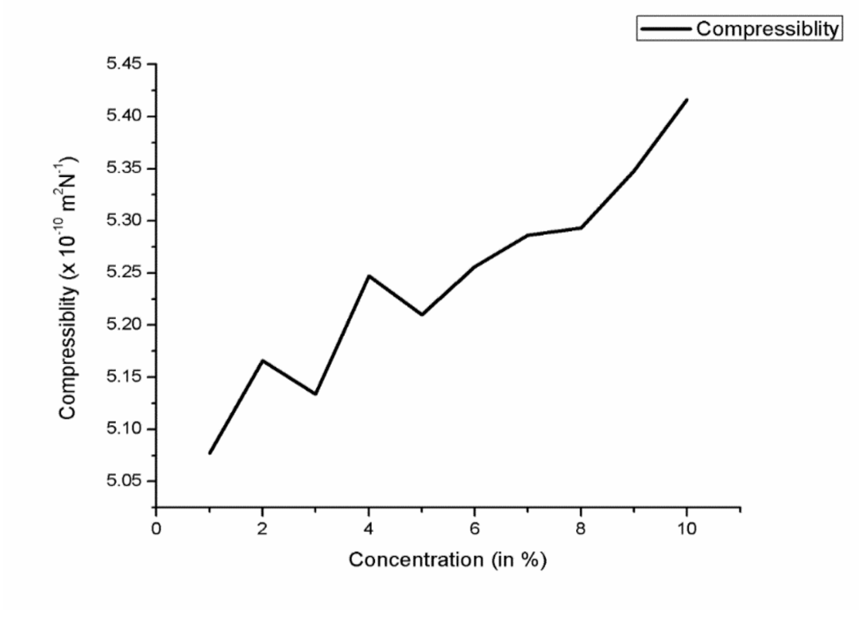
(Fig 4.1) Concentration vs Velocity



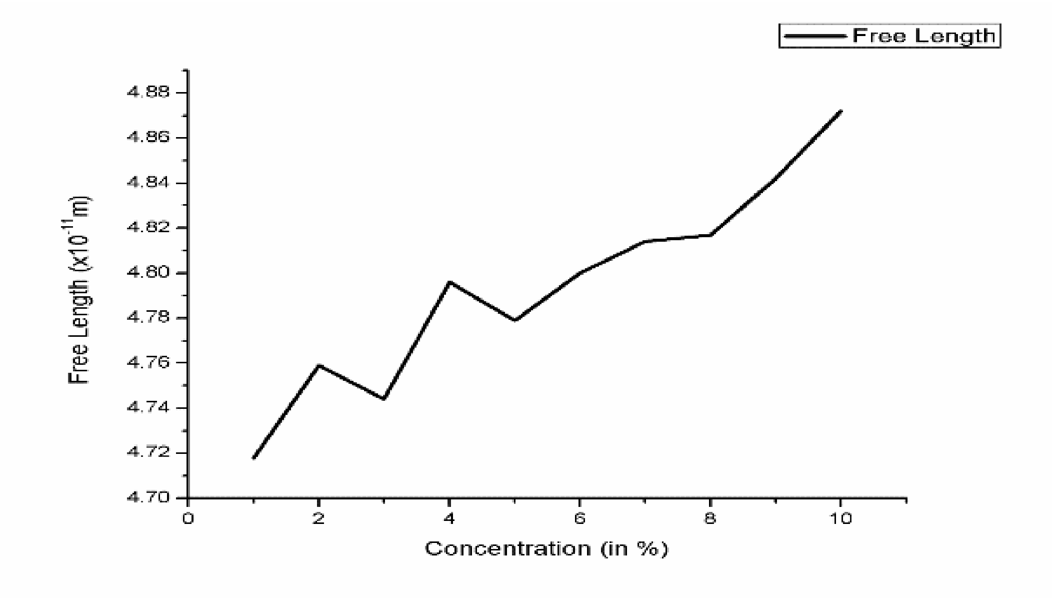
(Fig 4.2) Concentration vs Density



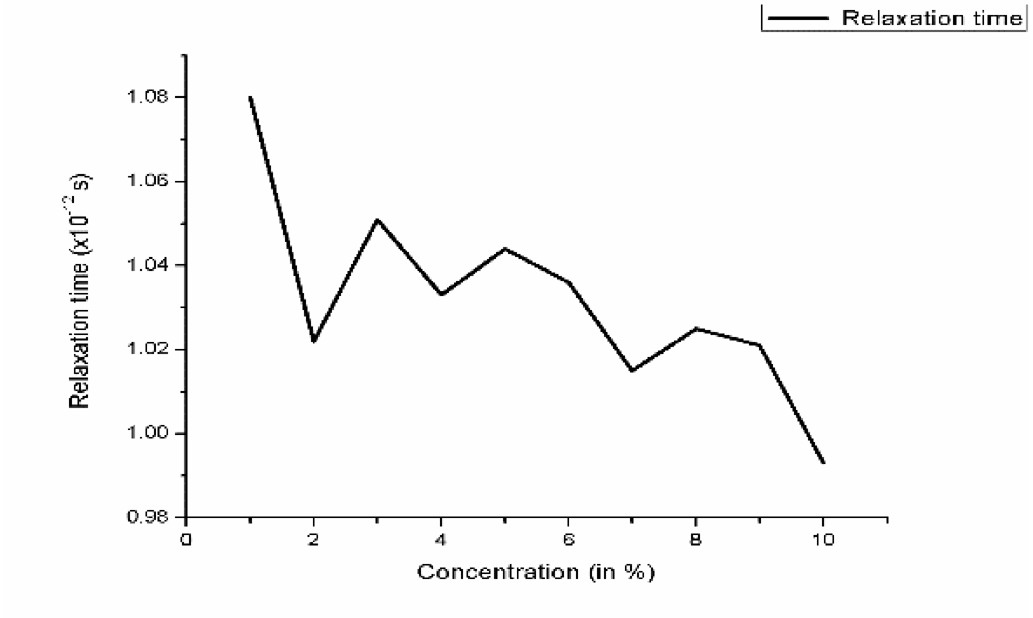
(Fig 4.3) Concentration vs Viscosity



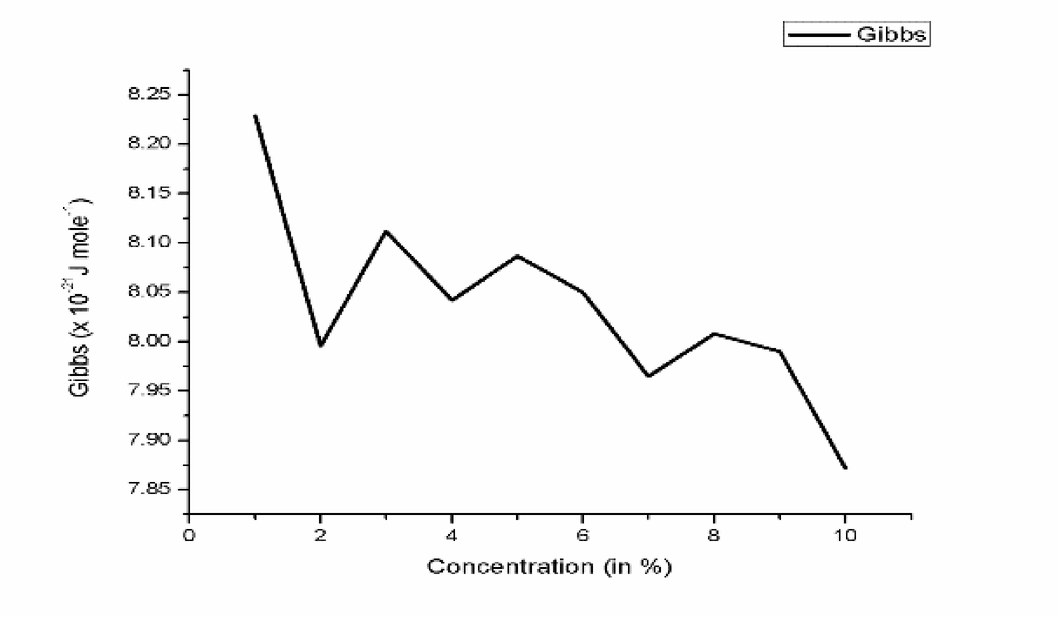
(Fig 4.4) Concentration vs Compressibility



(Fig 4.5) Concentration vs Free length



(Fig 4.6) Concentration vs Relaxation Time



(Fig 4.7) concentration vs Gibbs free energy

It is found that ultrasonic velocity (U) decreases with the increasing concentration of curcumin in the Figure (4.1). The structural changes of molecules in the mixture take place due to the existence of electrostatics field between the interacting molecules[52]. Thus the structural arrangement of molecules results in the effect of Adiabatic compressibility (βa), which shows an inverse behaviour.

The increase in free length with the increase in concentration of curcumin is due to the loose packing of the molecules inside the shield, which may be brought about by weakening of molecular interaction which is shown in the figure (4.5).

The increase in free length results in a decrease in velocity. This is also in accordance with the expected increase in adiabatic compressibility following a decrease in velocity showing there by weakening intermolecular interaction.

The relaxation time decreases with increase in concentration of curcumin which is shown in Figure (4.6). The relaxation time that is in the order of 10^{-12}s due to structural relaxation process[53], showing the presence of molecular interaction.

The reduction of Gibbs free energy in the binary systems indicates that the need for smaller time for the cooperative process or the rearrangement of molecules in the mixtures decreases the energy leads to dissociation[54] as shown in figure (4.7).

CONCLUSION

Acoustic properties of adiabatic compressibility(βa), Free length(Lf), relaxation time(τ) and gibbs free energy(G) are determined which explain how these interactions occur and responsible for breaking and making of the structure in the solution. The trends in the variation of parameters derived from velocity(U), density(ρ) and viscosity(η) at temperature 308K suggests existence of molecules interaction in the chosen binary mixture. It is concluded that there exists a weak molecular interaction between the components in the benzyl propionate and curcumin.

REFERENCE:

1. Warren, B. E. (1937), J. Applied Physics, 8,645.
2. Compton, A. H. And Allison, S. K. 'X-rays in Theory and Experiment' (Newyork: D. Van Nostrand Co., Inc., 1935), pp. 781-782.
3. G. W. Stewart, Phys. Rev., 37, 9(1931); E. Amaladi, Phuysik. Z., 32, 914(1931); H. H. Meyer, Ann. Physek, 5,701(1930); S. Katzoff, J. Chem. Phys; 2, 841(1934); J. D. Bernal and R. H. Fowler, ibid, 1,515(1933); J. Morgan and B. E. Warren, ibid; 6,666(1938).
4. A. Joffe, Ann. Physik, 72, 461 (1923); J. Frenkel, Z. Physik, 35,652 (1926).
5. Oster, G., and Kirkwood, J. G., J. Chem., Phys., II (1943), 175.
6. Smyth, C. P., and Stoops, W. N., J. Am. Chem. Soc., 51(1929), 3330.
7. Philippe, R., and Piette, A. M., Bull Soc. Chem., Belg., 64(1995), 600.
8. Malecli, J., J. Chem., Phys., 43(1965), 1351.
9. Bellamy, L. J., and Pace, R. J., Specitrochim Acta, 22(1966), 525.
10. Copurn, W. C., and Grunwald, E. J., Am. Chem. Soc., 81(1959),6145.
11. Brown, I. Fock, W., and Smit, F., Aust. J. Chem., 17(1964), 1106.

12. Haskell, R. W., Hollinger, H. B and Van Ness, H. C., J. Phys., Chem., 72(1968), 4534.

13. Bordewijk, P., "Fluid Structure and Dielectric behaviour of the mono alcohols", Ph.D., thesis, University of Leiden, 1968.

14. Reddy, K. S., and Naidu, P. R., J. Chem. Thermodynamics(1976), 1208.

15. Prakash, S., Srivastau, S. B., and Prakash, O., Ind. J. Pure and Apopld. Phys., 13(1975), 19.

16. Ravindraa Prasad, K., Ravimahar, E. L., and Reddy, K. G. Acoust, Lett., 4(1981), 170.

17. Subba Rao, S., and Gobala Krishnan, R. Acoust, Lett., 2(1978), 69.

18. Gopal K. And Prabhakara Rao, N. Acoust Lett., 4(1981), 164.

19. Ramanjappa, T., and Raja Gopal, K., Proc. Latl. Sympoium on Acoustis(1986), 57.

20. Sabesan, R., Ramadurai, R and Rangan, R., J. Acoust. Soc. (India), 11(1983), 5.

21. Vradarajan, R., and Bharathi, G., J. Pure and Appl. Ultrasonics, 9(1987), 15.

22. Sabesan, R., Vradarajan, R., and Natarajan, M., Proc. Natl. Symposium on Acoustic, Tiruchy, 1987, 282.

23. P. Vigoureux, Ultrasonics, Chapman and Hall Ltd, London (1952).

24. T. Robert Beyer, V. Stephen Letcher, Physical ultrasonics Academic Press, New York (1969).

25. E. G. Richardoss, Ultrasonic Physics, Elseveir, London (1952).

26. N. V. Temperley and D. H. Trevena, Ellis Horwood Ltd, Liquids and other properties, John wiley and sons, England (1978).

27. A. B. Bhattia, Ultrasonic Absorption , Oxford (1967).

28. Chandra Bhan Singh, Avanesh Kumar and Soran Singh (2012).

29. Dash Ashok Kumar and Paikaray Rita (2014) 'Study of Molecular Interaction in Binary mixture of Dimethyl Acetamide with Diethyl Ether using Ultrasonic and Viscosity probes', Research Journal of Chemical Science vol. 4, No. 3, pp. 45-53.

30. Ubagaramary. D, Muthu Vijayan Enich, Mullainathan. S and Kesavaswamy (2018) 'Acoustical properties of molecular interactions in 1-propanol, 1butanol and 1-pentanol with tetrahydrofuran in cyclohexane at various temperatures', vol. 29, No. 17, pp. 3276-3281.

31.Nabaparna Chakraborty, Monika Rani and Juglan. K.C ('Ultrasonic Investigation of Dichloromethane with Ethanolamine at various temperatures', vol. 20, pp. 2825-2829.

32. Kolhe .R.K and Bhosale .B.B (2020) 'Molecular Interaction study in Binary mixtures of DMSO and 1-octanol using ultrasonic method at various concentrations and temperatures' vol. 11, No. 5, pp. 750-757.

33. Nabil M. Abdel Jabbar and Farouq S. Mjalli (2017) 'Ultrasonic study of binary aqueous mixtures of three common eutectic solvents', An International Journal of Physics and Chemistry of Liquids, pp. 1-18.

34. Singh K.P and Singh .S (2018) 'Thermodynamic and acoustic properties of binary mixtures of PEGDME 250 with 1-propanol and 1-butanol at 293, 303 and 313 °K', An International Journal of Physics and Chemistry of Liquids, pp. 1-21.

35. Mohabansi N.P, Satone A.K, Gulafsha A.I. Sheikh and Komal Vairagade (2020) 'Excess Thermodynamic Parameters of 1-[2-(Dimethylamino)-1-(4Methoxyphenyl)Ethyl] Cyclohexan-1-ol in aqueous Na2SO4', International Journal of Researches in Biosciences, Agriculture and Technology, vol. 3, No. 8, pp. 26-34.

36. Dandwate S.R and Deshmukh S.B (2018) ‘Excess Thermodynamic properties of Binary liquid mixtures of DMSO with Methanol at different temperatures’, International Journal of Universal Print, vol. 4, No. 4, pp. 196-201.

37. Syed Ibrahim P.S, S. Chidambaravinayagam, J. Senthil Murugan and J. Edward Jeyakumar (2019) ‘Studies on some Acoustical and Thermodynamic properties of Ternary liquid mixtures of Meta Methoxy Phenol (MMP), 1propanol and n-Hexane at different temperatures using ultrasonic techniques’, Journal of Information and Computational Science, vol. 9, No. 7, pp. 391-399.

38.V. Vanathi, S. Mullainathan, S. Nithiyanatham, V. Ramasamy and L. Palaniappan (2019) ‘Ultrasonic velocity, density, viscosity for the ternary mixture of (benzene+Chloroform+Cyclohexane) at different temperatures’, pp. 1-6.

39. Sudhir P. Dange and Omprakash P. Chimankar (2020) ‘Molecular Interaction study in Binary mixture of Riboflavin with Methanol at 298K’, vol. 7, No. 2, pp. 555-557.

40. Pallavi B. Nalle, R.G. Dorik and K.M. Jadhav (2019) ‘Acoustical and excess parameter studies of piperine with MgCl2’, Journal of Pure and Applied Ultrasonics, vol. 41, No. 2, pp. 27-35.

41. T Karunakar, CH Srinivasu and K Narendra (2013) ‘Thermo Acoustic and Infrared study of Molecular Interactions in Binary mixture Aniline+1butanol’, Journal of Pure and Applied Physics, vol. 1, No. 1, pp. 5-10.

42. R.C. Verma and Vinod Kumar Yadav (2014) ‘The study of Excess molar volume and deviation in viscosity of binary mixtures of Ethyl Propionate in Butanol-1 and pentanol-1 at 308K ultrasonically’, Journal of Chemical, Biological and Physical Sciences, vol. 4, No. 3, pp. 1988-1991.

43. L. Palaniappan and S. Nithiyanantham (2020) ‘Molecular Interactions from the Experimental and Validation with Estimated Theoretical sound velocity’, pp. 277-285.

44. SK. Md Nayeem, M. Kondaiah, K. Sreekanth and D. Krishna Rao (2015) ‘Acoustic and volumetric investigatuins in aromatic, cyclic and aliphatic ketones with dimethyl sulphoxide at 308.15K’, Arabian Journal of Chemistry, pp. 1-12.

45. Subhraraj Panda (2020) ‘Ultrasonic study on dextran in aqueous media at 313K at different frequencies’, Adalya Journal, vol. 9, No. 3, pp. 456-462.

46. R. Chithra Devi and R. Mathammal (2019) ‘Thermodynamic Behaviour of Ternary mixtures of Acrylonitrile in Benzene with N-N-dimethyl aniline at 303K, 308K and 313K’, vol. 8, No. 12, pp. 158-165.

47. Nikam PS, Hasan Mehdi. Ultrasonic velocity and adiabatic compressibility of monochloric acetic acid in aqueous ethanol at various temperatures. Journal of Chemical and engineering Data. 1988; 88:165-169.

48. Nikkam PS, Hasan Mehdi. Ultrasonic velocity and apparent molar compressibility of trichloroacetic acid in aqueous ethanol. Asian Journal of Chemistry. 1993; 5(02):319-321. 15.

49. Venkateswarlu P, Raman GK. Sound velocities and isentropic compressibilities of 1, 2-dibromoethane + ketone at 303.15K. Journal of pure and applied ultrasonics. 1985; 7(02):31-34.

50. Kumar Naidu Vijaya B, Rao Sadasiva A, Rao Chowdoji K. Ultrasonic velocity study in some glycols and polyglycols in formamide solutions. Journal of Acoustical Society of India. 2000; 28(1-4):297-300.

51. Maurya VN, Arora Diwinder Kaur, Maurya Avadhesh Kumar, Gautam RA. Measurement of ultrasonic velocity, density, viscosity and refractive index of liquids using experimental techniques. Word of Sciences J. 2013; 02:27-48.

52.B. Hemalatha, Ultrasonics studies at different Temperatures, Springer 2009,947-955.

53.Thomas M. Bender and R. Pecora, A dynamic light scattering study of the tert-butyl alcohol-water system, ACS Publications 1986,90;1700-1706.

54.A N kannappan & R Palani ,Acoustical behavior of gyclerine,dextrose,sucrose in Na_2CO_3 and $NaHCO_3$,buffer solution.Indian Journal of Pure & Applied Physics 2017;45:573-579.

AN ANALYSIS ON THERMO-ACOUSTIC BEHAVIOUR OF BINARY LIQUID MIXTURE WITH VARIOUS TEMPERATURES USING ULTRASONIC TECHNIQUE

A project report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI

In partial fulfillment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

M. UMA MAHESWARI

Reg. No: 19SPPH10

Under the supervision and guidance of

Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this project work entitled **"AN ANALYSIS ON THERMO-ACOUSTIC BEHAVIOUR OF BINARY LIQUID MIXTURE WITH VARIOUS TEMPERATURES USING ULTRASONIC TECHNIQUE"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** in partial fulfillment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the year 2020-2021 by

M. UMA MAHESWARI **Register No: 19SPPH10**

Padmavati S.P

Signature of the Guide

Padmavati S.P

Signature of the SSC Coordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

A. Nirmala Shirley

Signature of the Examiner

ACKNOWLEDGEMENT

"GIVE THANKS TO THE LORD FOR HE IS GOOD"

First of all, I thank the Lord Almighty for his blessing and grace to complete this comprehension work.

I am deeply indebted to our Principal **Rev. Dr. Sr. A. S. J. LUCIA ROSE M. Sc., PGDCA., M. Phil., Ph. D.,** for the encouragement she bestowed upon us.

I wish to express my sincere thanks to our Director of SSC, **Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil.,** for her support in my work.

I would like to express my special thanks of gratitude to **Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D.,** Head of the Department, for her inspirational words and encouragement to complete this project.

I am thankful to **Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,** SSC Coordinator and my guide, for the continuous support, patience, motivation, and immense knowledge. Her guidance had encouraged me to do this project successfully.

I am grateful to my parents and my sister who have provided me through moral and emotional support to complete my work.

An endeavor over a long period can be successful only with the advice and supports of many well-wishers. I take this opportunity to express my gratitude and appreciations to all these people.

Abstract:

The Ultrasonic velocity (U), Density (ρ), Viscosity (η) have been measured for binary liquid mixtures of Benzyl Propionate with DMSO at 308K, 313K, 318K, 323K, 328K and 333K. From these data some of acoustical parameters such as Adiabatic compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free volume (V_f), and Internal pressure (π_i) have been computed using standard relations. The variations in ultrasonic velocity and other parameters play a significant role in understanding the solute-solvent, intra and intermolecular interactions between the constituent molecules.

LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Symbols, Abbreviations & Nomenclature	**Meanings**
H^E	Excess of mixing for several alcohols
U	Ultrasonic Velocity
K	Wave number
K_s	Adiabatic bulk modulus
ρ	Density
η	Viscosity
ρ_0	Ambient hydrostatic pressure
ρ_{mix}	Density of binary mixtures
P	Acoustic pressure
A	Cubical expansion coefficient
β_{ad}	Adiabatic compressibility
γ	Ration of specific heats
ω	Angular frequency
ξ	Particle displacement
ξ_0	Peak value of the particle displacement
m	Molecular weight
U_T	Isothermal sound velocity
R	Gas constant
Π_i	Internal Pressure

Symbols, Abbreviations & Nomenclature	**Meanings**
T	Temperature
N_A	Avogadro number
R_m	Molar refraction
Z_i	No. of atoms in the i^{th} molecules
A_i	Additive volume
W	Sound velocity
T_c	Critical Temperature
T_0	Melting point
V_0	Volume per mole
V_f	Free volume
V_α	Available volume
V_{OA}, V_{OB}	Molar volume of the components A, B
L_f	Free length
L_{mix}	Free length in binary mixtures

CHAPTER I

CHAPTER-1

THE LIQUID STATE

1.1 INTRODUCTION

While it is often said that a liquid is intermediate in its properties between a solid and a gas, this statement should not be understood to mean that every property of a liquid is intermediate in value between those of the other two states. If the actual figures are compared, it is found that in the great majority of cases the value of any property of a liquid is approximately equal either to that of the solid or to that of the gas. The intermediateness, then, is a statistical one-a liquid has some of the properties of a solid, and some of the properties of gas. The most obvious resemblance between liquids and gases is their lack of rigidity neither offers permanent resistance to a shearing stress. The immediate consequence of this is that neither a liquid nor a gas possesses shape of its own, but always offer a resistance to shearing stress.

Between liquids and solids, the most prominent resemblance is that both possess cohesion, which enables each to maintain a free surface, whereas a gas will always completely fill any container. A second, and hardly less fundamental, property common to liquids and solids, is their relative incompressibility compared to gases. While the compressibility of solids are usually of the order or of10^{-6} atm^{-1}, those of liquids are only slightly larger (about10^{-5} atm^{-1}).

The compressibility of a gas, on the other hand, is roughly equal to the reciprocal of the pressure, or, at a pressure of one atmosphere, about 10^{5} times as great as that of liquid. Closely allied to the second similarity between liquids and solids is the third: their similarity in density. The density change which takes place when a solid melts is usually of the order of 10 to 50 percent, but on vapourization the density decreases by a factor of 100 or 1,000.

From these simple facts considerable information can be obtained about the nature of the molecular arrangement in liquids. From the density, for example, the mean distance between molecules can be calculated. Taking Argon as a typical example, the molar volumes of the solid, liquid and gas at the boiling point are respectively 24.3 cc, 28.1 cc and 7.050 cc. As a first molecules of the liquid and gas are arranged like those of the solids in a face centered cubic lattice. To obtain the correct densities it is then necessary to assume that the distance between nearest neighbours is 3.84 A° in the solid 4.03 A° in the liquid 25.4 A° in the gas. In the solid, the molecules are in contact. In the liquid, there is a little space (about 5 percent of the molecular diameter) between molecules is about six times the molecular diameter.

Since the forces between molecules are short range forces, and act through a distance of only two or three times the molecular diameter, it is immediately obvious that in the gas these forces are of little importance. Any such regular arrangement of molecules as that we have assumed will therefore be destroyed by the thermal motions of the molecules, and the usual assumption that the molecules of a gas are arranged in space and are randomly distributed.

In the solid, on the other hand, the close-packed arrangement of the molecules prevents any molecule moving from moving far from its original position, which results in turn in the rigidity of the crystal. At the same time the low compressibility of the solid is due to the fact that there is no free space between the molecules, so that any compression must be accomplished by reducing the size of the molecules themselves. If the liquid maintains the arrangement we have assumed, it is difficult to see how to explain its fluidity. The molecules are packed so closely together that no interior molecule can change its position by much more than can the molecule of the solid. The only conceivable way in which flow could take place would be by the simultaneous displacement of a whole plane molecule. Such a motion, however, would require the simultaneous lengthening of a great number of intermolecular distances and hence a large energy of activation for the flow process. To avoid this difficulty it is obviously necessary to assume that a few molecules move at a time, but this in turn implies that it must be relatively easy for molecules to become displaced from the regular lattice.

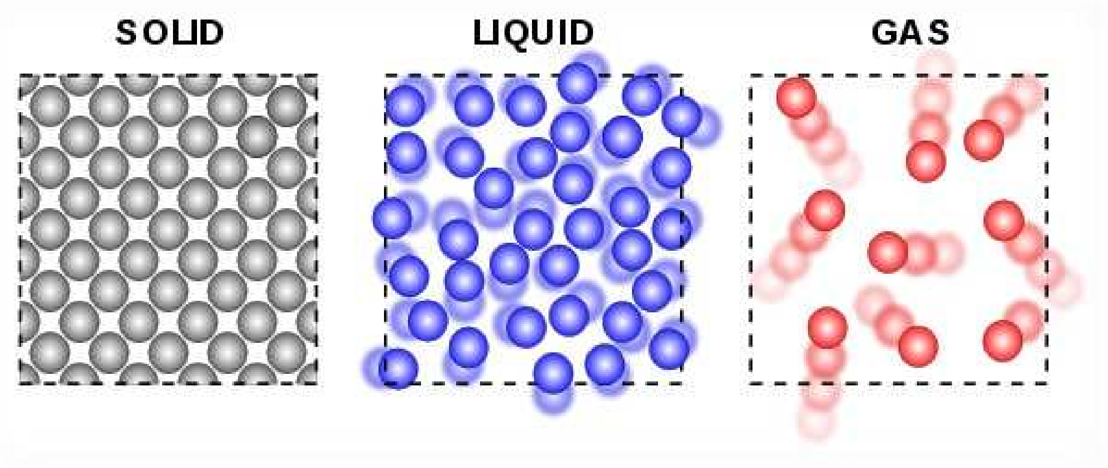


Fig 1.1: Relative spacing of molecules in solid, liquid and Gaseous Phases

On the other hand, the problem of packing so many spheres into a given volume does not permit any great variation from the regular closed packed structure. In fact the only reasonable modifications which can be made are two in number. First, there may be local irregularities caused by groups of molecules coming closer together, leaving wider spaces elsewhere in the structure. Second, there may be gradual distortion of the structure as we go from molecule to molecule, so that although the pattern in the immediate neighbourhood of a given molecule be quite regular, the pattern is irregular at a distance.

1.2 SHORT AND LONG RANGE ORDER

The tendency of a liquid molecule to surround itself with a more or less definite number of neighbouring molecules at a near a definite distance shows that if we consider a region in the liquid so small that it contain only a few molecules, - say about 20 – these molecules must be arranged very nearly in as regular fashion as in the corresponding crystal. On the other hand, if the size of the region is enlarged, the irregularities mount up, and the positions of the molecule no longer can be related to a lattice of the type occupied by the molecules in the crystal. The regularity exhibited by the crystal is now generally referred to as long range order, since the positions of molecules many diameters away from a central molecule can be predicted from a knowledge of the position of the central molecule and the molecules immediately surrounding it.

In the liquid, on the other hand, this long range order has disappeared. Nevertheless, since the arrangement of the molecules immediately surrounding the central atom is reasonably definite, we can say that the liquid still possesses short range order. The crystal, of course, has short range order as well as long range order, but in the gas phase even the short range order has disappeared.

We can, therefore, state as an experimental fact that the melting of a crystal is accompanied by the disappearance of long range order, and the evaporation of a liquid is accompanied by the disappearance of short range order.

1.3 THE LOOSE PACKING OF RIGID SPHERES

Many of the features of liquids are shown by a simple collection of rigid spheres. If the spheres are packed carefully to make the volume occupied a minimum, them a regular crystal-like lattice-either hexagonal or cubic is formed. But if the volume available to the spheres is greater than that required for close packing, the regularity of the structure will disappear. This has been demonstrated in two dimensions by a number of experimenters[1] who have studied the distribution of spheres and other objects distributed on a flat surface. The three dimensional problem has been studied experimentally by Morrell and Hildebrand [2] by suspending hard gelatin spheres in a solution of the same density. These experiments gave radial distribution curves which were extremely close to those obtained by X-ray diffraction in liquids.

It would appear from this experimental evidence that the principal factor in the determination of the radial distribution function in a liquid is the volume occupied by the molecules themselves, that is to say, the repulsive forces between the molecules rather that their attraction.

1.4 THEORIES OF LIQUID STATE

The readiness with which liquids flow and diffuse suggests a random molecular structure analogous to the gas. On the other hand the cohesion and compactness exhibited by liquids indicate a structure resembling that of a solid. The similarities between a liquid and a solid make one to consider the two states of matter collectively as a “condensed matter” while the properties of fluidity shared by liquid and gas connect them collectively as “fluids”. Hence liquid state theories are broadly of two types.

1. Considering it as a condensed gas so that the interaction between the neighbouring molecules may be calculated through “pair potential functions” and
2. Considering it as a disordered solid lattice.

1.5 MOLECULAR INTERACTION IN LIQUIDS

There are two kinds of interaction

1. Dispersion interaction and
2. Dipole-dipole interaction in liquids.

In the case of non polar molecules the average dipole moment averaged over all phases of electronic motions is zero while the instantaneous dipole moment is never zero.

If two non-polar molecules are placed near each other, the instantaneous dipole moment will interact and will produce some potential energy, which may be positive (or) negative. Such interaction between the molecules is termed as dispersion interaction and is present in all the aggregates of molecules irrespective of the nature of the atoms and molecules.

The second category of interaction is specific. It requires a Hydrogen atom attached to a fairly high electronegative atom and an atom at an optimum distance with non bonded electrons (ion-pairs). This results in the formation of complexes between molecules while the dispersion interaction leads to positive contributions to excess thermodynamic quantities, the latter category makes negative contribution.

The determination of sound velocity, density, viscosity etc., leads to an understanding of the nature and type of molecular interactions especially in binary mixtures of liquids through the excess thermodynamic quantities. Normal liquids obey certain empirical rules such as Trouton's rule, The heat of vaporization at the boiling point is nearly equal to $85 \pm 10\ \mathrm{JK^{-1} mole^{-1}}$, the associated liquids (having hydroxyl group), do not obey these empirical rules. The deviation is due to association of molecules found in the vapour to form larger molecules in liquids. In the case of alcohols and acids, the links between the individuals are provided by hydrogen bonds.

The protic dipolar liquids are ordinarily intermolecular hydrogen bonded. This class of liquids has been extensively studied, the best example being water. Aliphatic and aromatic alcohols and amines, carboxylic acids and amides are typical representatives of this class of liquids. The liquids of this class possess an entropy of vaporization which is 30% higher than for normal non-associated liquids. A notable exception is the carboxylic acids.

The alcohols show regularly changing liquid properties as the aliphatic chain length is increased (or) as the number of hydroxyl groups is increased. For example, the di-electric constant drops as the chain length increases, but increases with the increase in number of hydroxyl groups.

When two liquids are mixed, the solution is said to be ideal if there is no volume change (or) enthalpy change on mixing. But in practice, solutions of liquids are never ideal. The deviation from ideality is much more marked in the case of associated solutions. The thermal energy is less than the interaction energy. The thermal perturbation cannot disturb the association very much. In a binary system of associated liquids, a distortion occurs depending on the concentration. The distortion in the structure of the associated molecules leads to large changes in the physical properties such a dielectric constant, viscosity, free volume etc. Considerable dissociation must occur when alcohols are mixed with diluents, the hydrogen bonds are broken and this explains the positive heats of reactions.

Self associations in alcohols are shown on fig 1.2. The earliest model of self association in alcohols is that of Oster and Kirkwood[5], which assumed long chain association with free rotations of the O.H. around the H-bond in such a situation,

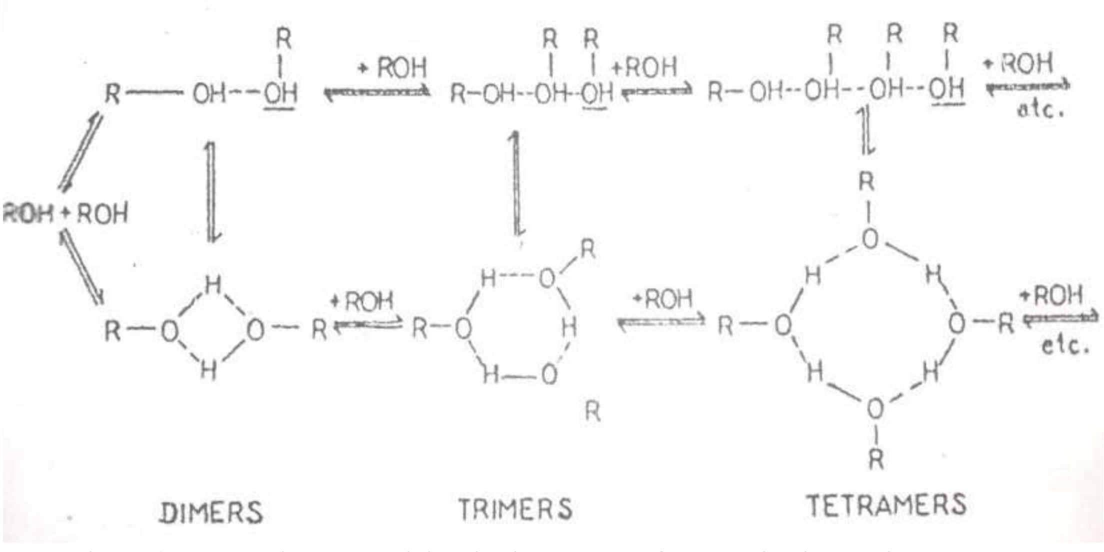


Fig 1.2: Posssible equilibria in the self-association of alcohols

Dipole moment of the alcohol solution should be greater than that of its monomer unit, which is not the case always [6,7]. In the most alcohols, dilution with non polar solvents resulted in a dip in dipole moment at a definite concentration [8], which means qualitatively that dilution leads to the formation of cyclic multimers of lesser dipole moment. Bellamy and Pace [9] and Coburn Oxrunwald [10] were of the view that such cyclic structures must be multimers and not dimmers because of unfavourable bonding angles in dimers. Since the cyclic form possesses one additional H-bond compared to the open (or) linear form, the change in enthalpy AH^o for cyclic form should be greater than that corresponding to the open structure. Hence it is possible to look for specific information from the experimental studies of enthalpy and entropy. Such studies [11,12] also do not provide sufficient data to permit a decision in favour of or against a particular model. Bordewijk [13], from his dielectric studies showed in mono alcohols, the large multimers are cyclic, probably tetramers, without of plane Oxygen and Hydrogen atoms.

Though there are plenty of data available on the ultrasonic behavior of mono alcohols [14-19] and in mixtures with inert solvents, they do not provide enough information on the model of mono alcohols.

Since the ultrasonic velocity is very sensitive to change in the free volume, it is desirable to look at the data on ultrasonic compressibility's of liquids from the thermo-dynamic point of view. The change in free volume results in a large change in the internal pressure of the liquids and hence the enthalpy of the system. The ease with which one can distort the fluid structure is determined by the energy holding the lattice together. In H-bonded liquids, it is reasonable to assume that this internal energy is related directly to the number of H-bonds per unit volume. The ultrasonic wave propagation in such liquids should result on the distortion of the fluids structures. Based on this concept, Sabesan et.al [20] studied the internal pressure and excess of mixing (H^E) for several alcohols including cyclo hexanol, amyl alcohol, Isoamyl alcohol, Isopropanol, n-butonol, 2-butonol, Isobutanol and tert-butanol in dioxin at different concentrations at 303, 308 and 313K. The positive values of H^E for the systems reported was explained as arising due to the stronger, self associations that was broken, rather strongly by dioxin compared to n-heptane (or) n-hexane. Among that the isomer alcohols, the n-compounds were found to have less H^Eat a given concentration and temperature, than the corresponding isomer. The role of free volume in systems involving propylene, glycol in several interacting systems was analyzed by Varadarajan and Bharathi [21]. The length of the side chain of hexanols was found to have a definite influence on the excess enthalpy values, on mixing with the interacting solvents [22].

1.6 VELOCITIES OF ULTRASONIC WAVES IN LIQUIDS

The first extensive measurements of ultrasonic velocity in organic liquids were done by Parthasarathy. He arrived at the assumptions that the aromatic compounds usually have higher velocities than the corresponding aliphatic compounds, although their densities are higher velocity in liquids of high density is low, but not in proportion, the increase in density being to some extent set off by an accompanying decrease in compressibility, polar molecules favour high velocities, long molecules give rise to higher velocity, a double bond of unsaturation tends to lower velocity and in similar derivatives changes from a light to a heavy atom lowers velocity. The results in many organic liquids indicate that as a rule an increase in density is to some extent balanced by an accompanying increase in β_0[23]. Nevertheless, since a number of inconsistencies developed from some of these rules, no quantitative derivations were possible [24]. However, Schaaffs had contradicted Parthasarathy’s rule arguing that the aromatic substances have generally higher velocities than aliphatics. Increasing density through a homologous series ought to decrease u, but, in fact does not. In halogen compounds the abnormal in molecular weight accounts for the observed fall in U through a series. Increase in molecular volume and the density go hand in hand. These are the factors, which cause the increase of U when heavier atoms are substituted and not increased in molecular weight per sec. There is real evidence that dipole moment is of important in this connection [25]. The velocity of ultrasonic waves in liquids varies from about 900 to $2000ms^{-1}$. The value of U also depends on the temperature and pressure. For most pure liquids at temperatures far from the critical values the value of U decreases as the temperature increases. Water is an exception to this general rule and in this case U increases by about 2 ms^{-1} for each Kelvin rise in temperature and reaches a maximum at 346 mK, above this temperature, U decreases as the temperature rises further. As far as pressure changes are concerned, the velocity U increases in an approximately linear way with pressure for all liquids. This is simply as consequence of the fact that the bulk modulus increases as the molecules are squeezed closer together. For water U increases by about 0.2 ms^{-1} for every increases of one atmosphere [26].

In ultrasonic work, it is convenient to work with plane waves of small amplitude. When an ultrasonic waves passes through a liquid, the pressure and density of an element of liquid vary periodically with time. The variations in P and ρ may be assumed reversible and adiabatic. An ultrasonic wave is propagated as a longitudinal wave in a liquid because the particles of the liquid oscillate in the same direction in which the wave is moving. This is because the liquid possesses only one elastic modulus, the bulk modulus K. The propagation velocity, U, of the wave depends on this modulus and on the density ρ_0 of the liquid according to the equation,

$$U = \sqrt{\frac{Ks}{\rho_0}} \tag{1.1}$$

where K_s is the adiabatic bulk modulus. The above equation holds for small excess pressure amplitudes for which ρ_0 can be considered to remain a constant. This excess or acoustic pressure P is equal to the difference between the instantaneous pressure P and the ambient hydrostatic pressure ρ_0 i.e.,

$$P = P - \rho_0 \qquad (1.2)$$

Let us consider a plane wave traveling in a liquid in the x-direction. Its propagation is given by the well known equation,

$$\frac{\partial^2 p}{\partial t^2} = U^2 \frac{\partial^2 p}{\partial X^2} \qquad (1.3)$$

As the wave proceeds, each particle of the liquids sutlers a certain displacement from its mean position, we denote this particle displacement we denote this particle displacement by 'ξ'. The corresponding particle velocity v in the medium is given by $v = \frac{\partial \xi}{\partial t}$ and the particle acceleration by

$$a = \frac{\partial v}{\partial t} = \frac{\partial^2 \xi}{\partial t^2} \qquad (1.4)$$

In equation (1.3), the propagation of sound wave has been described in terms of the acoustic pressure, p. This equation is also satisfied by other quantities such as velocity potential cp, particle displacement ~ and particle acceleration

$$\frac{\partial^2 \xi}{\partial t^2} = U^2 \frac{\partial^2 \xi}{\partial X^2} \qquad (1.5)$$

We consider the typical solution

$$\xi = \xi_0 . \exp j\,(\omega t - kx) \qquad (1.6)$$

In this equation ξ_0 represents the peak value of the particle displacement, $\omega = 2\pi f$ f is the angular frequency and $k = \frac{\omega}{U} = 2\frac{\pi}{\lambda}$ is the wave number [27, 28].

CHAPTER II

CHAPTER-2

LITERATURE SURVEY

2.1 REVIEW

Dash Ashok Kumar et al.,(2014) [29] proposed that the ultrasonic velocity (U), density (ρ) and coefficient of viscosity (η) of binary mixture of dimethyl acetamide (DAMC) and diethyl ether at temperature 308K have been measured at different frequencies (2MHZ, 4MHz 6MHZ and 8MHZ). Adiabatic compressibility (K_s), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i) and their respective excess values have been computed for entire range of concentration and are interpreted to explain molecular interaction occurring in the liquid mixture. Relaxation time (τ), excess enthalpy (H^E) and absorption coefficient (α/f2) have been calculated and discussed. On the basis of the experimental values of density, ultrasonic velocity, related acoustical parameters and their excess values for the binary liquid mixture, it is concluded that there exists dipole-dipole, dipole-induced dipole and dispersion interactions in the binary liquid mixture of DMAC diethyl ether.

D. Ubagaramary et al.,(2018) [30] discovered that the functions of ultrasonic velocity, density and viscosity for ternary liquid mixtures of 1-proponol, 1- butanol and 1-pentanol with tetra hydro furan are determined by 303.15 K-313.15 K. This data is used to calculate various parameters like the excess free volume, excess internal pressure and Gibb’s free energy, which is used to discuss molecular interactions in the ternary liquid mixtures.

Nabaparna Chakraborty et al.,(2020) [31] revealed that the Velocity of sound and density of binary liquid mixture of Dichloromethane with Ethanolamine have been calculated at different range of temperatures for various concentrations.

Liquid-liquid interaction is confirmed by obtaining experimental values of fundamental parameters; ultrasonic velocity and density. Then these parameters are used to determine various other dependent parameters such as acoustic impedance (Z), intermolecular free length (L_f), adiabatic compressibility (β_{ad}), Rao's constant (R), Wada's constant (W), Vander Waal's constant (b), effective molecular weight and Relative strength. Graphs are plotted for all parameters versus mole fraction. The linear variation of most of the acoustical parameters shows the absence of complex formation in the mixture. The decrease in ultrasonic velocity indicates that there is weak interaction between the molecules of the mixture. The solution tested, consisting of Dichloromethane and Ethanolamine, was selected in order to obtain data on the molecular interaction between their constituent particles.

R. K. Kolhe et al.,(2020) [32] proposed that the viscosity **(η),** density (ρ) and ultrasonic velocity (U) of dimethylsulphoxide with 1-Octanol have been measured at different concentrations and temperatures from 303.15K to 318.15K. Above measured data is used to calculate the parameters like adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), free volume (V_f), and available molar volume ($V\alpha$). These calculated parameters are helpful to explain the strength of interaction among the molecules of liquid binary mixture under investigation. From observed values of ultrasonic speed, viscosity and density of mixture, other parameters such as adiabatic compressibility, acoustic impedance, free length, free volume and available volume for binary mixtures of dimethylsulphoxide with 1-Octanol at various temperatures, it is found that, molecular association is present among the molecules of liquid combinations.

Nabil M. Abdel Jabbar et al.,(2017) [33] proposed that the ultrasonic velocities have been measured for different binary mixtures of common choline chloride-based deep eutectic solvents (DESs), namely, reline, glyceline and ethaline with water, in the range of temperature: 303.15–353.15 K. The experimental data measurements with different mole fractions of DES–water solutions were utilised in fitting four different models for speed of sound. These models correlate the speed of sound with some physical properties such as molar volumes, molar components sound velocity, densities, molecular weights, collision factors etc. A close match was obtained with these models with an average relative error of less than 4% for all data points used. It was observed that the ultrasonic velocity increases with the concentration of DES solvent and decreases with temperature. Moreover, this study roughly indicated that the intermolecular interactions in reline and ethaline aqueous mixtures exist in the form of disruption of dipole–dipole interactions (that varies considerably as a function of DES mixture composition and solution temperature). On the other hand, the interactions on the molecular level in glyceline aqueous solution are mainly due to dipole–dipole intermolecular forces. The speed of sound and density data of different aqueous solutions of three common choline chloride-based DESs were measured as a function of temperature within the range 323.15–353.15 K.

K. P. Singh et al.,(2018) [34] the work presented in this paper deals with the study of thermodynamic properties of new working fluids for absorption machines, mainly for characterization of absorbent–refrigerant pairs that could improve the cycle performance. The study of atomic motion in liquids plays an important role in understanding the solid-like behaviour of liquids. The accurate measurement of the energy changes due to scattering can be used to study the dynamical behaviour of liquids. Measurements of the ultrasonic velocity (u), density (ρ) and viscosity (η) for binary mixtures of polyethylene glycol 250 dimethyl ether with 1-propanol and 1-butanol have been made at three temperatures (T = 293, 303 and 313 K) over the entire composition range in order to investigate the nature of intermolecular interactions between the components of these liquid mixtures. Non-linear variation of derived quantities with the mole fraction supports the molecular interaction occurring between component molecules. From above studies, it is concluded that presence of strong interaction through hydrogen bonding between unlike molecules is characterised by non-linear behaviour of excess values of Gibbs's free energy of activation for viscous flow (ΔG^{*E}) and internal pressure (π_i^E).

N. P. Mohabansi et al.,(2020) [35] discovered that the Density(ρ), Viscosity(η), Ultrasonic Velocity(U) and Surface Tension(γ) of an aqueous-consolute, Na2SO4 solution of [2-(dimethylamino)-1-(4-methoxyphenyl) ethyl] cyclohexan-1-ol (Venlafaxine) 0.0201,0.0402,0.0804,0.1608 mol/kg were measured at 293.15, 303.15 and 313.15K. The resulting data were used to calculate various acoustical parameters, acoustic impedance (Z), adiabatic compressibility (β), Intermolecular free length (L_f), Wada's Constant (W), Rao's Constant (R), free volume (V_f), Relative Association (RA) were calculated which provides valuable information regarding drug-electrolyte (Na2SO4) interaction. The excess parameters viz. partial molar volume and excess adiabatic compressibility (β^E), excess inter molecular free length (L_f^E), excess free volume (V_f^E) were also calculated. These calculations help in predicting the intermolecular interactions. In an aqueous 2-(dimethylamino)-1-(4-methoxyphenyl)ethyl]cyclohexan-1-ol and co-solute Na2SO4 solution, ultra-sonic velocity, density, viscosity and surface tension are measured at 293.15, 303.15 and 313.15K.

S. R. Dandwate et al.,(2018) [36] in the present study attempt has been made to determine acoustic and thermodynamic parameters for binary liquid mixture of DMSO with methanol at 295.15 K, 300.15 K, 305.15 K, 310.15 K and 315.15 K temperatures. The excess values of isentropic compressibility, acoustic impedance, and internal pressure have been calculated using experimental data of ultrasonic velocity, density and viscosity. Molecular interactions in mixture form have been discussed depending upon deviations in excess values. Experimental data have been validated using Redlich-Kister polynomial equation. The values of excess isentropic compressibility have been found negative over entire concentration range at all temperatures.

P. S. Syed Ibrahim et al.,(2019) [37] deal the values of ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary liquid mixtures containing meta methoxy phenol and 1-propanol in n-hexane at different temperature 303 K,308 K and 313 K at a fixed frequency of 2MHz., experimentally. Using the experimental data of velocity, density and viscosity, various acoustical and thermodynamical parameters like Gibb's free energy, entropy, molecular interaction parameter, stability constant and excess property like solvation number are either calculated or computed. All these parameters have been discussed to throw light on intermolecular interactions between the component of ternary mixtures. The dependence of excess property in particular solvation number of the ternary mixture is compared and discussed in the context of intermolecular interaction and other factors. The result is interpreted in terms of molecular interactions under the influence of ultrasonic sound. From this present study it is concluded that the values of solvation number support the molecular reactions rather than the ionic reactions and henceforth interaction will be allowed due to dipole-dipole interactions and dipole – induced dipole interactions and nature of the hydrogen bonding and some extent due to steric effect of the substituent present in the benzene ring between MMP and 1-propanol in n hexane and these facts are substantiated by the values of thermodynamic properties such as ΔG^0 & ΔS.

V. Vanathi et al.,(2019) [38] proposed that the ultrasonic velocity (U), density (ρ), viscosity (η) for the ternary mixture of benzene þ chloroform þ cyclohexane in the whole range of composition has been carried out at various temperatures 303.15, 308.15 and 313.15K. From the measured parameters U, ρ and η, some derived parameters β_{ad}, L_f, V_f, π_i, Z, R,W with molar enthalpy (Hm) and apparent molar volume (ϕv) are also estimated. The decreasing trend of η, R,W, Hm, and ϕv with concentrations and other parameters are in increasing trend were observed. The trend of acoustical and physico-chemical parameters confirm the dynamics of molecules at higher temperature and the magnitude of intermolecular interactions among the constituents of the mixtures always reflects the nature of substance. The role of enthalpy and apparent molar volume has been used to determine their thermal response. The sign and magnitude of these properties are evident for the nature of interactions between component molecules. In summary, the ultrasonic velocity, density and viscosity measurements on ternary organic mixtures at various temperatures are carried out.

Sudhir P. Dange et al.,(2020) [39] reported that the Ultrasonic velocity (u), density (ρ) and viscosity (η) at 2 MHz in the binary mixtures of Riboflavin with methanol in the concentration range (0 to 0.1 M) and at temperature of 298K using ultrasonic interferometer technique. The experimental parameters, ultrasonic velocity, density and viscosity were used to calculate various acoustic and thermodynamic parameters. The obtained results support the nature and strength of molecular interaction, Physico-chemical behaviour in the binary liquid mixture of Riboflavin and Methanol. The Non-linear variation of thermo-acoustical parameters with molar concentration reveals that, there exist intermolecular forces in the binary liquid mixture of Riboflavin and methanol.

Pallavi B. Nalle et al.,(2019) [40] discovered that the ultrasonic velocity, density and viscosity of drug Piperine with MgCl2 have been measured as a function of number of moles n = (0.7009, 1.4018, 2.1027, 2.8036 and 3.5045) at 323.15 K, 328.15 K and 333.15 K. The experimentally collected data have been used to calculate various acoustical, thermodynamic and excess parameters such as excess values of adiabatic compressibility, excess intermolecular free length, excess specific acoustic impedance, excess relaxation amplitude and excess relaxation time have been calculated. Above excess parameters are fitted to the Redlich-Kister equation.
The results of acoustical, thermodynamic and excess properties reveal the existence

of strong molecular interaction in the mixtures. The drug works as a structure breaker (it breaks the structure of MgCl2) and there is ion formation in the system. Acoustic, thermodynamic and excess parameter of mixture reflects the structural deformation in terms of intermolecular interaction. As the isentropic compressibility goes on increasing in a negative manner, the prepared solvent mixture maleic acid and methanol (60/40) can be used for the bleaching purpose of coconut coir fibres.

T Karunakar et al.,(2013) [41] revealed that the ultrasonic velocity and density measurements for binary mixtures of aniline + 1-butanol at T= (303.15 – 318.15) K, are conducted at atmospheric pressure. Some thermo acoustical parameters like adiabatic compressibility (β), molar volume (V_m), inter molecular free length (L_f) and acoustic impedance (Z) have been calculated from experimental measurements. The results have been used qualitatively to explain the molecular interaction between the components of these mixtures. Further, the results are further supported by FT-IR spectra. From the data of ultrasonic velocity and density various acoustical parameters of the mixtures of aniline with 1-butanol at 303.15, 308.15, 313.15 and 318.15 K were calculated.

R. C. Verma et al.,(2014) [42] proposed that Density, Ultrasound velocity and viscosities of Ethyl propionate with butanol-1 and pentanol-1 have been measured over entire range of composition at 308 K and atmospheric pressure. The computed acoustic and thermodynamic properties of Ethyl propionate in higher alcohols will give the excess values of issentropic compressibility, molar volume and viscosity. The excess value will decided the nature and extent of molecular interaction of Ethyl propionate in butanol-1 and pentanol-1.

L. Palaniappan et al.,(2020) [43] proposed that the ultrasonic velocity, density and viscosity measurements carried out for the binary mixtures of toluene, m-xylene with some butanols at 303 K. Various theoretical models have been applied to these binary systems; evaluate the sound velocity values and compared with the experimental values. The validity of Nomoto theory (NT), Van Deal-

Vangeal (IMR) and Free length theory (FLT) is checked and a comparative study of the above models is made. The non-ideal behaviour of the system is explained in terms of molecular interactions of the constituents of the mixture. The interactions further, evident with percentage deviation, molecular interaction parameter and goodness fit test. Among the three theories taken up for the prediction of sound velocity, Namoto Relation is found to yield excellent comparison with the experimental value for the systems investigated.

Sk. Md Nayeem et al.,(2015) [44] proposed that the ultrasonic velocities (U), and densities (ρ), of binary liquid mixtures of dimethyl sulphoxide (DMSO) with ketones such as acetophenone (AP), cyclohexanone (CH), and 3-pentanone (3P), including pure liquids, over the entire composition range have been measured at 308.15 K. Using the experimental data, deviation in ultrasonic velocity, Δu, deviation in isentropic compressibility, Δk_s, excess molar volume, V_m^E, excess intermolecular free length, L_f^E and excess acoustic impedance, Z^E, partial molar volumes, $V_{m,1}$, $V_{m,2}$, and excess partial molar volumes, $V^E_{m,1}$, $V^E_{m,2}$, have been calculated. Molecular interactions in the systems have been studied in the light of variation of excess/deviation values of calculated properties and these properties have been fitted to Redlich–Kister type polynomial equation. The observed positive values of V_m^E, Δk_s, L_f^E and negative values of Δu, Z^E for all the binary liquid mixtures studied clearly indicate the presence of the dominance of weak physical interactions between the components of molecules. Further, FTIR spectra support the conclusions drawn from deviation/excess properties. Moreover, theoretical values of ultrasonic velocity in the mixtures have been evaluated using various theories and such values were compared with experimental velocities to verify the applicability of such theories to the systems investigated.

Subhraraj Panda (2020) [45] proposed that the measurement of ultrasonic velocity is helpful to interpret solute-solute, solute-solvent interaction in aqueous medium. The ultrasonic speed (U), density (ρ) and viscosity (η) at 313 K have been determined using ultrasonic interferometer at four different frequencies *i.e.* 1MHz, 5MHz, 9MHz and 12 MHz, pycnometer and Ostwald's viscometer of dextran in aqueous medium respectively. All the three measurements were carried out in a water bath of constant temperature with an uncertainty of ±0.1 0C. The derived acoustical parameters such as free volume (V_f), internal pressure (π_i), absorption coefficient (α), molar sound velocity (R) and molar sound compressibility (W) have been determined from experimental data. The outcomes are described in terms of molecular interaction between the solution components. Ultrasonic speed, density and viscosity have been measured for aqueous dextran solution at different frequencies in constant temperature.

R. Chithra Devi et al.,(2019) [46] proposed that the density (ρ), viscosity and ultrasonic velocity (u) in ternary liquid mixture of acrylonitrile (AN) with benzene in N-N-di methyl aniline have been measured at (303,308 and 313)K respectively, over the entire composition range by using an ultrasonic interferometer for measuring velocity at 2MHz frequency. From the experimental data various acoustical and thermodynamical parameters such as; adiabatic compressibility(β), Intermolecular free length (Lf), Specific acoustic Impedance (Z), relative association (RA) and molar sound velocity have been computed using the standard relations. The results have been analysed on the basis of variation in thermodynamic parameters. These parameters are found to be very sensitive in exploring the interaction between the component molecules, which enable to have better understanding of the liquid mixtures. Since the system show similar trends for evaluated parameter so the constituent ternary mixture at different temperatures. The results have been interpreted in terms of dipole induced dipole interaction. The results obtained for the present study indicates that the molecular interaction is present in the liquid mixtures.

CHAPTER III

CHAPTER-3

MATERIALS AND METHODS

3.1 INTRODUCTION

Ultrasonic, thermo-physical and thermodynamic properties of liquid mixtures are of great significance in obtaining an in depth knowledge of inter and intra-molecular interactions, structural and physiochemical behaviour and also in verifying various liquid state theories which attempt in estimating the properties of liquid mixtures. Systematic study of thermodynamic properties of solutions with a new type of multi-frequency ultrasonic interferometer is done for precise measurement of the velocity of sound in liquids. The path length in the cell is varied by motion of a reflector, at the electrical reaction of the cell upon the oscillator is used to fix standing wave position at a standard frequency, and their locations are determined with a suitable cathetometer.

An investigation in the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been found to be an excellent quantitative way to elicit information about molecular structure and intermolecular forces in liquid mixtures. This has given impetus to the theoretical and experimental investigation of excess thermodynamic properties of liquid mixtures. Measurement of physiochemical properties such as density and ultrasonic velocity of pure components and their binary mixtures are being increasable used as tools for investigations of the properties of pure components and the nature of intermolecular interactions between the components of liquid mixtures. The significance reasons for the study of thermo-physical and thermodynamic properties of multi-component liquid mixtures are as follows:

- They provide way for studying the physical forces acting between molecules of different species.
- The study of liquid mixtures provides appearance of new phenomena, which are absent in pure liquids. The most interesting of these are the new types of phase equilibria, which are introduced by the variation in the promotion of the pure components.
- Liquid mixtures are the most direct source for studying the various parameters. The study of thermo-physical and thermodynamic properties of liquid mixtures helps in obtaining in depth knowledge about molecular interactions.

3.2 THEORY

Ultrasonic interferometer is a simple and direct device which yields accurate and consistent data, from which one can determine the velocity of ultrasonic sound in a liquid medium with a high degree of accuracy. A crystal-controlled interferometer (model M-83S) supplied by Mittal Enterprises, New Delhi, operating frequency 2 MHz has been used to measure the ultrasonic velocity.

3.3 ULTRASONIC

Ultrasonic sound refers to sound pressure with a frequency greater than the human available range (20 Hz to 20 KHz). When an ultrasonic wave propagates through a medium, the molecules in that medium vibrate over short distance in a direction parallel to the longitudinal wave. During this vibration, momentum is transferred among molecule. This causes the wave to pass through the medium.

3.4 ULTRASONIC INTERFEROMETER

An Ultrasonic Interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy.

Fig 3.1: Experimental setup for ultrasonic interferometer

The salient features of ultrasonic interferometer are given below:

- It is a simple in design, rugged and gives very accurate and reproducible results.
- Experiments may be performed over a wide range of temperature from -30 ^{0} C to +80 ^{0} C on all liquids except those which reacts with the plating of cell and crystal.
- Nearly 10 ml of experimental liquid is required.
- There is no danger of any change such as depolymerisation, due to ultrasonic effect since a very small ultrasonic energy is required.

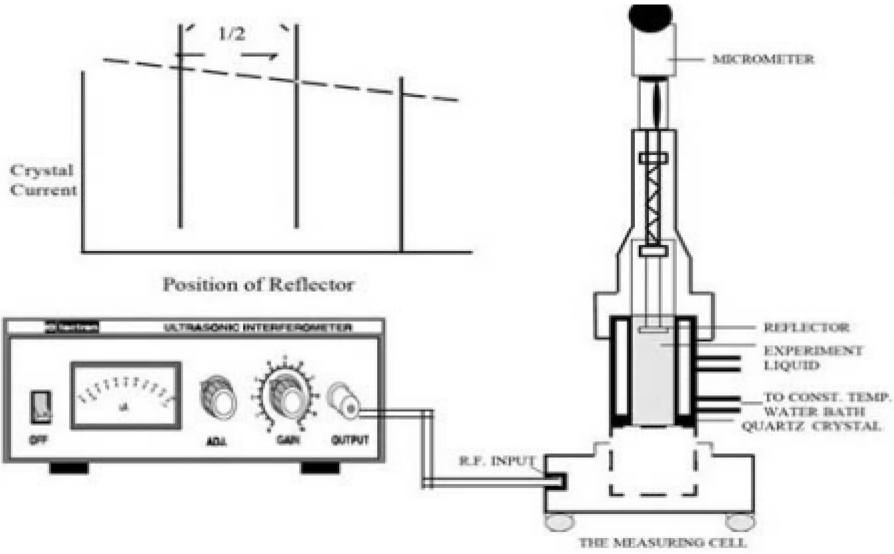


Fig 3.2: Cross section of the liquid cell and graph plotted position of reflector versus crystal current

In an ultrasonic interferometer, the ultrasonic waves are produced by the piezoelectric methods. At a fixed frequency variable path interferometer, the wavelength of the sound in an experimental liquid medium is measured, and from this one can calculate its velocity through that medium. The ultrasonic cell consists of a double walled brass cell with chromium plated surfaces having a capacity of 10 ml. The double wall allows water circulation around the experimental liquid to maintain it at a known constant temperature. The micrometer scale is marked in units of 0.01 mm and has an overall length of 25 mm. Ultrasonic waves of known frequency are produced by a quartz crystal which is fixed at the bottom of the cell. There is a movable metallic plate parallel to the quartz plate, which reflects the waves. The waves interfere with their reflections, and if the separation between the plates is exactly an integer multiple of half wave length of sound, standing waves are produced in the liquid medium. Under these circumstances, acoustic resonance occurs. The resonant waves are a maximum in amplitude, causing a corresponding maximum in the anode current of the piezoelectric generator. The ultrasonic interferometer consists of the following mainly two parts:

3.4.1. The high frequency generator.

3.4.2. The measuring cell.

3.4.1 The high frequency generator

The high frequency generator is designed to excite the quartz crystal fixed at the bottom of the measuring cell at its resonant frequency to generate ultrasonic waves in the experimental liquid filled in the “measuring cell”. A micrometer to observe the changes in current two controls for the purpose of sensitivity regulation and initial adjustment of the micrometer are provided on the panel of the high frequency generator.

3.4.2 The measuring cell

The measuring cell is specially designed for maintaining the temperature of the liquid constant during the experiment. A fine digital micrometer screw (LC 0.001 mm) has been provided at the top, which can lower or raise the reflector plate in the liquid within the cell through a known distance. It has a quartz crystal fixed at its bottom.

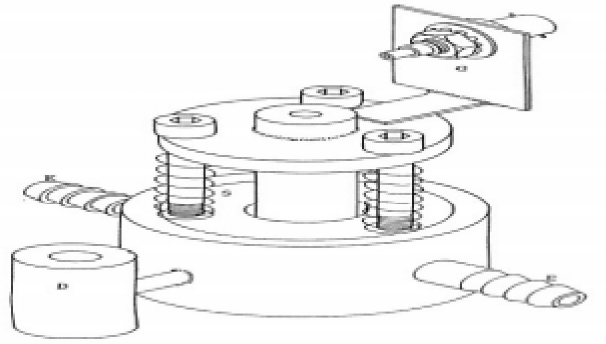


Fig 3.3: Ultrasonic interferometer cell liquid mixtures

3.5 WORKING PRINCIPLE

The principle used in the measurement of velocity (U) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by quartz crystal fixed at the bottom of the cell. These waves are reflected by a movable metallic plate kept parallel to the quartz crystal. If the separation between these two plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and anode current of the generator become a maximum. If the distance is now increased or decreased and the variation is exactly one-half wavelengths$(\lambda/2)$ or multiple of it, anode current become maximum from the knowledge of wavelength (λ) the velocity (U) can be obtained by the relation:

$$\text{Velocity} = \text{Wavelength} \times \text{Frequency}$$

$$U = \lambda \times f \tag{3.1}$$

3.6 ADJUSTMENT OF ULTRASONIC INTERFEROMETER

For initial adjustment two knobs are provided on high frequency generator, one is marked with "ADJ" to adjust the position of the needle on the ammeter and the knob marked "GAIN" is used to increase the sensitivity of the instrument for greater deflection, if desired. The ammeter is used to notice the number of maximum deflection while micrometer is moved up or down in liquid.

3.7 PROCEDURE

- Unscrew the knurled cap of cell and lift it away from double walled construction of the cell. In the middle position of it pour experimental liquid and screw the knurled cap. Wipe out excess liquid overflowing from the cell.

- Insert the cell in the heavy base socket and clamp it with the help of a screw provided on its side.
- Connect the high frequency generator with cell by coaxial cable provided with the instrument. In ultrasonic interferometer frequency selector knob should be positioned at desired frequency (same frequency as that of liquid cell chosen).
- Move the micrometer slowly in either clockwise or anticlockwise direction till the anode current on the ammeter on the high frequency generator shows a maximum or minimum.
- Note the reading of micrometer corresponding to the maximum or minimum (which is sharper) in microammeter. Take about 50 reading of consecutive maximum or minimum and tabulate them.
- Take average of all differences ($\lambda/2$).
- Once the wavelength (λ) is known the velocity (U) in the liquid can be calculated with the help of the relation.

3.8 SAMPLE CALCULATIONS

Sample: water

Average ($\lambda/2$): 0.375mm.

Ultrasonic velocity in sample: $U = \lambda \times f = 1480$ m/sec.

Density of the liquid = 996.458 Kg/m^3

Adiabatic compressibility (β_{ad}) = $1/\rho v^2 = 1/996.458 \times (1480)^2$

$\beta_{ad} = 4.58 \times 10^{-10}$ N/m^2.

3.8.1. Measurement of the density

The density (ρ) of the liquid mixture was determined by a specific gravity bottle of 5ml capacity. The specific gravity bottle with the liquid mixture was immersed in a temperature controlled water bath. The density was determined using the relation:

$$\rho_2 = (w_2/w_1)\rho_1 \qquad (3.2)$$

where w_1, w_2, ρ_1 and ρ_2 are masses of distilled water, mass of liquid mixture, density of distilled water and density of liquid mixture respectively.

3.8.2. Measurement of the viscosity

The viscosity measurements were done through Ostwald’s viscometer. The viscometer is filled with reference liquid (distilled water) and then immersed in water bath. The water in the viscometer is allowed for some time to attain the experimental temperature. Using a suitable arrangement, the water is sucked above the marked level and then it is allowed to flow freely. The time taken for the flow of water is noted. The water is replaced with a mixture, whose viscosity is to be determined. Using the same procedure, the time taken for flow of liquid mixture at the experimental temperature was determined. Using the time taken for the distilled water and mixture, the viscosity of unknown liquid mixture is determined.

$$\eta_s/\eta_w = \rho_s/\rho_w \text{ x } t_s/t_w \qquad (3.3)$$

where η_w, ρ_w and t_w are the viscosity, density and time flow of water respectively and η_s, η_s and t_s are the viscosity, density and time flow of unknown liquid mixture respectively. Viscosity is an important transport property for process design in petroleum, petrochemical, chemical and other chemical industries involving fluid transportation, mixing agitation, heat exchange and concentration. The estimation of the viscosity of a mixture is more difficult than of the pure compound. The prediction of the viscosity of liquid mixtures is a goal of long standing with both experimental and theoretical importance. Many industrial, chemical processes or laboratory works need experimental data of viscosity at any given temperature and composition for the liquid mixtures.

3.9 THEOTERTICAL METHOD FOR THE ESTIMATION OF ACOUSTICAL THERMODYNAMIC PARAMETERS OF LIQUID AND LIQUID MIXTURES

3.9.1 Adiabatic compressibility (β_{ad})

The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. These changes are related to the compressibility of the medium by thermodynamic relation;[47]

$$\beta_{ad} = 1/\nu[\partial\nu/\partial p] \qquad (3.4)$$

It can also be calculated from the speed of sound (U) and the density of the medium (ρ) using the equation of Newton Laplace as;

$$\beta_{ad} = 1/u\rho^2 \text{ Kg}^{-1} \text{ ms}^2 \qquad (3.5)$$

3.9.2 Free length (L_f)

The intermolecular free length is the distance covered by sound wave between the surfaces of the neighbouring molecules. It is measure of intermolecular attractions between the components in binary mixture. The increase or decrease in free length indicates weakling and strengthen of intermolecular attraction. As the ultrasonic velocity increase due to the increases in concentration, the interaction free length has to decrease and vice-versa. It is related to ultrasonic velocity and density as;[48]

$$L_f = K/(\rho U)^{1/2} \text{ m} \qquad (3.6)$$

The adiabatic compressibility of a liquid can be expressed in terms of the intermolecular free length which is the distance between the surfaces of the neighbouring molecules and is given by the relation,[49]

$$L_f = K_T\, \beta^{1/2} \qquad (3.7)$$

where, $K_T = (93.875+0.345T) \times 10^{-8}$

3.9.3. Free volume (V_f)

Free volume is one of the significant factors in explaining the variations in the physio-chemical properties of liquids and liquid mixtures. The free space and its dependent properties have close connection with molecular structure and it may show interesting features about interactions, which may occur when two or more liquids are mixed together. This molecular interactions between like and unlike molecules are influenced by structural arrangements along with shape and size of the molecules.

A liquid may be treated as if it were composed of individual molecules each moving in a volume V_f in an average potential due to its neighbours. That is, the molecules of a liquid are not quite closely packed and there are some free spaces between the molecules for movement and the volume V_f is called the free volume. Eyring and Kincaid defined the free volume as the effective volume in which particular molecule of the liquid can move and obey perfect gas laws. Free volume in terms of Ultrasonic velocity (U) and the Viscosity of the liquid (η) as;[50]

$$V_f = [M_{eff} U/K\eta]^{1/2} \quad m^3\ mol^{-1} \qquad (3.8)$$

where

M_{eff} is the effective molecular weight.

$M_{eff} = M_iX_i$ in which Mi and Xi are the molecular weight and the mole fraction of the individual constituents respectively. K is a temperature independent, constant which is equal to 4.28 x 109 for all liquids.

3.9.4. Relaxation time (τ)

Relaxation time is the time taken for the excitation energy to appear as translational energy and it depends on temperature and on impurities. The dispersion of the ultrasonic velocity in binary mixture reveals information about the Characteristic time of the relaxation process that causes dispersion. The relaxation time (τ) can be calculated from the relation;[51]

$$\beta = 4/3\ \beta\eta \qquad (3.9)$$

3.9.5. Internal Pressure (π_i)

The measurement of internal pressure is important in the study of the thermodynamic properties of liquids. The internal pressure is the cohesive force, which is a resultant of force of attraction and force of repulsion between the molecules. Cohesion creates a pressure within the liquid of value between 103 and 104 atmospheres. Internal pressure also gives an idea of the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent arise through hydrogen bonding, charge transfer, Columbic (or) Vander Waal's interaction. The term a/v^2 in Vander Waal's equation being the measure of attractive force of the molecule is called the cohesive (or) internal pressure.

The internal pressure is the single factor which varies due to all type of solvent-solute, solute-solute and solvent-solvent interactions. The internal pressure, (πi) can be calculated by using equation;[52]

$$\Pi_i = bRT\ [K\eta/U]^{1/2}[\rho^{2/3}/M^{7/6}]\ \ Nm^{-2} \qquad (3.10)$$

where K is a constant. T is the absolute temperature. η is the viscosity in NSm^{-2}. U is the ultrasonic velocity in ms^{-1} and ρ is the density in kgm^{-3} of the liquid.

CHAPTER IV

CHAPTER-4

RESULT AND DISCUSSION

Table 4.1, 4.3, 4.5, 4.7, 4.9, 4.11 show that the values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) of DMSO in Benzyl Propionate at 308K, 313K, 318K, 323K, 328K and 333K.

Table 4.2, 4.4, 4.6, 4.8, 4.10, 4.12 show that the values of Adiabatic compressability (β_{ad}), Free length (L_f), Free volume (V_f), Relaxation time (τ) and Internal pressure (π_i) of DMSO in Benzyl Propionate at 308K, 313K, 318K, 323K, 328K and 333K.

It may be noted that in six different temperature, the Adiabatic compressibility (β_{ad}) decreases with increase in composition of DMSO in Benzyl Propionate indicating the possibility of stronger interaction at higher composition. It is also observed that, the interactions are more at lower temperature as compared to higher.

In accordance with the view that the ultrasonic velocities increases with decrease in free length and vice versa.

The density is found to be increased with increasing the mole fraction of DMSO in Benzyl Propionate. However, it decreases in all cases as the temperature is increased.

Adiabatic compressibility shows an inverse behaviour compared to the ultrasonic velocity in the mixtures with increase in concentration and also increases in temperature [53].

The addition of interaction molecules breaks up the molecular clustering of the other, releasing several dipoles for the interactions. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes takes place due to the existence of electrostatic field. Thus structural arrangement of molecules results in increasing β with increasing temperature, thereby showing progressively intermolecular interactions [54].

The values of π_i increases with the increase in mole fraction of DMSO in Benzyl Propionate and also π_i increases with the increase in temperature. The increase in π_i with increase in concentration of DMSO indicates that the increase of cohesive forces in the binary liquid mixture.

The values of τ decrease with the increases of mole fraction of DMSO in a higher concentration which indicates the strong molecular interaction [55].

Table 4.1: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) for Benzyl propionate + DMSO at 308K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) $10^{-3}Nsm^{-2}$
X_1	X_2			
1.000	0.000	1371.2	1031.6	3.969
0.810	0.189	1404.4	1031.8	1.762
0.615	0.384	1401.3	1041.6	1.772
0.420	0.579	1425.3	1050.8	1.809
0.213	0.787	1423.6	1061.8	1.765
0.000	1.000	1455.6	1072.6	1.152

Table 4.2: Values of Adiabatic Compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free Volume (V_f) and Internal Pressure (π_i) for Benzyl propionate + DMSO at 308K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Free length $\times 10^{-11}$ m	Relaxation time $\times 10^{-12}$ s	Free volume $\times 10^{-8}$ $m^3\ mol^{-1}$	Internl Pressure $\times 10^{8}$ Nm^{-2}
X_1	X_2					
1.000	0.000	5.155	4.754	2.728	4.824	4.790
0.810	0.189	4.914	4.641	1.155	14.439	3.565
0.615	0.384	4.888	4.629	1.155	11.927	4.142
0.420	0.579	4.685	4.532	1.130	9.642	4.901
0.213	0.787	4.647	4.514	1.094	7.738	5.948
0.000	1.000	4.401	4.392	0.676	11.071	6.115

Mole fraction Vs Ultrasonic velocity

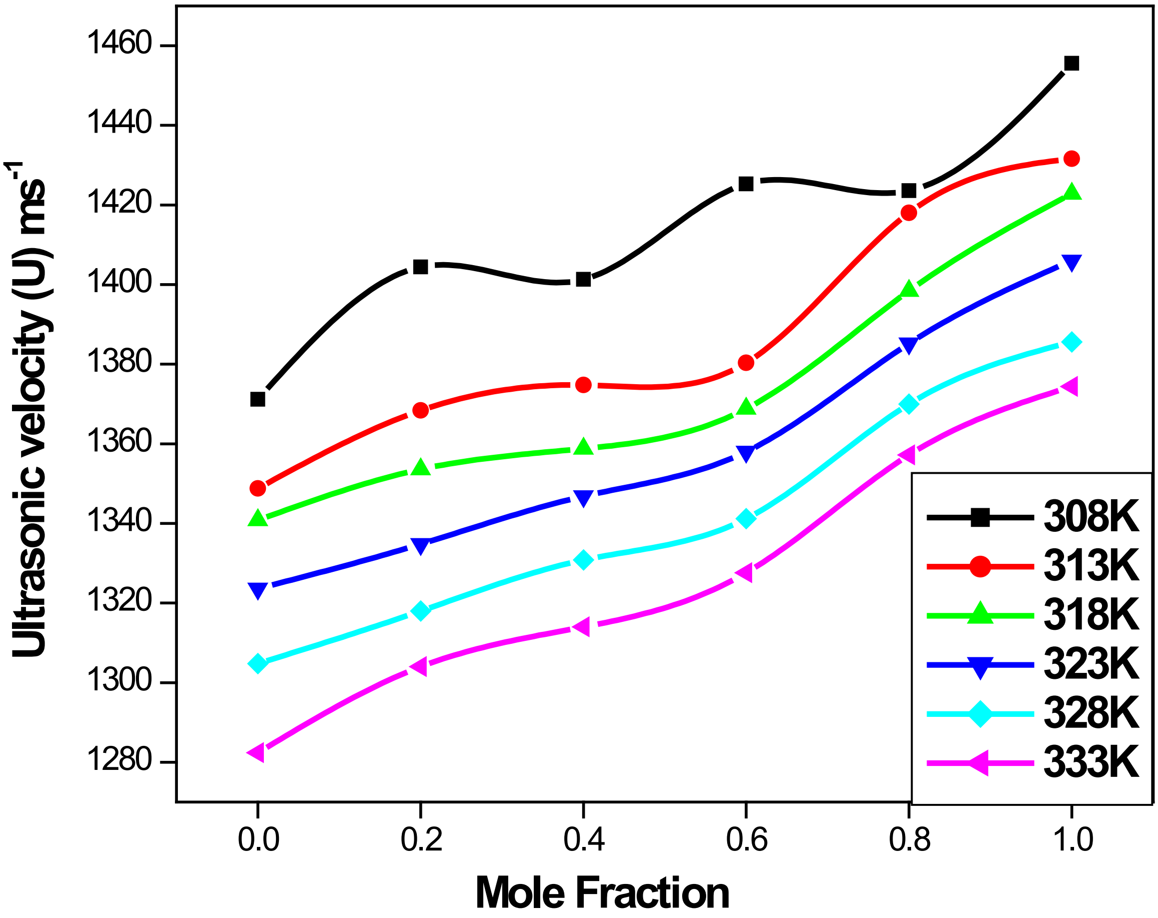


Table 4.3: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) for Benzyl propionate + DMSO at 313K

Mole fraction		**Ultrasonic velocity (U) ms^{-1}**	**Density (ρ) 10^{-3} Kgm^{-3}**	**Viscosity(η) $10^{-3} Nsm^{-2}$**
X_1	**X_2**			
1.000	0.000	1348.8	1031	3.873
0.810	0.189	1368.4	1031.6	1.709
0.615	0.384	1374.8	1041.6	1.726
0.420	0.579	1380.3	1050.6	1.777
0.213	0.787	1418	1061.6	1.724
0.000	1.000	1431.6	1072.4	1.110

Table 4.4: Values of Adiabatic Compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free Volume (V_f) and Internal Pressure (π_i) for Benzyl propionate + DMSO at 313K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Free length $\times 10^{-11}$ m	Relaxation time $\times 10^{-12}$ S	Free volume $\times 10^{-8}$ $m^3\ mol^{-1}$	Internal Pressure $\times 10^{8}$ Nm^{-2}
X_1	X_2					
1.000	0.000	5.332	4.877	2.753	4.882	4.846
0.810	0.189	5.176	4.806	1.180	14.536	3.614
0.615	0.384	5.079	4.7611	1.169	12.046	4.195
0.420	0.579	4.995	4.722	1.184	9.438	5.015
0.213	0.787	4.685	4.573	1.076	7.974	5.984
0.000	1.000	4.549	4.506	0.674	11.417	6.150

Mole fraction Vs Density

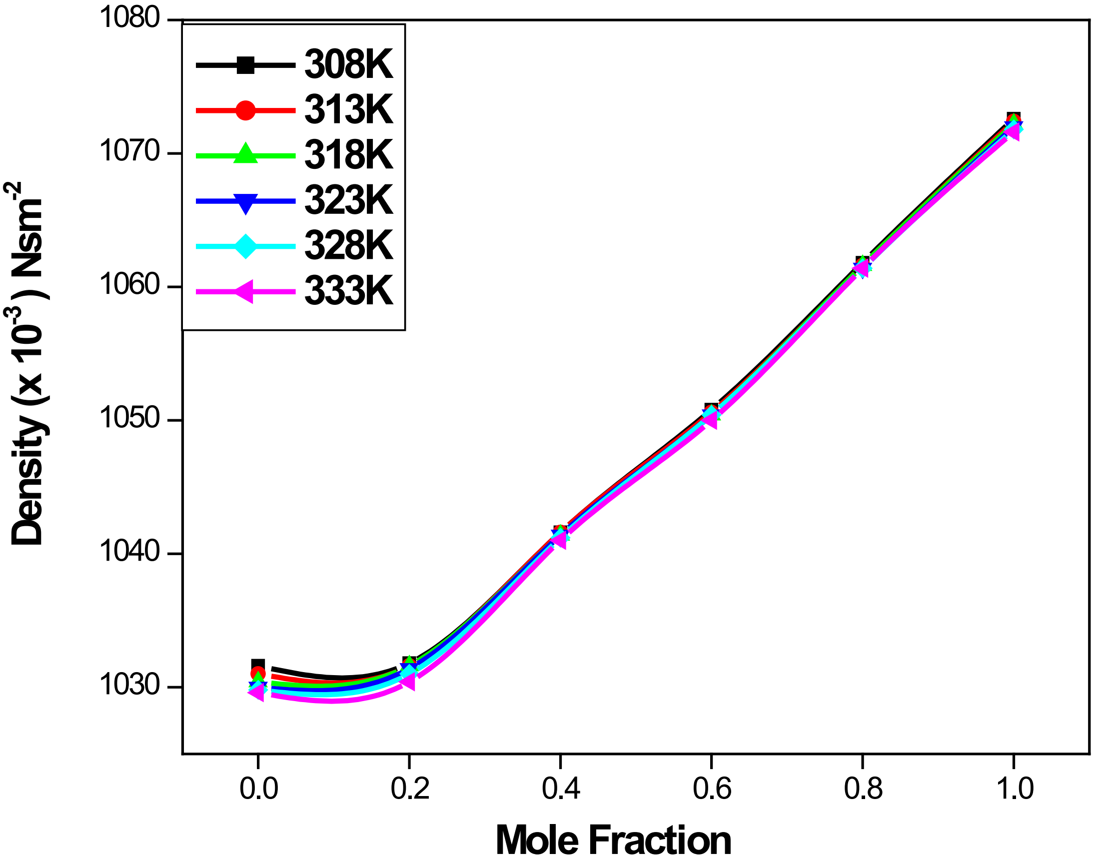


Table 4.5: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (ƞ) for Benzyl propionate + DMSO at 318K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) $10^{-3}\mathrm{Nsm}^{-2}$
X_1	X_2			
1.000	0.000	1340.8	1030.4	3.782
0.810	0.189	1353.6	1031.6	1.678
0.615	0.384	1358.8	1041.4	1.689
0.420	0.579	1368.8	1050.4	1.729
0.213	0.787	1398.4	1061.6	1.665
0.000	1.000	1422.8	1072.2	1.061

Table 4.6: Values of Adiabatic Compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free Volume (V_f) and Internal Pressure (π_i) for Benzyl propionate + DMSO at 318K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Free length $\times 10^{-11}$ M	Relaxation time $\times 10^{-12}$ s	Free volume $\times 10^{-8}$ $m^3\ mol^{-1}$	Internal Pressure $\times 10^{8}$ Nm^{-2}
X_1	X_2					
1.000	0.000	5.398	4.952	2.722	5.014	4.878
0.810	0.189	5.291	4.902	1.184	14.704	3.658
0.615	0.384	5.201	4.860	1.171	12.233	4.239
0.420	0.579	5.082	4.804	1.172	9.715	5.046
0.213	0.787	4.817	4.677	1.069	8.226	6.016
0.000	1.000	4.607	4.574	0.652	12.101	6.127

Mole fraction Vs Viscosity

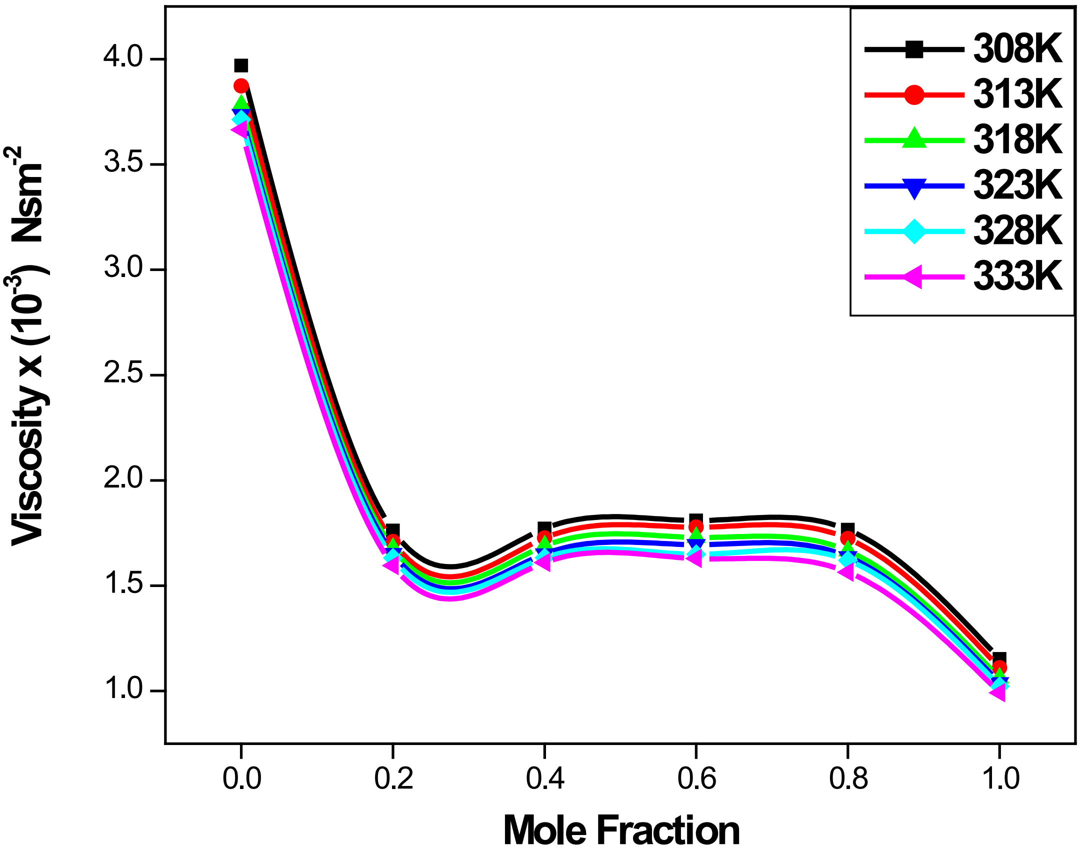


Table 4.7: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η), for Benzyl propionate + DMSO at 323K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) $10^{-3}Nsm^{-2}$
X_1	X_2			
1.000	0.000	1323.6	1030	3.737
0.810	0.189	1334.8	1031.4	1.653
0.615	0.384	1346.8	1041.4	1.651
0.420	0.579	1358	1050.4	1.695
0.213	0.787	1385.2	1061.4	1.637
0.000	1.000	1406	1072	1.039

Table 4.8: Values of Adiabatic Compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free Volume (V_f) and Internal Pressure (π_i) for Benzyl propionate + DMSO at 323K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Free length $\times 10^{-11}$ m	Relaxation time $\times 10^{-12}$ s	Free volume $\times 10^{-8}$ $m^3 mol^{-1}$	Internal Pressure $\times 10^{8}$ Nm^{-2}
X_1	X_2					
1.000	0.000	5.542	5.061	2.761	5.007	4.956
0.810	0.189	5.442	5.015	1.199	14.734	3.713
0.615	0.384	5.294	4.946	1.165	12.491	4.276
0.420	0.579	5.162	4.885	1.166	9.894	5.095
0.213	0.787	4.911	4.765	1.072	8.319	6.087
0.000	1.000	4.718	4.670	0.654	12.263	6.195

Mole fraction Vs Adiabatic compressibility

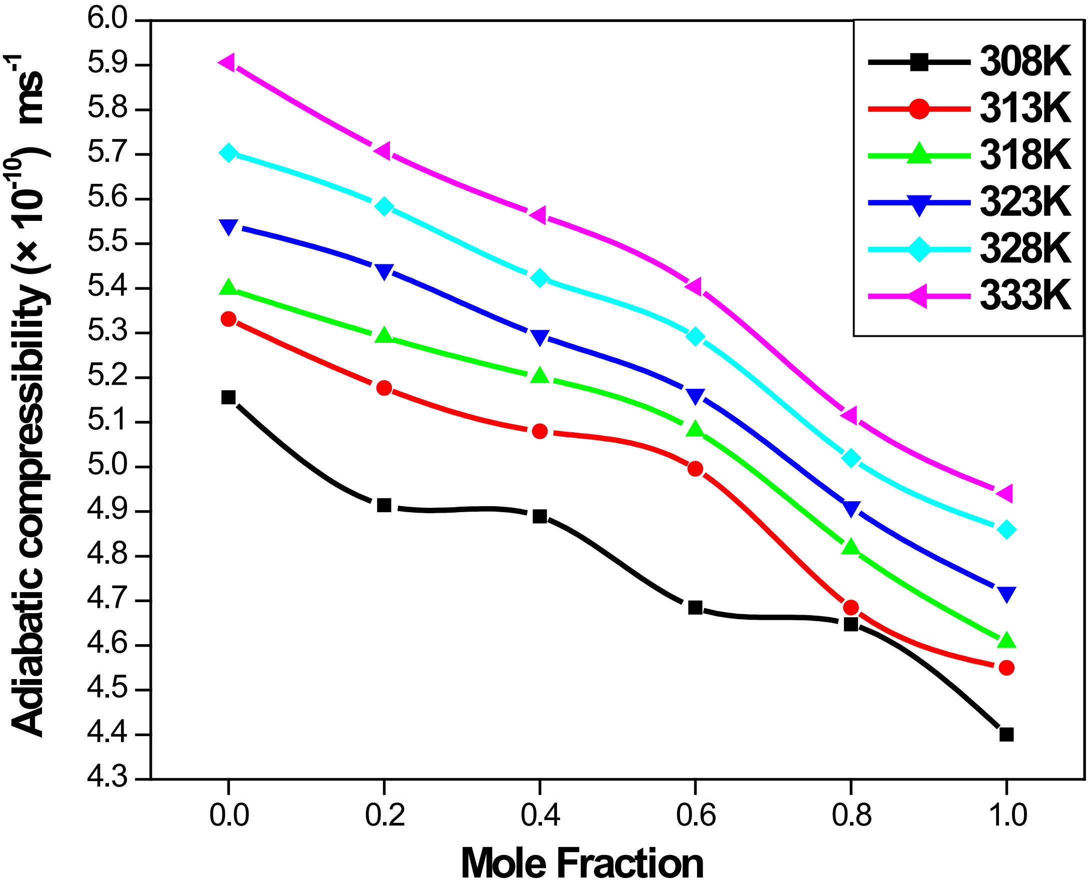


Table 4.9: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (ɳ) for Benzyl propionate + DMSO at 328K

Mole fraction		**Ultrasonic velocity (U) ms^{-1}**	**Density (ρ) 10^{-3} Kgm^{-3}**	**Viscosity(η) $10^{-3}Nsm^{-2}$**
X_1	**X_2**			
1.000	0.000	1304.8	1029.8	3.713
0.810	0.189	1318	1031	1.632
0.615	0.384	1330.8	1041.2	1.633
0.420	0.579	1341.2	1050.4	1.648
0.213	0.787	1370	1061.4	1.620
0.000	1.000	1385.6	1071.8	1.022

Table 4.10: Values of Adiabatic Compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free Volume (V_f) and Internal Pressure (π_i) for Benzyl propionate + DMSO at 328K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Free length $\times 10^{-11}$ m	Relaxation time $\times 10^{-12}$ s	Free volume $\times 10^{-8}$ $m^3\ mol^{-1}$	Internal Pressure $\times 10^{8}$ Nm^{-2}
X_1	X_2					
1.000	0.000	5.704	5.179	2.824	4.948	5.052
0.810	0.189	5.584	5.125	1.215	14.726	3.769
0.615	0.384	5.423	5.050	1.181	12.477	4.344
0.420	0.579	5.292	4.989	1.163	10.122	5.134
0.213	0.787	5.019	4.859	1.084	8.3106	6.184
0.000	1.000	4.859	4.781	0.662	12.304	6.284

Mole fraction Vs Free length

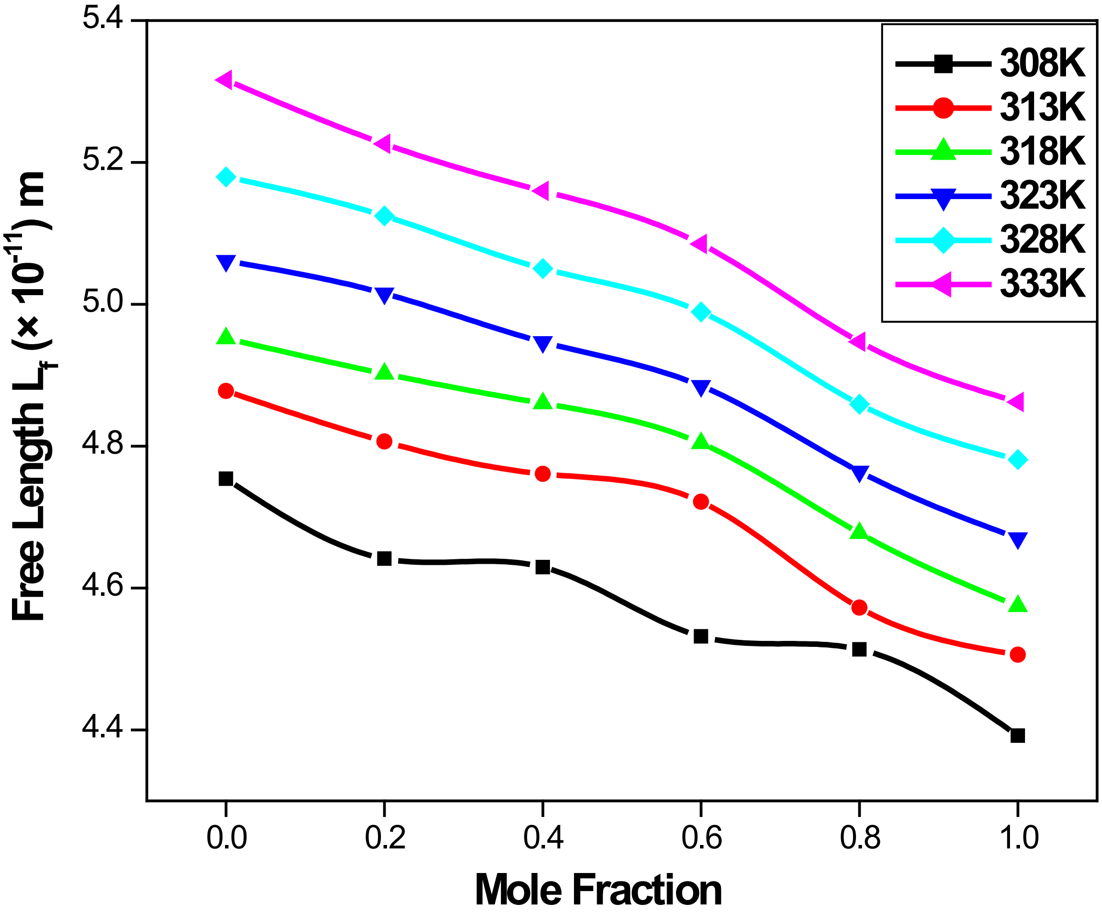


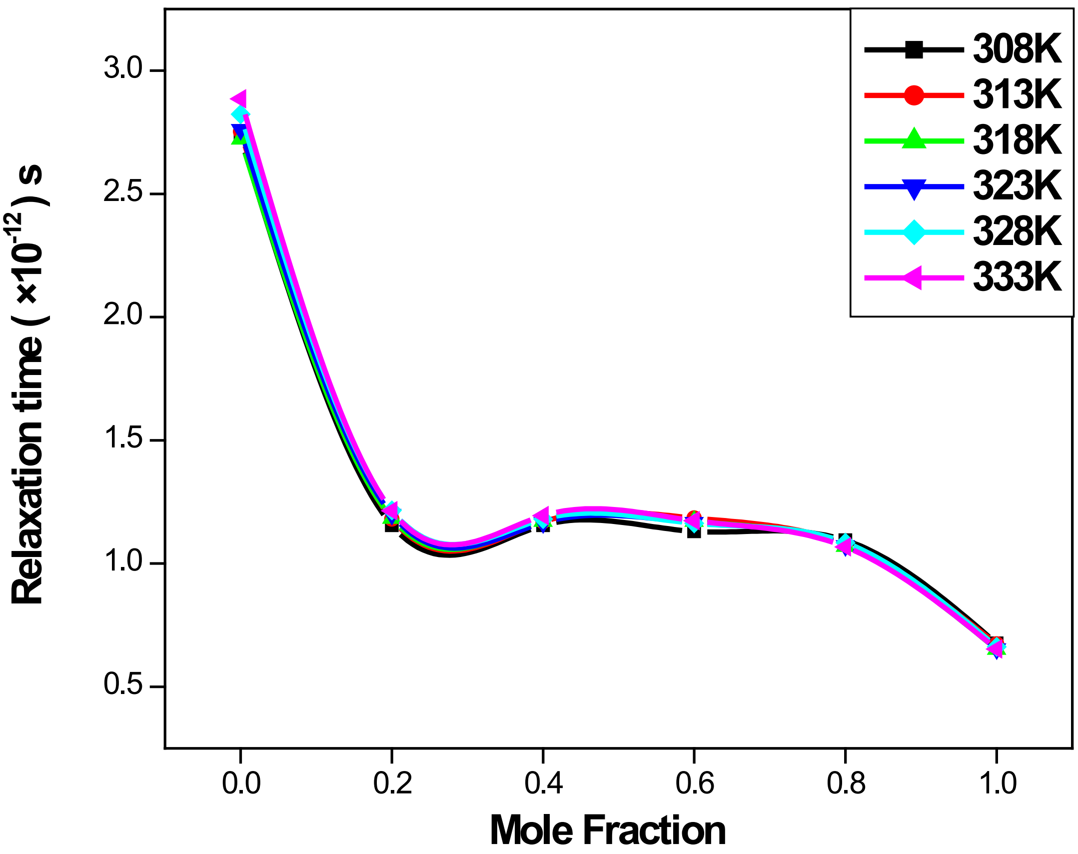
Table 4.11: Values of Ultrasonic velocity (U), Density (ρ) and Viscosity (η) for Benzyl propionate + DMSO at 333K

Mole fraction		Ultrasonic velocity (U) ms^{-1}	Density (ρ) 10^{-3} Kgm^{-3}	Viscosity(η) $10^{-3}Nsm^{-2}$
X_1	X_2			
1.000	0.000	1282.4	1029.6	3.664
0.810	0.189	1304	1030.4	1.595
0.615	0.384	1314	1041	1.610
0.420	0.579	1327.6	1050	1.629
0.213	0.787	1357.2	1061.4	1.564
0.000	1.000	1374.4	1071.6	0.992

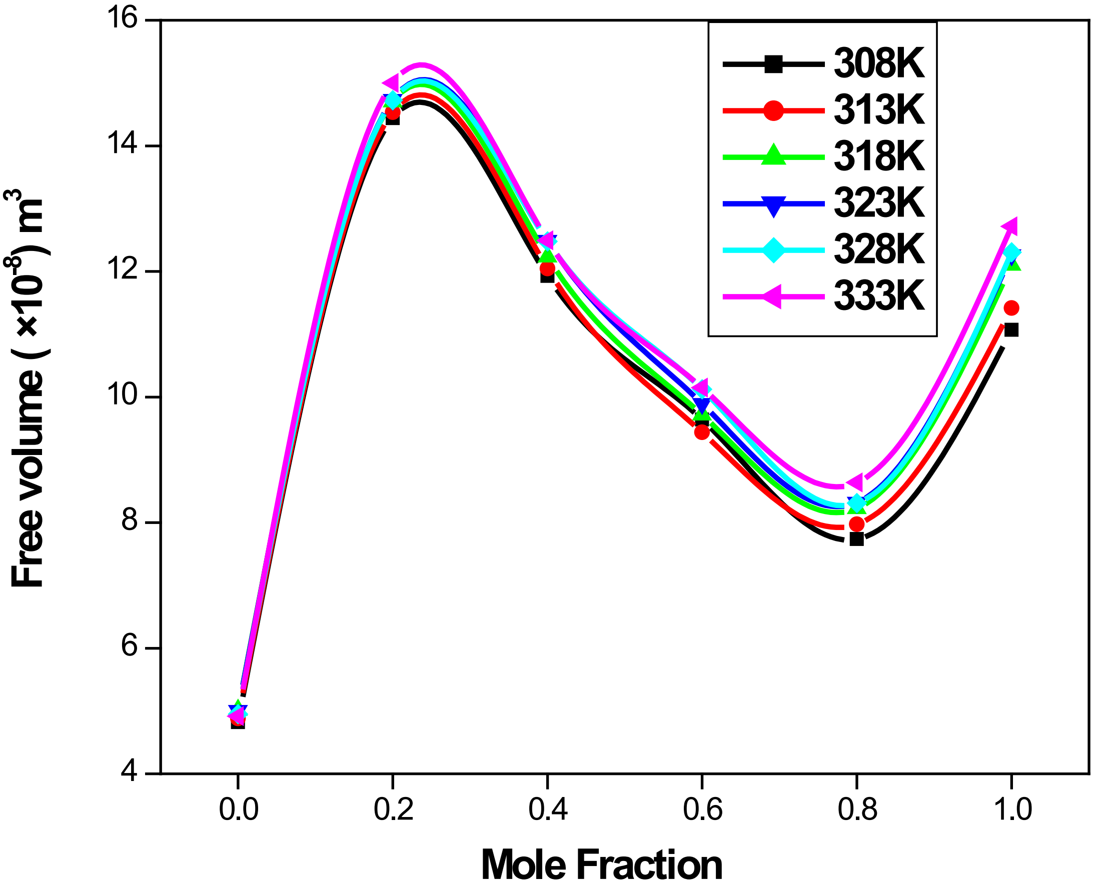
Table 4.12: Values of Table 4.6: Values of Adiabatic Compressability (β_{ad}), Free length (L_f), Relaxation time (τ), Free Volume (V_f) and Internal Pressure (π_i) for Benzyl propionate + DMSO at 333K

Mole fraction		Adiabatic compressibility ($\beta_{ad} \times 10^{-10}$) ms^{-1}	Free length $\times 10^{-11}$ m	Relaxation time $\times 10^{-12}$ s	Free volume $\times 10^{-8}$ $m^3 mol^{-1}$	Internal Pressure $\times 10^{8}$ Nm^{-2}
X_1	X_2					
1.000	0.000	5.905	5.316	2.885	4.918	5.138
0.810	0.189	5.707	5.225	1.214	15.001	3.802
0.615	0.384	5.564	5.159	1.195	12.496	4.407
0.420	0.579	5.404	5.085	1.174	10.15	5.206
0.213	0.787	5.115	4.947	1.067	8.637	6.198
0.000	1.000	4.940	4.862	0.654	12.717	6.309

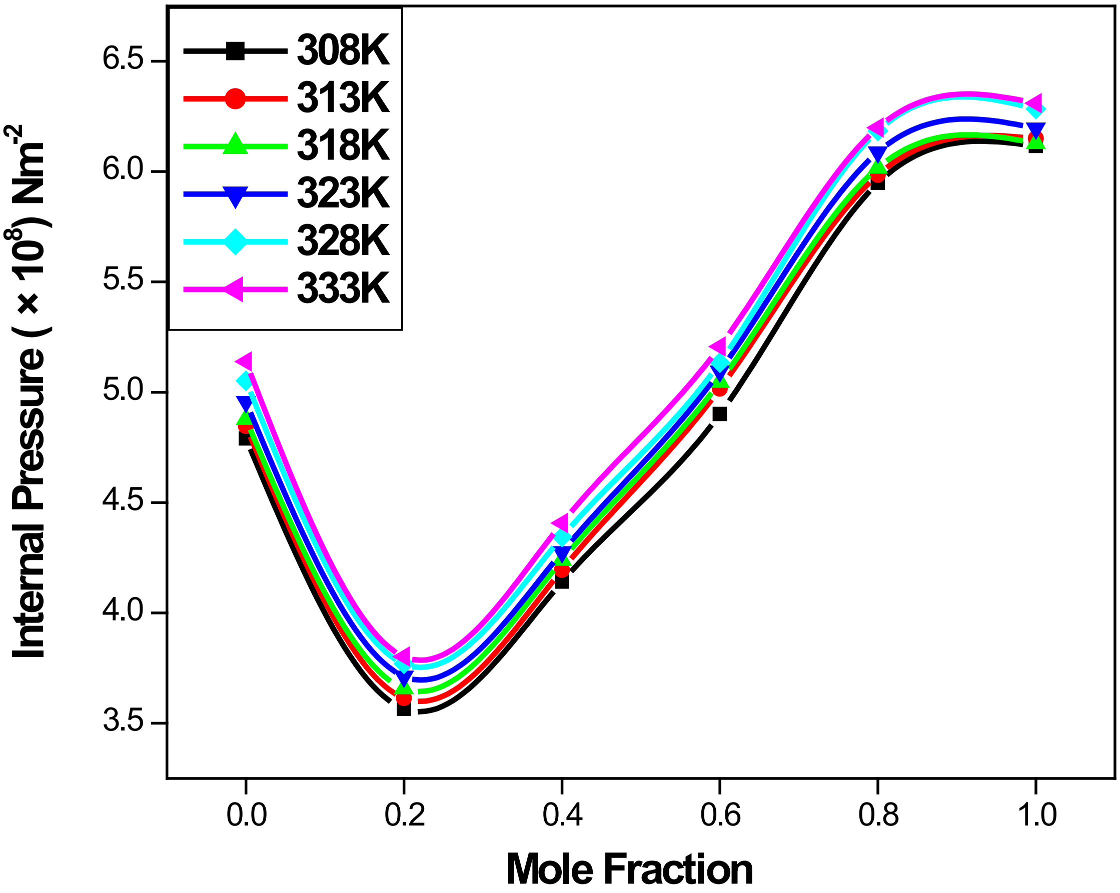
Mole fraction Vs Relaxation time



Mole fraction Vs Free volume



Mole fraction Vs Internal Pressure



CONCLUSION

Acoustic properties of Adiabatic compressability (β_{ad}), Free length (L_f), Relaxation time (τ) are determined which explain how these interactions occur and responsible for breaking and making of the structure in the solution. The trends in the variation of parameters derived from Ultrasonic velocity (U), Density (ρ), Viscosity (η) at different temperatures 308K, 313K, 318K, 323K, 328K and 333K over entire composition range suggest existence of molecules interaction in the chosen binary mixture.

REFERENCE:

1. Warren, B. E. (1937), J. Applied Physics, 8,645.
2. Compton, A. H. And Allison, S. K. ‘X-rays in Theory and Experiment’ (Newyork: D. Van Nostrand Co., Inc., 1935), pp. 781-782.
3. G. W. Stewart, Phys. Rev., 37, 9(1931); E. Amaladi, Phuysik. Z., 32, 914(1931); H. H. Meyer, Ann. Physek, 5,701(19z30); S. Katzoff, J. Chem. Phys; 2, 841(1934); J. D. Bernal and R. H. Fowler, ibid, 1,515(1933); J. Morgan and B. E. Warren, ibid; 6,666(1938).
4. A. Joffe, Ann. Physik, 72, 461 (1923); J. Frenkel, Z. Physik, 35,652 (1926).
5. Oster, G., and Kirkwood, J. G., J. Chem., Phys., II (1943), 175.
6. Smyth, C. P., and Stoops, W. N., J. Am. Chem. Soc., 51(1929), 3330.
7. Philippe, R., and Piette, A. M., Bull Soc. Chem., Belg., 64(1995), 600.
8. Malecli, J., J. Chem., Phys., 43(1965), 1351.
9. Bellamy, L. J., and Pace, R. J., Specitrochim Acta, 22(1966), 525.
10. Copurn, W. C., and Grunwald, E. J., Am. Chem. Soc., 81(1959),6145.
11. Brown, I. Fock, W., and Smit, F., Aust. J. Chem., 17(1964), 1106.
12. Haskell, R. W., Hollinger, H. B and Van Ness, H. C., J. Phys., Chem., 72(1968), 4534.
13. Bordewijk, P., “Fluid Structure and Dielectric behaviour of the mono alcohols”, Ph.D., thesis, University of Leiden, 1968.
14. Reddy, K. S., and Naidu, P. R., J. Chem. Thermodynamics(1976), 1208.
15. Prakash, S., Srivastau, S. B., and Prakash, O., Ind. J. Pure and Apopld. Phys., 13(1975), 19.
16. Ravindraa Prasad, K., Ravimahar, E. L., and Reddy, K. G. Acoust, Lett., 4(1981), 170.
17. Subba Rao, S., and Gobala Krishnan, R. Acoust, Lett., 2(1978), 69.
18. Gopal K. And Prabhakara Rao, N. Acoust Lett., 4(1981), 164.

19. Ramanjappa, T., and Raja Gopal, K., Proc. Latl. Sympoium on Acoustis(1986), 57.
20. Sabesan, R., Ramadurai, R and Rangan, R., J. Acoust. Soc. (India), 11(1983), 5.
21. Vradarajan, R., and Bharathi, G., J. Pure and Appl. Ultrasonics, 9(1987), 15.
22. Sabesan, R., Vradarajan, R., and Natarajan, M., Proc. Natl. Symposium on Acoustic, Tiruchy, 1987, 282.
23. P. Vigoureux, Ultrasonics, Chapman and Hall Ltd, London (1952).
24. T. Robert Beyer, V. Stephen Letcher, Physical ultrasonics Academic Press, New York (1969).
25. E. G. Richardoss, Ultrasonic Physics, Elseveir, London (1952).
26. N. V. Temperley and D. H. Trevena, Ellis Horwood Ltd, Liquids and other properties, John wiley and sons, England (1978).
27. A. B. Bhattia, Ultrasonic Absorption , Oxford (1967).
28. Chandra Bhan Singh, Avanesh Kumar and Soran Singh (2012).
29. Dash Ashok Kumar and Paikaray Rita (2014) ‘Study of Molecular Interaction in Binary mixture of Dimethyl Acetamide with Diethyl Ether using Ultrasonic and Viscosity probes’, Research Journal of Chemical Science vol. 4, No. 3, pp. 45-53.
30. Ubagaramary .D, Muthu Vijayan Enich, Mullainathan .S and Kesavaswamy (2018) ‘Acoustical properties of molecular interactions in 1-propanol, 1-butanol and 1-pentanol with tetrahydrofuran in cyclohexaone at various temperatures’, vol. 29, No. 17, pp. 3276-3281.
31. Nabaparna Chakraborty, Monika Rani and Juglan .K.C (2020) ‘Ultrasonic Investigation of Dichloromethane with Ethanolamine at various temperatures’, vol. 20, pp. 2825-2829.

32. Kolhe .R.K and Bhosale .B.B (2020) ‘Molecular Interaction study in Binary mixtures of DMSO and 1-octanol using ultrasonic method at various concentrations and temperatures’ vol. 11, No. 5, pp. 750-757.
33. Nabil M. Abdel Jabbar and Farouq S. Mjalli (2017) ‘Ultrasonic study of binary aqueous mixtures of three common eutectic solvents’, An International Journal of Physics and Chemistry of Liquids, pp. 1-18.
34. Singh K.P and Singh .S (2018) ‘Thermodynamic and acoustic properties of binary mixtures of PEGDME 250 with 1-propanol and 1-butanol at 293, 303 and 313 °K’, An International Journal of Physics and Chemistry of Liquids, pp. 1-21.
35. Mohabansi N.P, Satone A.K, Gulafsha A.I. Sheikh and Komal Vairagade (2020) ‘Excess Thermodynamic Parameters of 1-[2-(Dimethylamino)-1-(4-Methoxyphenyl)Ethyl] Cyclohexan-1-ol in aqueous Na_2SO_4’, International Journal of Researches in Biosciences, Agriculture and Technology, vol. 3, No. 8, pp. 26-34.
36. Dandwate S.R and Deshmukh S.B (2018) ‘Excess Thermodynamic properties of Binary liquid mixtures of DMSO with Methanol at different temperatures’, International Journal of Universal Print, vol. 4, No. 4, pp. 196-201.
37. Syed Ibrahim P.S, S. Chidambaravinayagam, J. Senthil Murugan and J. Edward Jeyakumar (2019) ‘Studies on some Acoustical and Thermodynamic properties of Ternary liquid mixtures of Meta Methoxy Phenol (MMP), 1-propanol and n-Hexane at different temperatures using ultrasonic techniques’, Journal of Information and Computational Science, vol. 9, No. 7, pp. 391-399.
38. V. Vanathi, S. Mullainathan, S. Nithiyanatham, V. Ramasamy and L. Palaniappan (2019) ‘Ultrasonic velocity, density, viscosity for the ternary mixture of (benzene+Chloroform+Cyclohexane) at different temperatures’, pp. 1-6.

39. Sudhir P. Dange and Omprakash P. Chimankar (2020) 'Molecular Interaction study in Binary mixture of Riboflavin with Methanol at 298K', vol. 7, No. 2, pp. 555-557.
40. Pallavi B. Nalle, R.G. Dorik and K.M. Jadhav (2019) 'Acoustical and excess parameter studies of piperine with $MgCl_2$', Journal of Pure and Applied Ultrasonics, vol. 41, No. 2, pp. 27-35.
41. T Karunakar, CH Srinivasu and K Narendra (2013) 'Thermo Acoustic and Infrared study of Molecular Interactions in Binary mixture Aniline+1-butanol', Journal of Pure and Applied Physics, vol. 1, No. 1, pp. 5-10.
42. R.C. Verma and Vinod Kumar Yadav (2014) 'The study of Excess molar volume and deviation in viscosity of binary mixtures of Ethyl Propionate in Butanol-1 and pentanol-1 at 308K ultrasonically', Journal of Chemical, Biological and Physical Sciences, vol. 4, No. 3, pp. 1988-1991.
43. L. Palaniappan and S. Nithiyanantham (2020) 'Molecular Interactions from the Experimental and Validation with Estimated Theoretical sound velocity', pp. 277-285.
44. SK. Md Nayeem, M. Kondaiah, K. Sreekanth and D. Krishna Rao (2015) 'Acoustic and volumetric investigatuins in aromatic, cyclic and aliphatic ketones with dimethyl sulphoxide at 308.15K', Arabian Journal of Chemistry, pp. 1-12.
45. Subhraraj Panda (2020) 'Ultrasonic study on dextran in aqueous media at 313K at different frequencies', Adalya Journal, vol. 9, No. 3, pp. 456-462.
46. R. Chithra Devi and R. Mathammal (2019) 'Thermodynamic Behaviour of Ternary mixtures of Acrylonitrile in Benzene with N-N-dimethyl aniline at 303K, 308K and 313K', vol. 8, No. 12, pp. 158-165.
47. Nikam PS and Hasan Mehdi 'Ultrasonic velocity and adiabatic compressability of Monochloric acetic acid in aqueous ethanol at various temperatures', Journal of Chemical and engineering Data. 1988; 88: 165-169.

48. Nikam PS and Hasan Mehdi 'Ultrasonic velocity and apparent molar compressability of trichloroacetic acid in aqueous ethanol', Asian Journal of Chemistry, 1993; 5(02): 319-321.
49. Venkateswarlu .P and Raman GK. 'Sound velocities and isentropic compressabilities of 1,2-dibromethane+Ketone at 303.15K', Journal of Pure and Applied ultrasonics, 1985; 7(02): 31-34.
50. Reddy Raveendranatha .K, Rama Murthy .S, Moorthy Rama .L 'Free volume and internal pressure study in aqueous solutions of methylene blue and auramine', The Journal of Acoustical society of India, 1991; 19(4): 22-25.
51. Kumar Naidu Vijaya .B, Rao Sadasiva .A and Rao Chowdoji 'Polyglycols in formamide solutions', Journal of Acoustical society of India, 2000; 28(1-4): 297-300.
52. Reddy Raveendranatha .K, Rama Murthy .S, Moorthy Rama .L 'Free volume and internal pressure study in aqueous solutions of methylene blue and auramine', The Journal of Acoustical society of India, 1991; 19(4): 22-25.
53. Niham P.S, Mole Interaction in binary mixture of bromobenzene with normal alkanols c_1-c_u,An ultrasonic study.
54. Bhatti Singh, Molecular association in some n-butanols systems.
55. Ashok Kumar Das, Studies of free volume, π_i, τ, H^E, α/fe in protic-aprotic binary mixture.

STRUCTURAL STUDIES OF ZnSe THIN FILMS SYNTHESIZED BY SILAR METHOD

A project report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI.

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI .

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

G.VENKATESWARI

Reg. No : 19SPPH11

Under the supervision and guidance of

Dr. A. NIRMALA SHIRLEY M.Sc., M.Phil.,Ph.D.

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS),THOOTHUKUDI.

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this project work entitled **"STRUCTURAL STUDIES OF ZnSe THIN FILMS SYNTHESIZED BY SILAR METHOD"** is submitted to **ST.MARYS'S COLLEGE (AUTONOMOUS), THOOTHUKUDI,** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year 2020 -2021 by

G.VENKATESWARI **Register No : 19SPPH11**

A. Nirmala Shirley

Signature of the Guide

Signature of the SSC Coordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Signature of the Examiner

DECLARATION

I hereby state that the project entitled, **“STRUCTURAL STUDIES OF ZnSe THIN FILMS SYNTHESIZED BY SILAR METHOD”** is submitted to **ST.MARY’S COLLEGE (AUTONOMOUS) THOOTHUKUDI,** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY TIRUNELVELI,** for the award of the Degree of Master of Science in physics is my unique work and no part of this project has been submitted for any Degree , Diploma or other similar titles.

Station : Thoothukudi **G.VENKATESWARI**

Date : **Signature of the student**

ACKNOWLEDGEMENT

First of all ,I owe my special gratitude to the Lord Almighty for blessing me with the successful completion of this project work.

I am deeply indebted to our Principal **Dr. Sr. A. S. J . LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D.,** for the encouragement she bestowed upon us.

I wish to express my sincere thanks to our Director of SSC, **Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D.,** for her support in my work.

I would like to express my special thanks of gratitude to **Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D.,** Head of Department, Department of Physics, for her inspirational words and encouragement to complete this project.

I assure my words of thanks to **Mrs. P. PADMAVATHI M.Sc., M.Phil., SET.,** SSC Co-ordinator ,Department of Physics for her efficient and encouragement in successful completion of this project.

I would like to express my sincere gratitude to my guide

Dr. A. NIRMALA SHIRLEY M.Sc., M.Phil., Ph.D., Assistant Professor, Department of Physics(SSC) for the continuous support, patience, motivation, and immense knowledge. Her enthusiastic guidance and support for completion of this project successfully.

I am grateful to my parents for their moral and emotional support to complete my work.

An endeavour over a long period can be successful only with the advice and supports of many well – wishers. I take this opportunity to express my gratitude and appreciations to all these people.

Finally, I am thankful and fortune enough to get support from my seniors, friends and my classmates who extended their help regarding my project.

CONTENTS

CHAPTER NO **PAGE NO**

CHAPTER I INTRODUCTION

1.4 MATERIALS

CHAPTER II

CHAPTER III

REFERENCES

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

LEDs – Light Emitting Diodes
ETA – Estimated Time of Arrival
DLC – Differential Leucocyte Count
SILAR – Successive Ionic Layer Adsorption and Reaction
AFM – Atomic Force Microscopy
PH – Potential of Hydrogen (or) Power of Hydrogen
XRD – X-ray Diffraction
HR-TEM – High Resolution Transmission Electron Microscopy
SAED – Selected Area Electron Diffraction
XPS – X-ray Photoelectron Spectroscopy
EIS – Electron Impedance Spectroscopy
PEC – Photo Electro Chemical
CIGS – Copper Indium Gallium Diselenide
SEM – Scanning Electron Microscopy
EDS – Energy Dispersive Spectroscopy
CBD – Chemical Bath Deposition
FTIR – Fourier Transform Infrared
PL – Photoluminescence
TFSCs – Thin Film Solar Cells
EPR – Extended Producer Responsibility
PKSC – Perovskite Solar Cell
ETL – Electron Transport Layer
PCE – Power Conversion Efficiency

UV – Ultra Violet

PCBD – Photo-assisted Chemical Bath Deposition

NPCBD – Non-Photo-assisted Chemical Bath Deposition

HH – Hydrazine hydrate

NR – Nano Rod

NRAs – Nano Rod Arrays

FTO – Fluorine-doped Tin Oxide

QDs – Quantum Dots

FE-SEM – Field Emission Scanning Electron Microscopy

NSs – Nano Sheets

NPs – Nano Particles

3D – Three Dimensional

MB – Methylene Blue

AF – Acid Fuchsine

QY – Quantum Yield

CVD – Chemical Vapour Deposition

TACVD – Thermally Activated Chemical Vapour Deposition

DC – Direct Current

PVD – Physical Vapour Deposition

MF – Molecular Formula

RF – Retention Factor

EDAX – Energy Dispersive X-ray Analysis

JCPDS – Joint Committee on Powder Diffraction Standards

SPM – Scanning Probe Microscopy

ASTM – American Society for Testing Materials

FWHM – Full Width at Half Maximum

CHAPTER -I

1.1 INTRODUCTION

A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness. The controlled synthesis of materials as thin films is a fundamental step in many applications. A familiar example is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently the metal layer is deposited using techniques such as sputtering. Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, Integrated passive devices, LEDs, optical coatings, hard coatings on cutting tools, and for both energy generation and storage. It is also being applied to pharmaceuticals, via thin-film drug delivery. A stack of thin films is called a multilayer. In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. Examples include multiferroic materials, and superlattices that allow the study of quantum phenomena.[1]

Over the past approximately two centuries, there has been significantly changing thin film deposition process. Indeed, Fraunhofer first observed generating of thin film layer over 195 years ago on the surface of glass . According to Wasa, Kitabatake and Adechi (2004), a thin film is a small-dimensional material on the substrate produced by intensifying, one-by-one, and ionic, molecular, atomic species of matter. The thickness of thin film is generally less than a number of microns. In fact, there is another type of film that is called thick film, which is known as a small-dimensional material formed by accumulating great grains, aggregates, clusters of ionic, molecular, atomic species or thinning a three-dimensional material. Factually, over the past 50 years, the thin films have been used for manufacturing optical coatings, electronic devices, decorative parts, and instrument hard coatings. The thin film is a conventional well-established material technology. In contrast, since the thin film technology is a main improvement of novel materials such as nanometre materials in the twenty-first century, it is still being developed on a daily basis (Wasa, Kitabatake and Adechi). [2]

1.2 DEPOSITION

Thin films are deposited by a wide variety of processes. However, the advantages of using thin films and deposition processes applications. Thin film is the general term used for coatings that are used to modify and increase the functionality of a bulk surface or substrate. Typical thicknesses range from 50 nm to 10 µm. They are used to protect surfaces from wear, improve lubricity, improve corrosion and chemical resistance, modify optical and electrical properties and provide a barrier to gas penetration. In many cases thin films do not affect the bulk properties of the substrate material. They can, however, totally change the optical, electrical transport, and thermal properties of a surface or substrate, in addition to providing an enhanced degree of surface protection. Thin film deposition technology and the science have progressed rapidly in the direction of engineered thin film coatings and surface engineering. Plasmas are used more extensively. Accordingly, advanced thin film deposition processes have been developed and new technologies have been adapted to conventional deposition processes. The market and applications for thin film coatings have also increased astronomically, particularly in the biomedical, display and energy fields.[3]

Thin films have distinct advantages over bulk materials. Because most processes used to deposit thin films are non equilibrium in nature, the composition of thin films is not constrained by metallurgical phase diagrams. Crystalline phase composition can also be varied to certain extent by deposition conditions and plasma enhancement. Virtually every property of the thin film depends on and can be modified by the deposition process and not all processes produce materials with the same properties. Microstructure, surface morphology, tribological, electrical, and optical properties of the thin film are all controlled by the deposition process. A single material can be used in several different applications and technologies, and the optimum properties for each application may depend on the deposition process used. Since not all deposit technologies yield the same properties or microstructures, the deposition process must be chosen to fit the required properties and application. For example, diamond-like carbon (DLC) films are used to reduce the coefficient of friction of a surface and improve wear resistance, but they are also used in infrared optical and electronic devices.[3]

1.3 AIM OF THIS PROJECT

- To prepare the ZnSe thin film by SILAR method.
- To analyse the structure of the ZnSe thin film by X-ray diffraction.
- To analyse the elastic properties of ZnSe thin film by AFM.

1.4 MATERIALS

1.4.1 ZINC CHLORIDE($ZnCl_2$)

Zinc chloride is a chemical compound with the formula $ZnCl_2$. There exist nine different crystalline forms of zinc chloride that are currently known. These hydrates of $ZnCl_2$ are either white in colour or colourless. All of them are highly soluble in water. Zinc chloride exhibits hygroscopic qualities, i.e. it attracts and captures the water molecules in its environment. The five known hydrates of zinc chloride have the general formula $ZnCl_2(H_2O)_n$ where the values of n can be 1, 1.5, 2.5, 3, and 4. Solid $ZnCl_2$ exhibits polymorphism and can take on one of the following crystal structures: tetragonal, monoclinic, and orthorhombic.[4]

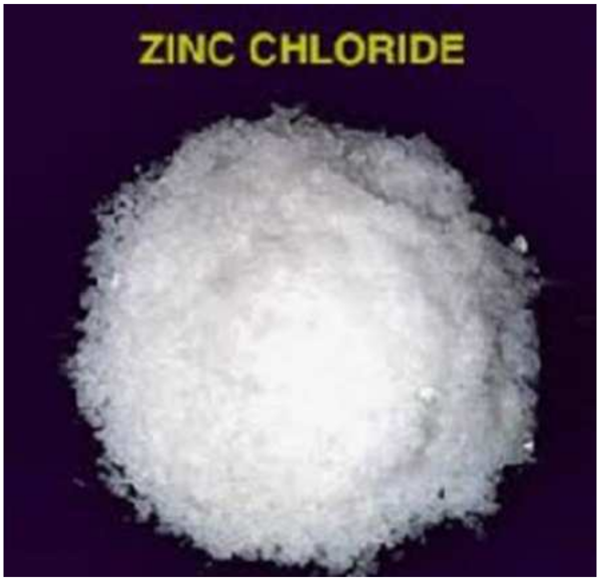


Fig 1.1 Zinc Chloride

1.4.1.1 STRUCTURE

Zinc chloride is an inorganic binary salt. A molecule of zinc chloride features ionic bonding between the zinc cation (Zn^{2+}) and the chloride anions (Cl^-). The structure of a $ZnCl_2$ molecule is illustrated below. It is important to note that the zinc-chlorine bond in $ZnCl_2$ possesses some covalent characteristics, which accounts for its low melting point and its solubility in ethereal solvents.[4]

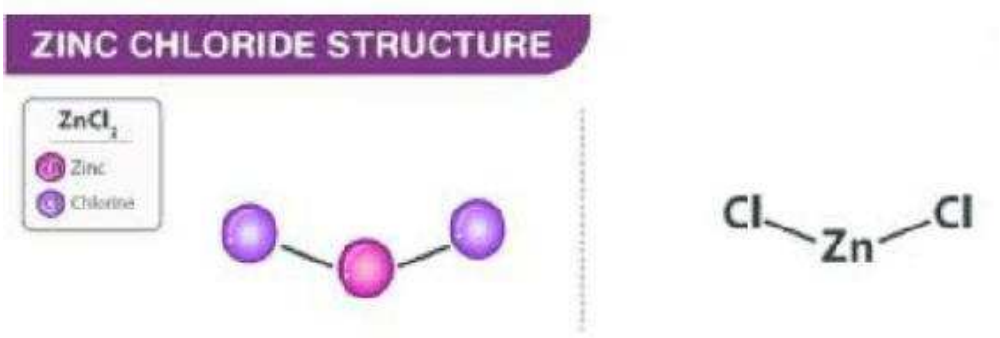


Fig 1.2 Structure of Zinc Chloride

1.4.1.2 PROPERTIES OF $ZnCl_2$

Chemical Data

Zinc Chloride	$ZnCl_2$
Molar Mass	136.315 grams per mole
Density	2.907 grams per cubic centimeter
Melting Point	563 K (290°C)
Boiling Point	1005 K (732°C)

Table 1.1 Properties of Zinc Chloride

1.4.1.3 Physical Properties

Zinc chloride is solid at room temperature and has a white crystalline appearance. It is odourless. The solubility of this compound in water corresponds to 432g/100g. It is also soluble in acetone, ethanol, and glycerol. The four polymorphs of $ZnCl_2$ feature a tetrahedral coordinate geometry between the Zn^{2+} ions and the Cl^{-} Molten zinc chloride is highly viscous and has a relatively low electrical conductivity value.[4]

1.4.1.4 Chemical Properties

When $ZnCl_2$ is dissolved in water, the resulting solution is acidic in nature. The pH of an aqueous solution of zinc chloride with a concentration of 6M is 1. This compound reacts with ammonia to form complexes. Examples include $Zn(NH_3)_4Cl_2$ and $ZnCl_2(NH_3)_2$. When heated, the hydrated form of zinc chloride loses water and small quantities of ZnCl(OH) are obtained.[4]

The chemical equation for this reaction is given by:

$$\mathbf{ZnCl_2.2H_2O \rightarrow ZnCl(OH) + H_2O + HCl}$$

1.4.1.5 USES OF $ZnCl_2$

Since it reacts with metal oxides to yield compounds with the general formula $MZnOCl_2$, zinc chloride is used as a flux/cleaning agent for soldering purposes. These fluxes have the ability to dissolve the layer of oxides on the surface of the metal. Some other uses of this compound are listed below. In its molten state, this compound acts as a catalyst for some aromatization reactions. For example, hexamethyl benzene can be obtained from methanol with the help of a molten $ZnCl_2$. Since it acts as a moderately strong Lewis acid, this compound can also serve as a catalyst for the Fischer indole synthesis reaction and some Friedel-Crafts acylation reactions. The

Lucas reagent is a solution of anhydrous zinc chloride and concentrated hydrochloric acid. This reagent is very useful in the preparation of alkyl chlorides. A mixture of zinc oxide and hexachloroethane is used in some smoke grenades. Upon ignition, these compounds react to form a smoke of zinc chloride, which serves as a smokescreen. $ZnCl_2$ is also useful in fingerprint detection since it forms an easily detectable complex with Ruhemann's purple. The aqueous solutions of this compound, when diluted, can be used for disinfecting purposes. It is a constituent of several antiseptic mouthwash products.[4]

1.4.2 SELENIUM DIOXIDE(SeO_2)

Solid SeO_2 is a one-dimensional polymer, the chain consisting of alternating selenium and oxygen atoms. Each Se atom is pyramidal and bears a terminal oxide group. The bridging Se-O bond lengths are 179 pm and the terminal Se-O distance is 162 pm. The relative stereochemistry at Se alternates along the polymer chain (syndiotactic).Selenium dioxide is the chemical compound with the formula SeO_2. This colorless solid is one of the most frequently encountered compounds of selenium.[5]

Fig 1.3 Selenium Dioxide

1.4.2.1 PROPERTIES

Solid SeO_2 is a one-dimensional polymer, the chain consisting of alternating selenium and oxygen atoms. Each Se atom is pyramidal and bears a terminal oxide group. The bridging Se-O bond lengths are 179 pm and the terminal Se-O distance is 162 pm.[3] The relative stereochemistry at Se alternates along the polymer chain. In the gas phase selenium dioxide is present as dimers and other oligomeric species, at higher temperatures it is monomeric.[4] The monomeric form adopts a bent structure very similar to that of sulfur dioxide with a bond length of 161 pm.[4] The dimeric form has been isolated in a low temperature argon matrix and vibrational spectra indicate that it has a centrosymmetric chair form.Dissolution of SeO_2 in selenium oxydichloride give the trimer $[Se(O)O]_3$. Monomeric SeO_2 is a polar molecule, with the dipole moment of 2.62 D pointed from the midpoint of the two oxygen atoms to the selenium atom. The solid sublimes readily. At very low concentrations the vapour has a revolting odour, resembling decayed horseradishes. At higher concentrations the vapour has an odour resembling horseradish sauce and can burn the nose and throat on inhalation. Whereas SO_2 tends to be molecular and SeO_2 is a one-dimensional chain, TeO2 is a cross-linked polymer. SeO_2 is considered an acidic oxide: it dissolves in water to form selenous acid.[4]

Often the terms selenous acid and *selenium dioxide* are used interchangeably. It reacts with base to form selenite salts containing the $SeO^{2-}{}_3$ anion. For example, reaction with sodium hydroxide produces sodium selenite:

$$\mathbf{SeO_2 + 2\ NaOH \rightarrow Na_2SeO_3 + H_2O}$$

1.4.2.2 USES

ORGANIC SYNTHESIS

SeO_2 is an important reagent in organic synthesis. Oxidation of paraldehyde with SeO_2 gives glyoxal and the oxidation of cyclohexanone gives cyclohexane-1,2-dione. The selenium starting material is reduced to selenium, and precipitates as a red amorphous solid which can easily be filtered off.[8] This type of reaction is called a Riley oxidation. It is also renowned as a reagent for "allylic" oxidation, a reaction that entails the following conversion.

This can be described more generally as;

$$\mathbf{R_2C{=}CR'\text{-}CHR''_2 + [O] \rightarrow R_2C{=}CR'\text{-}C(OH)R''_2}$$

where R, R', R" may be alkyl or aryl substituents. [5]

AS A COLORANT

Selenium dioxide imparts a red colour to glass. It is used in small quantities to counteract the colour due to iron impurities and so to create colourless glass. In larger quantities, it gives a deep ruby red colour. Selenium dioxide is the active ingredient in some cold-bluing solutions. It was also used as a toner in photographic developing. [5]

SAFETY

Selenium is an essential element, but ingestion of more than 5 mg/day leads to nonspecific symptoms.[5]

1.4.3 ZINC SELENIDE(ZnSe)

ZnSe can be made in both hexagonal (wurtzite) and cubic (zincblende) crystal structure. It is a wide-bandgap semiconductor of the II-VI semiconductor group. The material can be doped n-type doping with, for instance, halogen elements. Zinc selenide (ZnSe) is a light-yellow, solid compound comprising zinc (Zn) and selenium (Se). It is an intrinsic semiconductor with a band gap of about 2.70 eV at 25 °C (77 °F). ZnSe rarely occurs in nature, and is found in the mineral that was named after Hans Stille called "stilleite." [6]

Fig 1.4 Zinc Selenide

1.4.3.1 PROPERTIES

ZnSe can be made in both hexagonal (wurtzite) and cubic (zincblende) crystal structure. It is a wide-bandgap semiconductor of the II-VI semiconductor group. The material can be doped n-type doping with, for instance, halogen elements. P-type doping is more difficult, but can be achieved by introducing gallium.[6]

1.4.3.2 APPLICATIONS

ZnSe is used to form II-VI light-emitting diodes and diode lasers. It emits blue light. ZnSe doped with chromium (ZnSe:Cr) has been used as an infrared laser gain medium emitting at about 2.4 µm. It is used as an infrared optical material with a remarkably wide transmission wavelength range (0.45 µm to 21.5 µm). The refractive index is about 2.67 at 550 nm (green), and about 2.40 at 10.6 µm (LWIR). Similar to zinc sulfide, ZnSe is produced as microcrystalline sheets by synthesis from hydrogen selenide gas and zinc vapour. Another method of producing is a growth from melt under excessive pressure of inert gas (Ar usually). When free of absorption and inclusions it is ideally suited for CO2 laser optics at 10.6 µm wavelength. It is thus a very important IR material. In daily life, it can be found as the entrance optic in the new range of "in-ear" clinical thermometers, seen as a small yellow window. Zinc selenide can slowly react with atmospheric moisture if poorly polished, but this is not generally a serious problem. Except where optics are used in spectroscopy or at the Brewster angle, antireflection or beamsplitting optical coatings are generally employed. ZnSe activated with tellurium (ZnSe(Te)) is a scintillator with emission peak at 640 nm, suitable for matching with photodiodes. It is used in x-ray and gamma ray detectors. ZnSe scintillators are significantly different from the ZnS ones.[6]

CHAPTER – II

2.1 LITERATURE SURVEY

B.Güzeldir et.al said that the Successive Ionic Layer Adsorption and Reaction (SILAR) method has been used to deposit ZnSe thin film onto Si substrate to obtain the *Zn/ZnSe/n-Si/Au–Sb* sandwich structure. The X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) methods are used to investigate the structural and morphological properties of films. The XRD and SEM studies reveal that the films are covered well on Si substrate and have good polycrystalline structure and crystalline levels. The current–voltage (*I–V*) and capacitance–voltage (*C–V*) characteristics of this structure have been investigated as a function of the temperature (80–300 K) with 20 K steps. The ideality factor (*n*) and zero-bias barrier height (Φ_{b0}) value which obtained from *I–V* curves were found to be strongly temperature dependent. While Φ_{b0} increases with increasing temperature, *n* decreases. This behavior of the Φ_{b0} and *n* can be attributed to barrier inhomogeneities at the metal–semiconductor (*M–S*) interface. The temperature dependence of the *I–V* characteristics of the *Zn/ZnSe/n-Si/Au–Sb* structure can reveal the existence of a double Gaussian distribution. The mean barrier height and the Richardson constant values are obtained as 0.925 eV and 1.140 eV, 130 A/cm^2 K^2 and 127 A/cm^2 K^2, from the modified Richardson plot, respectively. Furthermore, the barrier height and carrier concentration are calculated from reverse bias C^{-2}–V measurements at 200 kHz frequency as a function of the temperature.[7]

Satish S.Patil et.al said that the facile hydrothermal route was directly employed to synthesize photoactive copper doped zinc selenide ($Zn_{1-x}Cu_{2x}Se$) thin films as function of copper ion concentration. The effect of Cu ion concentration on optical, morphological, structural, compositional and photoelectrochemical properties of $Zn_{1-x}Cu_{2x}Se$ thin films have been Investigated. Optical absorption elucidations revealed that, $Zn_{1-x}Cu_{2x}Se$ thin films shows direct allowed type of electronic transition with decrease in band gap energy from 2.45 eV to 2.09 eV with varying in Cu ion concentration respectively. A structural study of films confirms the generation of cubic zinc blende crystal structure with crystallite size in the range of 82 nm–58 nm. Decrease in defect level of synthesized material was explored by photoluminescence spectra. Alteration in surface morphology was observed from nanosphere to well grown nanoflakes. High resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) study reveals that formation of nanocrystalline $Zn_{1-x}Cu_{2x}Se$ thin film. X-ray photoelectron spectroscopy (XPS) analysis confirms the existence of Cu^{+}, Zn^{2+} and Se^{2-} elements in deposited $Zn_{1-x}Cu_{2x}Se$ thin film. The detailed electron impedance spectroscopy (EIS) studies were carried out and it is well support to the photoelectrochemical (PEC) performance of $Zn_{1-x}Cu_{2x}Se$ photoanode. From J-V measurements, Cu rich film photoanode shows better PEC performance with best photoconversion efficiency (η) 1.65% for sample CZS_5.[8]

DeryaBatibay et.al said that the thin film solar cells are an exciting topic for low cost and high efficient solar cells. Owing to the high price of the indium metal in the fabrication of copper indium gallium diselenide (CIGS) solar cells, $Cu_2ZnSn(SSe)_4$ thin films are used as a new material to reduce the cost and increase the efficiency. As an alternative absorber material for solar cell production, $Cu_2ZnTi(S{:}Se)_4$ thin films were deposited by the co-sputtering method at various temperatures. During the deposition, Cu, ZnSe and Ti targets were used as metal sources. The $Cu_2ZnTi(S{:}Se)_4$ thin films were annealed in $H_2S{:}Ar$ (1:9) atmosphere. The morphological, structural and optical properties of $Cu_2ZnTi(S:Se)_4$ thin films was analyzed using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) Raman spectroscopy and UV–Vis–NIR spectrometer. It was seen that the thin films had good optical absorption till the infrared region and the band gap of the $Cu_2ZnTi(S:Se)_4$ thin films were smaller than the conventional Cu_2ZnSnS_4 thin films. Furthermore, fabrication of a solar cell with 1.96% power conversion efficiency was reported using a $Cu_2ZnTi(S:Se)_4$ thin film as a low cost absorber layer.[9]

R.Khalfi et.al said that the Undoped ZnSe thin films were prepared using Chemical bath deposition method (CBD). All samples were deposited on glass substrates in acidic solution at 80 °C for 60, 120, 180 and 240 min. The effect of deposition time on the structural and optical properties of ZnSe thin layers were investigated by X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, atomic force microscopy (AFM), UV–Vis and photoluminescence (PL) spectroscopies. XRD patterns of the deposited thin films exhibited cubic structure with a preferred (111) orientation. The crystal quality and the average crystallite size were found to increase at higher durations of deposition. FTIR spectrum confirmed the presence of ZnSe vibration band. AFM analysis revealed that both of morphology and surface roughness were affected by time of deposition. According to UV–Vis results, all samples were transparent with average visible transmission values ranging from 55% to 72%. The optical band gap was found to decrease with increasing deposition time. The room temperature PL spectra indicated the presence of three emissions at 460, 575 and 630 nm.[10]

H H Hegazy et.al said that In this work, polycrystalline CuZnSn(S,Se)4 thin films were deposited on soda lime glass by a facile thermal evaporation method using a single source. The temperature dependence of electrical conductivity in the dark σD and under illumination σph has been evaluated over 290 K–425 K. The synthesized thin films exhibit a p-type semiconductor, regardless of the zinc ratio. The electrical conductivities for all compositions increase with increasing temperature indicating semiconducting behaviour of the material, and were explained by the thermionic emission model over grain boundary barriers. The grain boundary barrier energy decreases on exposure to light and was found to vary with Zn concentration. The photoconductivity increases with light intensity and the calculations reveal that the recombination process is bimolecular in nature. The persistent photoconductivity was measured and the decay process exhibited non-exponential behaviour, and then the concept of a differential lifetime was used. The temperature dependence of the differential lifetime was studied for all films. Understanding of the current results is quite important for polycrystalline solar cell thin films.[11]

Sinan Temel et.al said that In this study, zinc oxide, zinc sulfide and zinc selenide semiconductor thin films were produced by Chemical Bath Deposition technique with and without annealing. The structural, surface and optical properties of the obtained thin films were determined to specify effect of annealing on thin film properties. Characterization results indicated that, the produced zinc-based thin films have polycrystalline nature. Both zinc sulphide and zinc selenide thin films have cubic and zinc oxide thin films have hexagonal structure. The surface morphologies of all thin films are homogeneous and compact. The optical band gap values of the obtained thin films are close to the band gap of zinc-based semiconductors. The annealing processes neither improved the crystal structures nor altered the band gap values of zinc-based thin films. Agreeable to characterization results, production of zinc-based thin films via chemical bath deposition technique without annealing is facile, economic and energy efficient so can be used for many thin film applications.[12]

Mahesh P.Suryawanshi et.al said that A facile improved successive ionic-layer adsorption and reaction (SILAR) sequence is described for the fabrication of Cu2ZnSn(S,Se)4 (CZTSSe) thin-film solar cells (TFSCs) via the selenization of a precursor film. The precursor films were fabricated using a modified SILAR sequence to overcome compositional inhomogeneity due to different adsorptivities of the cations (Cu+, Sn4+, and Zn2+) in a single cationic bath. Rapid thermal annealing of the precursor films under S and Se vapor atmospheres led to the formation of carbon-free Cu2ZnSnS4 (CZTS) and CZTSSe absorber layers, respectively, with single large-grained layers. The best devices based on CZTS and CZTSSe absorber layers showed total area (~0.30 cm2) power conversion efficiencies (PCEs) of 1.96 and 3.74%, respectively, which are notably the first-demonstrated efficiencies using a modified SILAR sequence. Detailed diode analyses of these solar cells revealed that a high shunt conductance (Gsh), reverse saturation current density (Jo), and ideality factor (nd) significantly affected the PCE, open-circuit voltage (Voc), and fill factor (FF), whereas the short-circuit current density (Jsc) was dominated by the series resistance (Rs) and Gsh. However, the diode analyses combined with the compositional and interface microstructural analyses shed light on further improvements to the device efficiency. The facile layer-by-layer growth of the kesterite CZTS-based thin films in aqueous solution provides a great promise as an environmentally benign pathway to fabricate a variety of multielement-component compounds with high compositional homogeneities.[13]

Tingting Yao et.al said that the transition-metal doping in semiconductors is an important way to modulate their intrinsic properties or bring out new functionalities for applications. Here, elongated Mn-doped $ZnSe_{1-x}S_x$ nanocrystals are synthesized through a facile one-pot reaction under mild conditions. These $ZnSe_{1-x}S_x$ nanocrystals with a diameter of 2–4 nm have a cubic phase structure. EPR and PL spectra confirm the successful doping of Mn^{2+} into the $ZnSe_{1-x}S_x$ nanocrystals, based on the corresponding hyperfine splitting constants and emission bands. The temporal evolution of UV-vis absorption and PL spectra indicates the growth-doping mechanism for the formation of the doped nanocrystals. Surface coating of these nanocrystals with a shell increases the quantum yield up to 35%. And the dual-function role of 1-dodecanethiol is confirmed in the formation of the elongated Mn-doped $ZnSe_{1-x}S_x$ nanocrystals.[14]

Chaitali S. Bagade et.al said that the present work, we have synthesized nanocrystalline (CdZn)Se thin films by a simple and cost effective arrested precipitation technique. Systematic characterization of optostructural, morphological, compositional and photoelectrochemical property has been carried out. The optical band gap was evaluated from optical absorption spectra by using UV–Vis–NIR spectrophotometer. Estimated optical band gap lies in the range of 1.90–2.07 eV. X-ray diffraction pattern reveals that the deposited thin films were nanocrystalline in nature and exhibit cubic crystal structure. The dependency of microstructural parameters such as crystallite size, microstrain and dislocation density has been studied. Scanning electron microscopy images demonstrates that surface morphology can be improved with respect to deposition time. X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy confirmed that composition and stoichiometry of (CdZn)Se thin films. A maximum photo conversion efficiency 0.73 % was achieved in the (CdZn)Se cauliflower thin film based solar cell.[15]

Yu-PinLin et.al said that the work demonstrates the preparation of $Cu_2ZnSn(S_xSe_{1-x})_4$(CZTSSe) thin films by sputtering deposition using single-phase Cu_2ZnSnS_4 (CZTS) target followed by selenization/sulfurization treatment at 570 °C for 1 h. Afterward, the CZTSSe thin-film solar cell samples with the Mo/CZTSSe/CdS/*i*-ZnO/IZO/Al structure were prepared and their performances were evaluated. By varying the ratio of Se and S powders of heat treatment, the Cu-poor/Zn-rich CZTSSe layers with S/(S+Se) ratio in the range of 0.21–1 were achieved and the CZTSSe layers were the mixture of kesterite CZTS and CZTSe phases as revealed by the *x*-ray diffraction and the Raman spectroscopy analyses. UV-NIR spectroscopy indicated the bandgaps of CZTSSe samples are in the range of 1.06–1.45 eV when the S/(S+Se) ratio varies from 0.21 to 1. Hall measurement observed the best transport property with *p*-type carrier concentration of 2.17×10^{15} cm^{-3} and mobility of 8.9 cm^2 V^{-1} sec^{-1} in CZTSSe layer with S/(S+Se) ratio of 0.46. Under the AM1.5 illumination condition, the CZTSSe thin-film solar cell sample with S/(S+Se) ratio of 0.46 exhibited the best performance with open-circuit voltage of 0.506 V, short-circuit current density of 27.41 mA/cm^2, fill factor of 50% and conversion efficiency of 6.9%.[16]

Xin Li et.al said that For a typical perovskite solar cell (PKSC), the electron transport layer (ETL) has a great effect on device performance and stability. Herein, we manifest that low-temperature solution-processed ZnSe can be used as a potential ETL for PKSCs. Our optimized device with ZnSe ETL has achieved a high power conversion efficiency (PCE) of 17.78% with negligible hysteresis, compared with the TiO2 based cell (13.76%). This enhanced photovoltaic performance is attributed to the suitable band alignment, high electron mobility, and reduced charge accumulation at the interface of ETL/perovskite. Encouraging results were obtained when the thin layer of ZnSe cooperated with TiO2. It shows that the device based on the TiO2/ZnSe ETL with cascade conduction band level can effectively reduce the interfacial charge recombination and promote carrier transfer with the champion PCE of 18.57%. In addition, the ZnSe-based device exhibits a better photostability than the control device due to the greater ultraviolet (UV) light harvesting of the ZnSe layer, which can efficiently prevent the perovskite film from intense UV-light exposure to avoid associated degradation. Consequently, our results present that a promising ETL can be a potential candidate of the n-type ETL for commercialization of efficient and photostable PKSCs.[17]

D.D.Hile et.al said that the Photo-assisted chemical bath deposition (PCBD) and non-photo-assisted chemical bath deposition (NPCBD) methods were used to deposit ZnSe thin films on non-conducting glass substrates in an alkaline medium. Zinc acetate and sodium selenosulfatewere the starting precursors. Hydrazine hydrate (HH) was used as ligand for the deposition. Different HH volumes between 5 and 35 mL were used. The films were annealed at 300 °C for 2 h. The Glancing incidence X-ray diffraction results revealed hexagonal wurtzite structure. The estimated crystallites sizes were in the range of 4–14 nm and 6–19 nm for the NPCBD and PCBD, respectively. Changes in the films morphology were observed in both of the deposition methods. Energy dispersive X-ray analysis confirmed the presence of the Zn and Se. Raman spectroscopy also confirmed peaks of ZnSe.The bandgaps of the films were ranged from 1.5 - 2.8 eV in NPCBD and 2.3–2.6 eV in PCBD. Photoluminescence spectroscopy measurements revealed green-red emission which did not show significant changes with deposition method.[18]

QiZhang et.al said that As an important II–VI semiconductor, ZnSe is one of the first semiconductors discovered and is probably one of the most important electronic and optoelectronic materials with prominent applications in nonlinear optical devices, flat panel displays, light emitting diodes, lasers, logic gates, transistors, etc. In this article, we will provide a comprehensive review of the state-of-the-art research activities that focus on the rational synthesis, novel properties and unique applications of ZnSe nanostructures. We begin with a historical background of ZnSe, description of its structure, chemical and electronic properties, and its unique advantages in specific potential applications. This is followed by a survey of ZnSe nanostructures with various morphologies and their corresponding synthesis methods. Using various facile methods or techniques, nanoparticles, nanowires, nanobelts/nanoribbons, nanosheets, nanotubes, core/shell nanostructures, hierarchical nanostructures and of heterostructures ZnSe have been synthesized under specific growth conditions so far. Then, we discuss the critical experiments determining the optical and electrical properties of the nanostructures, as crucially they changes with synthetic conditions. Next, we highlight the recent achievements regarding to the potential applications of ZnSe nanostructures in light emitting diodes (LEDs), lasers, field emitters, photodetectors, sensors, photocatalysis, solar cells, vivo imaging, and so on. Finally, we conclude this review with some perspectives and outlook on the future developments in this area. Overall, this comprehensive review presents a systematic investigation on the controlled synthesis, novel properties and advanced applications of ZnSe nanostructures.[19]

Nader Ghobadi et.al said that We investigate the deposition temperature, pH and deposition time that govern evolution of the nanoparticle shape, size and density of ZnSe nanoparticle arrays. The nanoparticle arrays were grown on glass substrate using a facile chemical bath deposition method. The samples were also characterized by absorbance spectra for energy band gap determination and scanning electron microscopy. In comparison to other similar works, our method is simple, low cost and can be easily controlled. We find that temperature helps to tailoring the nanoparticle shape and has a critical role in comparison with other parameters such as pH and deposition time.[20]

M. Kamruzzaman said that the ZnO nanorod (NR) based inorganic quantum dot sensitized solar cells have gained tremendous attention for use in next generation solar cells. ZnO/ZnSe-core/shell NR arrays (NRAs) with various densities were grown on an Au@ZnO seed layer (Au = 0.0, 4.0, 8.0 and 16.0 nm) on glass supported fluorine-doped tin oxide (FTO) substrates using low cost hydrothermal and ion-exchange approaches. PbS quantum dots (QDs) were loaded into the ZnO/ZnSe core/shell NRAs *via* a successive ionic layer adsorption and reaction (SILAR) method. The morphology, structural and optical properties of the core/shell NRAs were investigated using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-vis spectroscopy measurements. It was observed that the density of the ZnO/ZnSe NRAs decreases with increasing Au buffer layer thickness. The absorption decreases along with a decrease in the ZnO/ZnSe NRA density. The ZnO NRs/PbS QD photoelectrode performs poorly; however, after introducing a ZnSe shell on the core-ZnO, the solar cells parameters changed according to the

ZnO/ZnSe NRA density. Values of η = ~0.88%, J_{SC} = 14.60 mA cm^{-2}, and V_{OC} = 190 mV, and η = ~0.25%, J_{SC} = 6.77 mA cm^{-2}, and V_{OC} = 115 mV were obtained for the highest and lowest NRA densities, respectively. Although the photovoltaic performance of these photoelectrodes is still inferior, further improvement of the device would be possible by suppressing surface defects, and through quality optimization of the ZnO/ZnSe NRAs, PbS QDs, counter electrode and electrolyte.[21]

XiaoyanLiu et.al said that the ZnO nanorods/ZnSe nanosheets heterostructure had been successfully fabricated by the spin coating method. The evolution of the structural, optical and photocatalytic properties of the samples with different spin coating times was comprehensively investigated. The X-ray diffraction (XRD) patterns showed that the relative intensities of ZnSe peaks increased gradually with the increase of spin coating times, but the ZnO peaks were relatively suppressed, which had a good agreement with the results of Raman spectra. The scanning electron microscope (SEM) and transmission electron micrograph (TEM) images further confirmed that the ZnSe nanosheets (NSs) had been successfully assembled on the top surfaces of the ZnO nanorods (NRs) and in the upper parts of the gaps between the rods. At room temperature, the ZnO/ZnSe heterostructures exhibited a relatively suppressed UV emission together with a dramatically enhanced deep-level emission. In addition, the heterostructures exhibited remarkable photocatalytic activities. The type-II staggered band alignment and defects formed at the ZnO/ZnSe interfaces should be the key factors for improved photocatalytic performance, and the probable photocatalytic mechanism was discussed in detail.[22]

Yi-Hsin Chen et.al said that the P-type micron size silicon wire (SiW) arrays coated with ZnSe nanoparticles (NPs) exhibiting enhanced photodetection and photocatalytic performances were synthesized. The SiWs were grown by combining catalytic etching with nanosphere lithography methods. ZnSe NPs were coated on SiWs with a chemical bath deposition (CBD) method. The high photodetection performance of three-dimensional (3D) heterostructured ZnSe NP/SiW arrays with immediate decay (>99.85%), on/off ratio ($>7 \times 10^2$) and photoresponse speed (<0.4 s) was recorded under a small applied voltage (80 µV). The immediate decay and on/off ratio increase with decreasing applied voltage and the photocurrent variations of ZnSe NPs/SiWs were larger than 0.3 µA at 1 V. The enhanced UV photocurrent response is attributed to a large surface-to-volume ratio and the presence of the fast conductive pathway of ZnSe NP/SiW shell/core heterostructures. ZnSe NPs/SiWs also showed superb photocatalytic properties with methylene blue (MB) and acid fuchsin (AF) as reagents. The photodegradation data exhibited high activities of 88% and 83% after 120 and 110 min, respectively. The CBD of ZnSe NPs on SiWs provides a facile route for the fabrication of well aligned 3D heterostructured ZnSe NP/SiW arrays with a high on/off ratio photocurrent and photocatalytic activity.[23]

M Kamruzzaman et.al said that the capture of solar energy has gained the attention for the next generation solar cell. ZnO/ZnSe NW arrays were synthesized on an FTO glass substrate using a simple and facile hydrothermal and ion-exchange approaches. The lead sulfide (PbS) QDs was infiltrated into ZnO/ZnSe NWs via SILAR method for making inorganic quantum dot sensitized

ZnO/ZnSe/PbS QDs solar cell. The surface morphology, structural, optical, and J-V characteristics have been investigated. The ZnO/ZnSe NW is a core–shell like structure, and the absorption edge shifted from the UV region (ZnO NWs) to the near infrared region for ZnO/ZnSe NWs/PbS QDs. For PbS QDs-sensitized solar cell, the obtained value of $\eta = 1.1\%$, $J_{sc} = 20.60$ mA/cm^2, $V_{oc} = 155$ mV, and FF = 34.7%, respectively. The photovoltaic performance of the device in this study is still inferior. However, it is the first report regarding to ZnO/ZnZe NWs/PbS QDs solar cell. The achieving high absorption and large short circuit current density may interest in further improvement of the device performance by suppressing surface defects, optimizing the quality of ZnO/ZnSe NWs and PbS QDs.[24]

Huaibin Shen et.al said that Here we report a new "green" method to synthesize $Zn_{1-x}Cd_xSe$ (x = 0–1) and stable red–green–blue tricolor $Zn_{1-x}Cd_xSe$ core/shell nanocrystals using only low cost, phosphine-free and environmentally friendly reagents. The first excitonic absorption peak and photoluminescence (PL) position of the $Zn_{1-x}Cd_xSe$ nanocrystals (the value of x is in the range 0.005–0.2) can be fixed to any position in the range 456–540 nm. There is no red or blue shift in the entire reaction process. Three similar sizes of alloyed $Zn_{1-x}Cd_xSe$ nanocrystals with blue, green, and yellow emissions were successfully selected as cores to synthesize high quality blue, green, and red core/shell nanocrystal emitters. For the synthesis of core/shell nanocrystals with a high quantum yield (QY) and stability, the selection of shell materials has been proven to be very important. Therefore, alternative protocols have been used to optimize thick shell growth. $ZnSe/ZnSe_xS_{1-x}$ and $CdS/Zn_{1-x}Cd_xS$ have been found as an excellent middle multishell to overcoat between the alloyed

$Zn_{1-x}Cd_xSe$ core and ZnS outshell. The QYs of the as-synthesized core/shell alloyed $Zn_{1-x}Cd_xSe$ nanocrystals can reach 40–75%. The Cd content is reduced to less than 0.1% for $Zn_{1-x}Cd_xSe$ core/shell nanocrystals with emissions in the range 456–540 nm. More than 15 g of high quality $Zn_{1-x}Cd_xSe$ core/shell nanocrystals were prepared successfully in a large scale, one-pot reaction. Importantly, the emissions of such thick multishell nanocrystals are not susceptible to ligand loss and stability in various physiological conditions.[25]

CHAPTER – III

3.1 METHODOLOGY

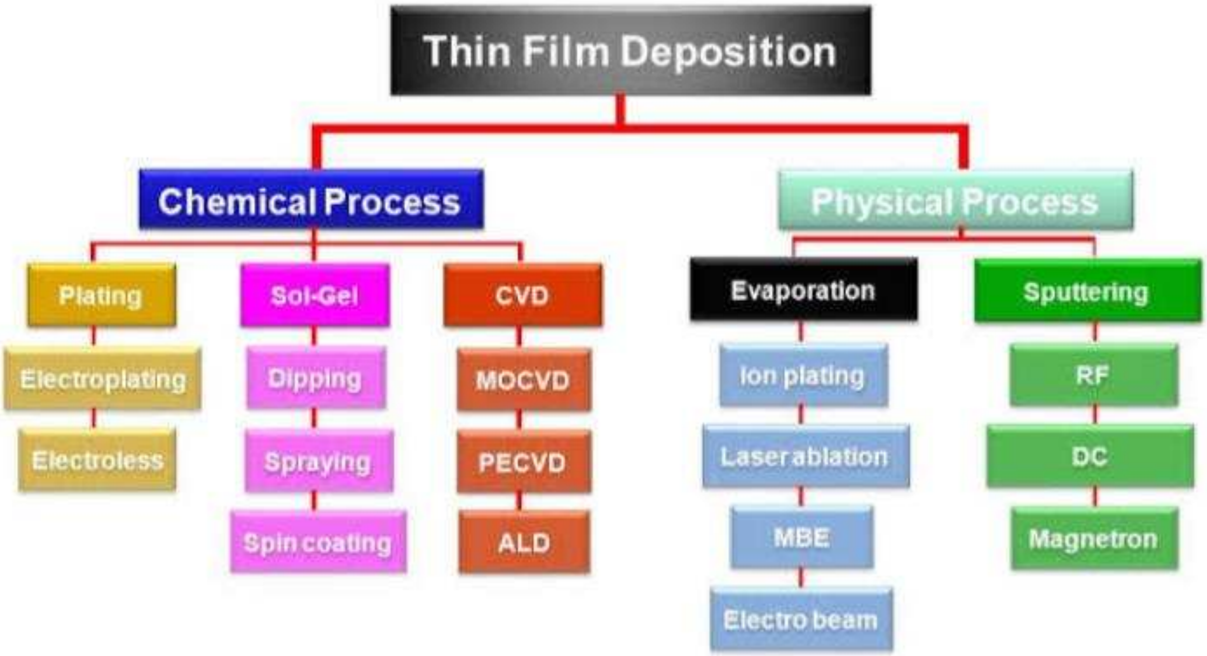


Fig 3.1 DEPOSITION METHODS

3.1.1 CHEMICAL PROCESS

3.1.1.1 ELECTROPLATING

Electroplating is a process that uses electric current to reduce dissolved metal cations onto an electrode surface, forming a thin film. Thin films are a layer of material that range in thickness from less than one nanometer to several micrometers. These thin films are used in a wide range of applications, ranging from solar cells to biosensor probes, and provide modified surface properties with minimal change in volume. However, it is essential that the thickness of the thin film is consistent and controllable. There are many different thin film deposition techniques commonly used to controllably deposit thin films, and each has its own benefits and drawbacks. In this video, we will introduce the electroplating technique, and demonstrate how to form a thin film using this method in the laboratory. Electroplating is performed in a set up like a galvanic cell which consists of two different metals, an anode and a cathode, connected by a salt bridge or porous membrane. These electrochemical cells have oxidation and reduction half-cell reactions that spontaneously occur at each of the metal electrodes, thereby generating electrical current. Electroplating relies on a similar concept. However, it reverses it by supplying current, thereby driving non-spontaneous redox reactions. The anode is made of the metal to be plated and is oxidized, creating dissolved ions. These ions flow through the electrolytic solution, which contains metal salts and other ions which permit the flow of electricity.[26]

3.1.1.2 SOL – GEL METHOD

The sol–gel deposition process includes synthesis techniques to produce a large quantity of nanosized material with modeled and controlled particle size, morphology, orientation, and crystal structure as well as optimized physical and chemical properties. It applies to the fabrication of metal oxide thin-films including chemical reaction, nucleation, growth, and aging, as an aqueous thin-film processing method (aqueous chemical growth). Tuning the thermodynamics and kinetics of nucleation, growth, and aging, and the precipitation conditions provides a simple and efficient control of the particle size and its distribution. The requirement of minimum surface energy drives nanoparticles to develop spherical morphology. However, in suitable synthesis (precursors) and dispersion conditions, the shape can be driven by the crystal symmetry and the chemical environment. Most process parameters influence the interfacial tensions which appear to play a prominent role. The control of the crystal structure is related with the nucleation kinetics. The more stable phase appears to be more sensitive to secondary growth after heteronucleation, such as the anatase–rutile transition.

The low-cost technique consists of heating the aqueous solution of metal salt or complex at given pH and temperature (<100 °C) in a closed bottle including substrates. Organic solvents or surfactants can also be used with the disadvantages of safety hazards, toxicity, and purity of the deposited film. For example, coatings of crystalline nanoparticulate of various textures have been grown with magnetite (Fe_3O_4), hematite (Fe_2O_3), CrO_3, Cr_2O_3, ZnO, Mn_2O_4, or RuO_2.[27]

3.1.1.3 CHEMICAL VAPOUR DEPOSITION (CVD)

Chemical vapor deposition (CVD) is parent to a family of processes whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface. The resulting solid material is in the form of a thin film, powder, or single crystal. By varying experimental conditions, including substrate material, substrate temperature, and composition of the reaction gas mixture, total pressure gas flows, etc., materials with a wide range of physical, tribological, and chemical properties can be grown. A characteristic feature of the CVD technique is its excellent throwing power, enabling the production of coatings of uniform thickness and properties with a low porosity even on substrates of complicated shape. Another important feature is the capability of localized, or selective deposition, on patterned substrates.CVD and related processes are employed in many thin film applications, including dielectrics, conductors, passivation layers, oxidation barriers, conductive oxides, tribological and corrosion-resistant coatings, heat-resistant coatings, and epitaxial layers for microelectronics. Other CVD applications are the preparation of high-temperature materials (tungsten, ceramics, etc.) and the production of solar cells, high-temperature fiber composites and particles of well-defined sizes. Recently, high Tc superconductors, and more recently carbon nanotubes, have also been made by this technique. Since oxygen activity in the vapor can be precisely controlled during the deposition, no annealing in oxygen is needed to achieve superconductivity. There exists a multitude of CVD processes, listed in Table 7.1. In thermally activated CVD (TACVD), the deposition is initiated and maintained by heat. However, photons, electrons, and ions, as well as a combination of these (plasma activated CVD), may induce and maintain CVD reactions. In this chapter, the underlying principles of TACVD are introduced. In addition, large-area deposition and selective CVD on patterned substrates are discussed.[28]

3.1.2 PHYSICAL PROCESS

3.1.2.1 THERMAL EVAPORATION

Thermal evaporation is a well-known method for coating a thin layer in which the source material evaporates in a vacuum due to high temperature heating, which facilitates the vapor particles moving and directly reaching a substrate where these vapors again change to a solid state. In this method, a charge holding boat or resistive coil is used in the form of a powder or solid bar. In order to get the high melting points necessary for metals, the resistive boat/coil is exposed to a large direct current (DC), where the high vacuum (below 10^{-4} Pa) supports the evaporation of the metal and further carrying it to the substrate. This technique is specially applicable for material with low melting points.[29]

3.1.2.2 SPUTTERING

Sputtering is a physical process in which atoms in a solid-state (target) are released and pass into the gas phase by bombardment with energetic ions (mainly noble gas ions). Sputtering is usually understood as the sputter deposition, a high vacuum-based coating technique belonging to the group of PVD processes. Furthermore, sputtering in surface physics is used as a cleaning method for the preparation of high-purity surfaces and as a method for analyzing the chemical composition of surfaces.The principle of Sputtering is to use the energy of a plasma (partially ionized gas) on the surface of a target (cathode), to pull the atoms of the material one by one and deposit them on the substrate.To do this, a plasma is created by ionization of a pure gas (usually Argon) by means of a potential difference (pulsed DC), or electromagnetic excitation (MF, RF); this plasma is composed of Ar+ ions which are accelerated and confined around the target due to the presence of a magnetic field. Each ionized atom, by striking the target, transfers its energy and rips an atom, having enough energy to be projected to the substrate.The plasma is created at relatively high pressures (10-1 - 10-3 mbar), but it is necessary to start from a lower pressure before the introduction of Argon, to avoid contamination due to the residual gases.The diversity of sputtering target shapes (circular, rectangular, Delta, tubular...) and the materials used allows creating all types of thin layers, including alloys during a single run.[30]

3.2 SILAR METHOD

The zinc selenide (ZnSe) thin films are deposited onto glass substrate using relatively simple and inexpensive successive ionic layer adsorption and reaction (SILAR) method. The films are deposited using zinc acetate sodium selenosulphate precursors. The concentration, pH, immersion and rinsing times and number of immersion cycles have been optimized to obtain good quality ZnSe thin films. The X-ray diffraction (XRD) study and scanning electron microscopy (SEM) studies reveals nanocrystalline nature alongwith some amorphous phase present in ZnSe thin films. Energy dispersive X-ray (EDAX) analysis shows that the films are Se deficient. From optical absorption data, the optical band gap 'Eg' for as-deposited thin film was found to be 2.8 eV and electrical resistivity in the order of 107 Ω cm.[31]

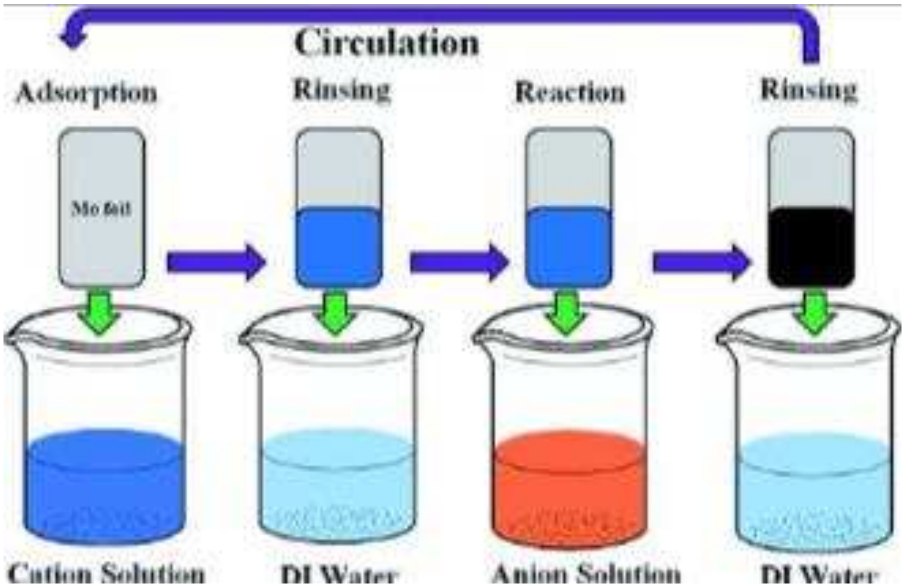


Fig 3.2 Schematic representation of SILAR METHOD

CHAPTER – IV

RESULT AND DISCUSSION

4.1 INTRODUCTION

The thin film can be characterised by using various techniques such as XRD, UV, SEM, TEM, AFM, PL. the ZnSe thin film subjected to XRD, AFM and SEM in this present work.

4.2 X – RAY DIFFRACTION(XRD)

X-ray diffraction is a powerful nondestructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the atomic positions within the lattice planes. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material. An online search of a standard database for X-ray powder diffraction patterns enables quick phase identification for a large variety of crystalline samples.

4.2.1 XRD Analysis

XRD is a technique used to find out the nature of the materials as crystalline or amorphous. It will define the quantification of cementitious materials. The XRD analysis is done with an X-ray source of Cu Kα radiation (λ = 1.5406 Å). It will analyze and identify the unknown crystalline compounds by Brag Brentano method. The different parameters such as scan step size, collection time, range, X-ray tube voltage and current should be fixed based on the specimen's requirement analysis. The standard database (JCPDS database) for XRD pattern is used for phase identification for a large variety of crystalline phases in the concrete specimens.

The Bragg equation, $n\lambda = 2d\sin\theta$ is one of the keystones in understanding X-ray diffraction .

n→ is an integer

λ→ is character wavelength of the X-ray impinging on the crystallize sample

d→is the interplaner spacing between rows of atoms

θ→ is the angle of the X-ray beam with respect to these planes

when this equation is satisfied X-ray scattered by the atoms in the plane of a periodic structure are in phase and diffraction occurs in the direction defined by the angle θ. In the simplest instance , an X-ray diffraction experiment consists of a set of diffracted intensities and the angles can be thought of a chemical fingerprint and chemical identification can be performed by comparing this diffraction pattern to a data base of known patterns.

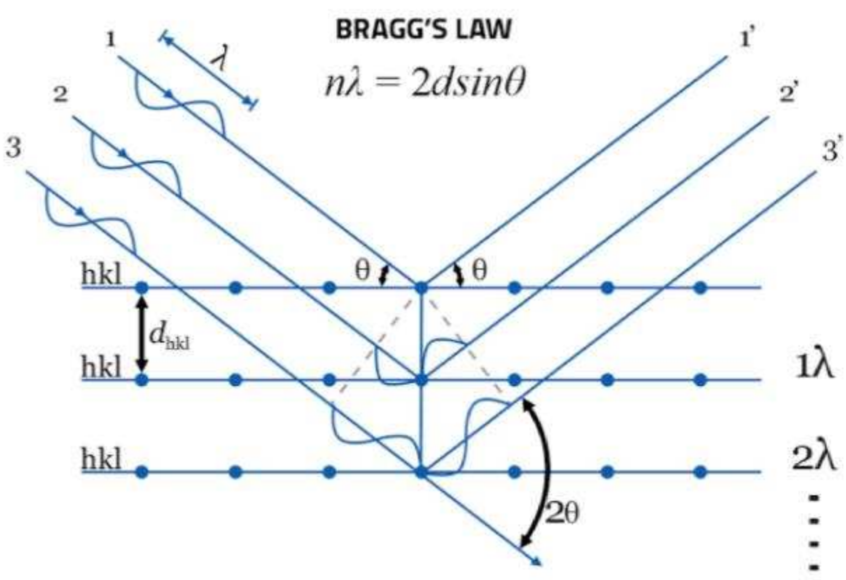


Fig 4.1 X-Ray Diffraction pattern

4.3 ATOMIC FORCE MICROSCOPY(AFM)

Atomic force microscopy (AFM) is a type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The information is gathered by "feeling" or "touching" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable precise scanning.

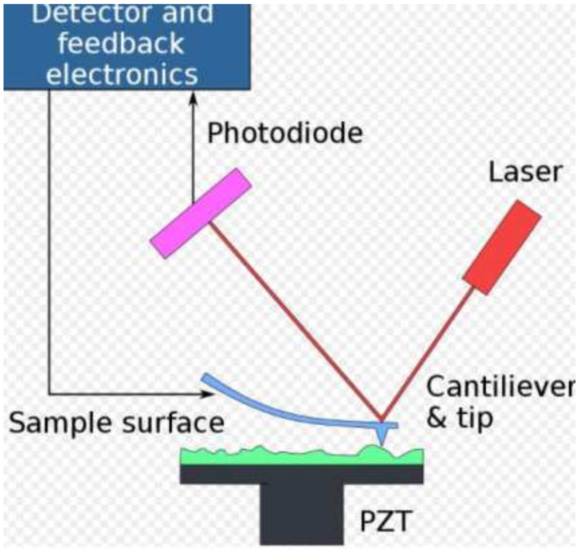


Fig 4.2Block diagram of AFM

4.4 SCANNING ELECTRON MICROSCOPY(SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern, and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector (Everhart-Thornley detector). The number of secondary electrons that can be detected, and thus the signal intensity, depends, among other things, on specimen topography. Some SEMs can achieve resolutions better than 1 nanometer.

Specimens are observed in high vacuum in a conventional SEM, or in low vacuum or wet conditions in a variable pressure or environmental SEM, and at a wide range of cryogenic or elevated temperatures with specialized instruments.

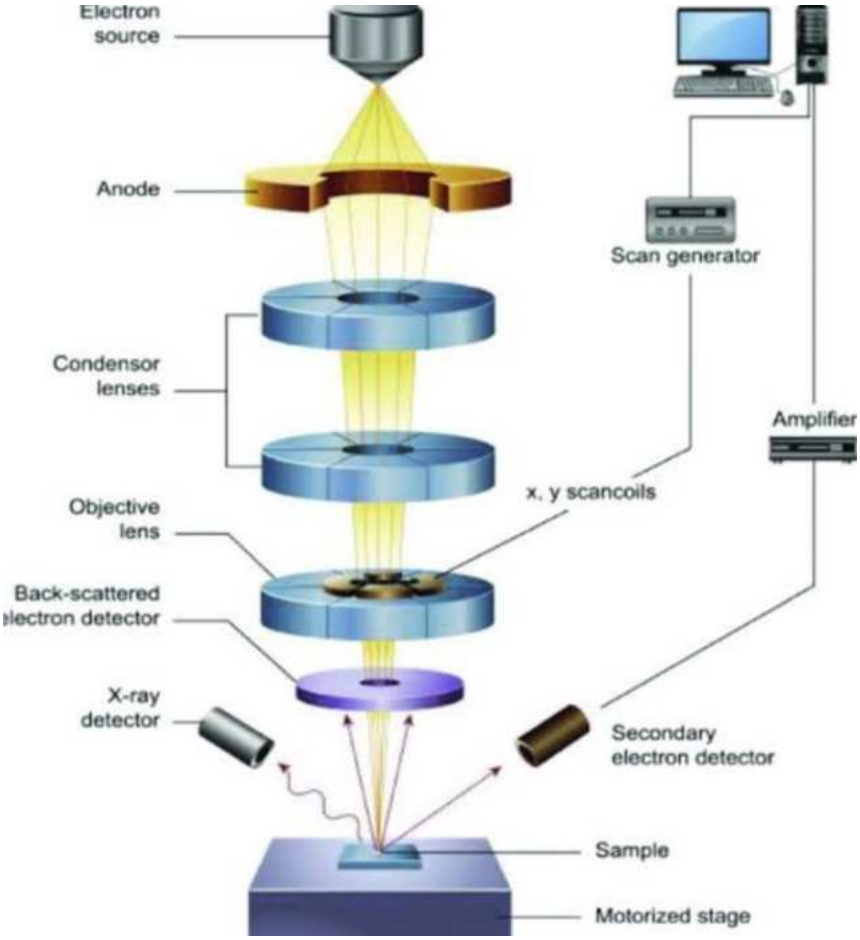


Fig 4.3 Schematic diagram of SEM

4.5 XRD PATTERN OF ZnSe PREPARED BY SILAR METHOD

To study structural properties of the deposited ZnSe thin films. X-ray diffraction (XRD) study was carried. The XRD pattern for the ZnSe thin film with the high density peaks absorbed at $2\theta = 27.223$ along the (111)hkl plane , $2\theta = 31.530$ along the (200) hkl plane, $2\theta = 65.908$ along the (400) hkl plane presented in the Fig 4.4 All diffraction peaks of the ZnSe thin film correspond to the characteristic zincblende structure of ZnSe thin film.

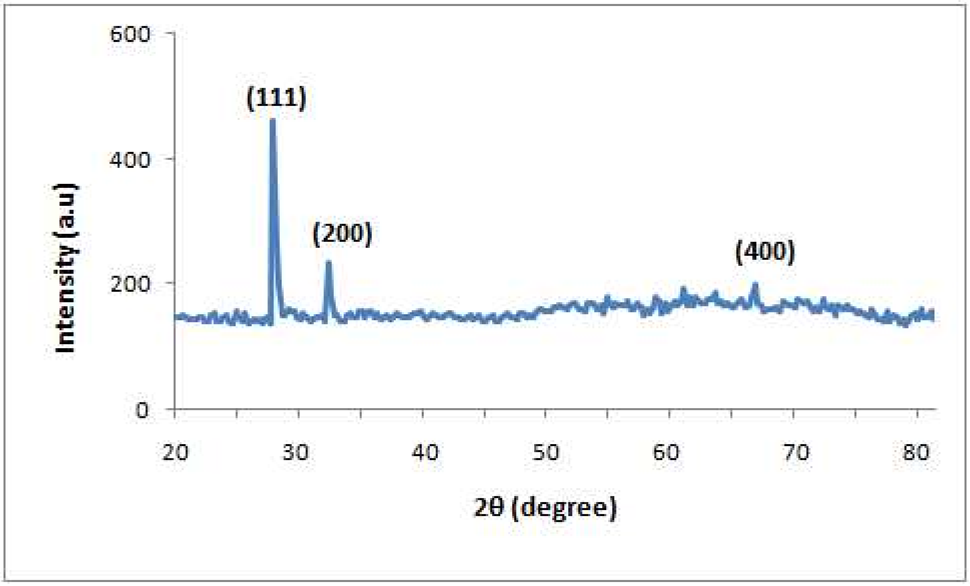


Fig 4.4 XRD pattern of ZnSe Thin Film

The observed ‘d’ values are compared with standard ‘d’ values using Joint Committee on Powder Diffraction Standards (JCPDS) diffraction file or American Society for Testing Materials (ASTM) data card for the same material synthesized by standard chemical methods. This analysis reveals the different phases present in the sample and Miller indices of the atomic planes. The lattice parameters ‘a’ , ‘b’ and ‘c’ for the unit cell of the phase present are then calculated using equations given by Kenon. The proportional amount of phases present can be determined from total intensities. Absence of reflection peaks indicates amorphous nature of the sample. A single reflection peak indicates an epitaxial growth, while many reflection peaks indicates heteroepitaxial (polycrystalline) growth. In case of a polycrystalline the average crystallite size is determined from Scherrer’s formula.

Using Fig4.3 to investigate structural properties of the deposited film, further analysis of XRD studies have been done. The crystallite size of thin film was calculated from XRD patterns by using Scherrer's formula given below

$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where

D = Crystallites size (nm)

β = (FWHM) (radians)

θ = Peak position (radians)

K = 0.9 (scherrer constant)

λ = 1.5406 nm (wavelength of the x-ray sources)

Using these formula grain size can be dertermined . The value of the grain size for (111) plane was found to be 3.0116nm, the grain size for (200) plane was found to be 2.626nm and the grain size for (400) plane value was obtained to be 1.441nm.

The grain size and dislocation density and microstrain of ZnSe thin film have been given in Table 1.3

The dislocation density has been calculated using crystallite size, by the equation

$$\text{Dislocation} = 1/D2$$

The microstrain has been calculated by the given formula,

$$\text{Microstrain} = \frac{\beta\cos\theta}{4}$$

Hkl	2θ (Degree)	Grain size (D)nm	Dislocation density (lines/m^2)	Microstrain
111	27.223	3.0116	0.11026	0.1151
200	31.530	2.626	0.14514	0.1319
400	65.908	1.441	0.48077	0.2406

Table 4.1 Structural parameters of ZnSe thin film

4.6 ATOMIC FORCE MICROSCOPY ANALYSIS

The Atomic Force Microscope(AFM) was developed in 1986 in order to overcome the limitations of Scanning Tunneling Microscope. The AFM is used to obtain the high resolution image of the individual atom on both conducting and insulating surfaces. The principle behind the AFM technique is the interaction between a double force sensing tip known as cantilever and the sample. The cantilever which contains the tip, scans the surface of the sample in a raster pattern to obtain the image of the sample.

When the mounted tip in the cantilever approaches the sample surfaces, it experiences a repulsive force. The repulsive force exists between tip and the sample produces a small bending on the cantilever. A laser beam is used to monitor the displacement of the cantilever. The laser beam incident on the cantilever gets reflected. The reflected laser beam is recorded using a position sensitive photodiode. A small bending in the cantilever leads in a corresponding change in the position of the reflected laser beam. The same is recorded by the photodiode. The signal received by the detector is then send as feedback into the

Piezoelectric Transducer, which helps the sample to move up and down. The movement of the sample helps to maintain a constant force between the sample and tip. By scanning the surface of the sample by raster pattern and recording the reflected laser beam using photodetector, topographical image of the sample is obtained. The image of the sample gives the information about the surface nature and subsurface nature of the sample. Fig 4.5 shows the topography of the Atomic Force Microscopy.

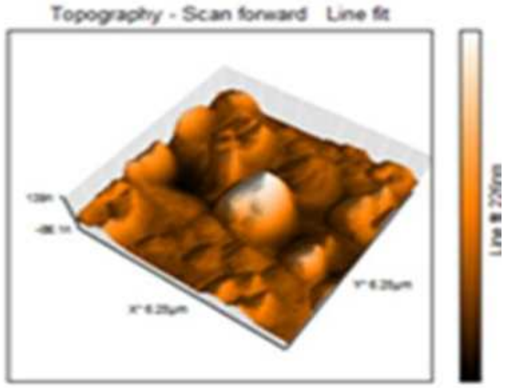


Fig 4.5 AFM image of ZnSe Thin Film

4.6.1 APPLICATIONS

It is most commonly used for imagining surface topography by recording the position of the sample relative to the tip and then recording the height of the probe that corresponds to a constant probe-sample interaction as well as the variety of mechanical, functional and electrical properties. For surface manipulation using tip forces, for example, scanning probe lithography. To measure the forces between the sample and the probe as a form of force spectroscopy, to examine physical and mechanical properties.

4.7 SCANNING ELECTRON MICROSCOPY ANALYSIS

Scanning Electron Microscopy (SEM) is a test process that scans a sample with an electron beam to produce a magnified image for analysis. The method is also known as SEM analysis and SEM microscopy, and is used very effectively in microanalysis and failure analysis of solid inorganic materials. Electron microscopy is performed at high magnifications, generates high-resolution images and precisely measures very small features and objects. Fig 4.6 shows the Morpology of the Scanning Electron Microscopy.

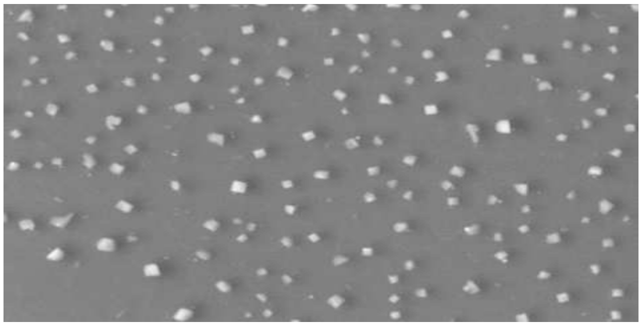


Fig 4.6 SEM image of ZnSe Thin Film

4.7.1 APPLICATIONS

The signals generated during SEM analysis produce a two dimensional image and reveal information about the sample, including external morphology (texture), chemical composition, when used with the EDS feature, and orientation of materials making up the sample. The EDS component of the system is applied in conjunction with SEM analysis to determine elements in or on the surface of the sample for qualitative information. It also measures elemental composition for semi-quantitative results and identifies foreign substances that are not organic in nature and coatings on metal.

CHAPTER – V

SUMMARY AND CONCLUSION

In this work ZnSe thin films were prepared by SILAR method and was characterised for various structural studies such as XRD, SEM and AFM.

The synthesised films were characterised by XRD. The grain size of ZnSe was calculated by De-scherrer's formula which proves that ZnSe thin film is a cubic structure. The average grain size of the thin film is about 2.3595nm. The Dislocation density of the thin film is about 0.2454 lines/m^2. The Microstrain of the thin film is about 0.1625. The miller indices values are found to be (111), (200), (400) well agree with the JCPDS files.

The surface roughness was measured by Atomic Force Microscopy. SEM studies reveal information about the surface topography and composition.

In future the prepared ZnSe thin film will be subjected to optical and electrical studies for solar cell applications.

REFERENCES

[1] https://en.m.wikipedia.org/wiki/Thin_film

[2] Thin Film Deposition Technologies: Introduction to Thin Films and Processes(2017).

[3] http://www.aiscience.org/journal/ijmpa

[4] byjus.com/chemistry/zinc chloride – zncl2

[5] https://en.m.wikipedia.org/wiki/selenium_dioxide

[6] https://en.m.wikipedia.org/wiki/zinc_selenide

[7]B.Guzeldir,M.Saglam,A.Ates"Analysis of the electrical characteristics of *Zn/ZnSe/n-Si/Au–Sb* structure fabricated using SILAR method as a function of temperature" 388(2010)394.

[8] Satish S.Patil,Sawanta S.Mali,Chang K.Hong,Popatrao N.Bhosale"Designing of novel efficient photoactive ternary Zn1-xCu2xSe thin film materials via hydrothermal route"104(2020)727.

[9] Derya Batibay, Yusuf Selim Ocak, Mustafa Fatih Genisel, Rasit Turan "Co-sputtered Cu2ZnTi(S:Se)4 absorbers for thin film solar cells"vol.145(2020).

[10] R.Khalfi, D.Talantikite-Touati, A.Tounsi, H.Merzouk "Effect of deposition time on structural and optical properties of ZnSe thin films grown by CBD method"vol.106(2020).

[11] H H Hegazy, I M Ashraf, H Algarni1 and Ahmad Umar "An investigation on photoconductivity of non-stoichiometric CuZnSn(S, Se)4 thin films for photovoltaic applications" (2019).

[12] Sinan Temel, Fatma Ö. Gökmen, Elif Yaman “An Energy efficient way to produce Zinc-based semiconductor Thin films via chemical bath deposition technique”vol.7(2019).

[13] Mahesh P. Suryawanshi, Uma V. Ghorpade, Umesh P. Suryawanshi, Mingrui He, Jihun Kim, Myeng Gil Gang, Pramod S. Patil, Annasaheb V. Moholkar, Jae Ho Yun, and Jin Hyeok Kim “Aqueous-Solution-Processed Cu2ZnSn(S,Se)4 Thin-Film Solar Cells via an Improved Successive Ion-Layer-Adsorption”(2017).

[14] Tingting Yao, Shufang Kou, Yanghui Sun, Qing Zhao and Jian Yang “Facile synthesis, optical properties and growth mechanism of elongated Mn-doped ZnSe1−xSxnanocrystals”(2012).

[15] Chaitali S. Bagade, Vishvanath B. Ghanwat, Sawanta S. Mali, Kishorkumar V. Khot, Chang K. Hong and Popatrao N. Bhosale “Synthesis of (CdZn)Se thin films by a facile aqueous phase route and their photoelectrochemical performance for solar cell application”(2016).

[16]Yu-PinLin,Tsung-EongHsieh,Yen-ChihChen Kun-PingHuang “Characteristics of Cu2ZnSn(SxSe1−x)4 thin-film solar cells prepared by sputtering deposition using single quaternary Cu2ZnSnS4 target followed by selenization/sulfurization treatment”vol.162(2017).

[17] Xin Li, Junyou Yang, Qinghui Jiang, Hui Lai, Shuiping Li, Jiwu Xin, Weijing Chu, and Jingdi Hou“Low-Temperature Solution-Processed ZnSe Electron Transport Layer for Efficient Planar Perovskite Solar Cells with Negligible Hysteresis and Improved Photostability”(2018).

[18] D.D.Hile, H.C.Swart, S.V.Motloung, T.E.Motaung, K.O.Egbo, L.F.Koaoa “Comparative study of photo- and non-photo-assisted chemical bath deposition of

Zinc Selenide thin films using different volumes of hydrazine hydrate"VOL.134 (2019).

[19] Qi Zhang, Huiqiao Li, Ying Ma, Tianyou Zhai "ZnSe nanostructures: Synthesis, properties and applications"VOL.83 (2016).

[20] Nader Ghobadi and Falah Dousi "Shape, size and configuration tuning in ZnSe nanostructure thin films through deposition temperature, pH controlling and deposition time"(2014).

[21] M. Kamruzzaman "The effect of ZnO/ZnSe core/shell nanorod arrays photoelectrodes on PbS quantum dot sensitized solar cell performance"(2019).

[22] Xiaoyan Liu, Jian Cao, Bo Feng, Lili Yang, Maobin Wei, Hongju Zhai, Huilian Liu, Yingrui Sui, Jinghai Yang, Yaohui Liu "Facile fabrication and photocatalytic properties of ZnO nanorods/ZnSe nanosheets heterostructure"vol.83(2015).

[23] Yi-Hsin Chen, Wun-Shan Li, Chun-Yi Liu, Chiu-Yen Wang, Yu-Cheng Chang and Lih-Juann Chen"Three-dimensional heterostructured ZnSe nanoparticles/Si wire arrays with enhanced photodetection and photocatalytic performances"(2013).

[24] M Kamruzzaman and J A Zapien "Synthesis and characterization of ZnO/ZnSe NWs/PbS QDs solar cell"(2017).

[25] Huaibin Shen, Hongzhe Wang, Changhua Zhou, Jin Zhong Niu, Hang Yuan, Lan Ma and Lin Song Li "Large scale synthesis of stable tricolor Zn1 − xCdxSe core/multishell nanocrystalsvia a facile phosphine-free colloidal method"(2011).

[26] Abdel Salam Hamdy Makhlouf, Rocio Rodriguez, in Advances in Smart Coatings and Thin Films for Future Industrial and Biomedical Engineering Applications(2020).

[27] F. Lévy, “Film Growth and Epitaxy: Methods” in Reference Module in Materials Science and Materials Engineering(2016).

[28] Jan-Otto Carlsson, Peter M. Martin, “Chemical Vapour Deposition”in Handbook of Deposition Technologies for Films and Coatings (Third Edition)(2010).

[29] Almas Bashir, Mohsin Ijaz, in Chemistry of Nanomaterials (2020).

[30] Sputtering: Process, Types, and Uses - Nanografi Nano (2019).

[31] https://www.scientific.net › paper-keyword › silar-method

STUDIES ON PHYSIOTHERAPY INSTRUMENTS

A field work report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS),THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirement for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

T.AROCKIA DEENA

Reg.No : 20SPPH02

Under the Guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this field work report entitled, "**STUDIES ON PHYSIOTHERAPY INSTRUMENTS**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirement for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020-2021** by **T. AROCKIA DEENA** (Register No: 20SPPH02)

Signature of Staff-In-Charge

Padmavathi P

Signature of the Co-Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous),
Thoothukudi - 628 001.

Padmavathi P 12/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, " **STUDIES ON PHYSIOTHERAPY INSTRUMENTS**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree , Diploma or other similar titles.

T.Arockia Deena

Signature of the Student

(T.AROCKIA DEENA)

Station: Thoothukudi

Date: 10.4.2021

ACKNOWLEDGEMENT

First and foremost, I feel obliged to our Almighty for his aid in the completion of this field project work successfully.

I am deeply indebted to our respected Principal Rev. Dr. Sr. A.S.J. LUCIA ROSE M.Sc., M.Phil., Ph.D., PDGCA., for providing me this wonderful opportunity to spread my wings through this project.

I would like to extend my gratitude to our Director of SSC, Rev Dr. Sr. F. MARY JOYCE BABY M.A., M.Phill., Ph.D., for her support and encouragement.

I would express my special gratitude to Rev.Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., HOD and Associate Professor for her encouragement to perform this project.

I wish to extend my heartfelt gratitude to Mrs. P. PADMAVATHI M.Sc., M.Phil., SET., SSC Co-ordinator, Department of Physics , for her encouragement in completing our project.

I cordially extend my sincere gratitude to Ms. A. VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her guidance and support in the completion of the field work report.

I am extremely thankful to Mr. RAMESH BABU Adminstrator AVM Hospital, Thoothukudi, for him help and support to complete my field work

CONTENT **Page.no.**

1 INTRODUCTION

1.1 Physiotherapy:

Physics is the study of matter motion, energy, and forces . It includes concepts of gravity, electricity, magnetism, heat, light, and radioactivity Physical therapy or physiotherapy involves treatment of diseases, disabilities and disorders and treating the evaluating, diagnosing the diseases using physical therapy treatments .For the treatment of different types of equipment are used by the physical therapists. These equipments are known as physiotherapy equipments. Most of these equipments and machines are mainly used to complete daily tasks easily and painlessly. Various types of therapies are used to heal different parts of the body.

1.2 Different types of physiotherapy equipments:

A therapist may require various kinds of machines and equipments to treat different types of disabilities. Some of the most important types of equipments used by the physical therapists are elaborated

- Infrared Radiation (IRR)
- Interferential therapy (IFT)
- Ultrasound therapy
- paraffin wax therapy

2 INFRARED RADIATION (IRR) IN PHYSIOTHERAPY

Fig. 2(a) Representing infrared radiation (IRR)

Infrared irradiation (IRR) is electromagnetic energy invisible to the human eye, having a wavelength between **760nm to 1mm**. In the electromagnetic spectrum, the infrared own the place **between visible light and microwaves.**

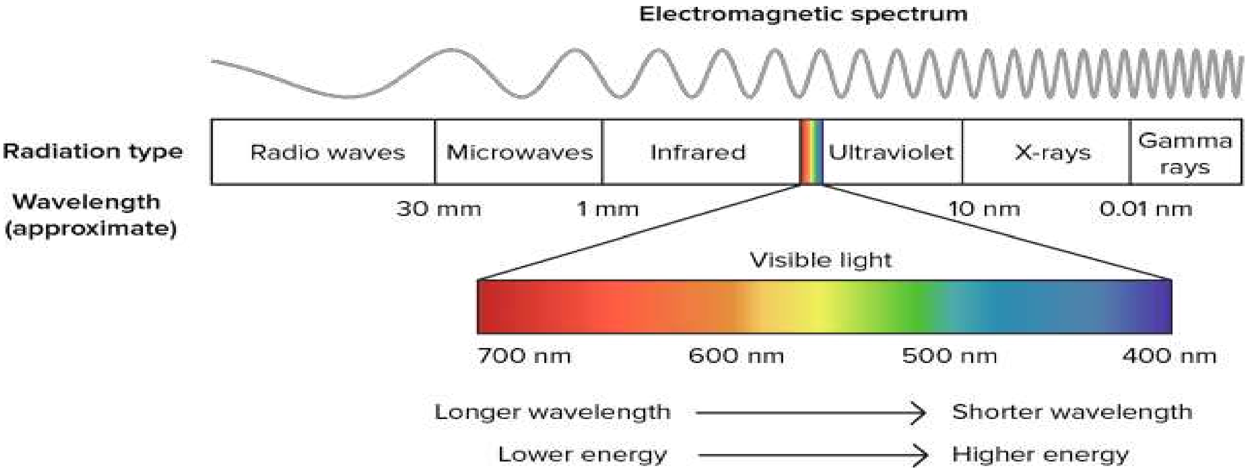


Fig.2 (b) Representing electromagnectic spectrum

It used for the relief of pain and stiffness and to enhance healing of soft tissue lesions and skin condition, by producing the superficial thermal effect in the tissues.

2.1 Production of IRR:

Any hot body emits infrared ray; the sun**, gas fires, coal fires, electric fires, hot water pipes,** etc. for therapeutic purpose, IRR produced by two types of generators- the **non-luminous and luminous generators.**

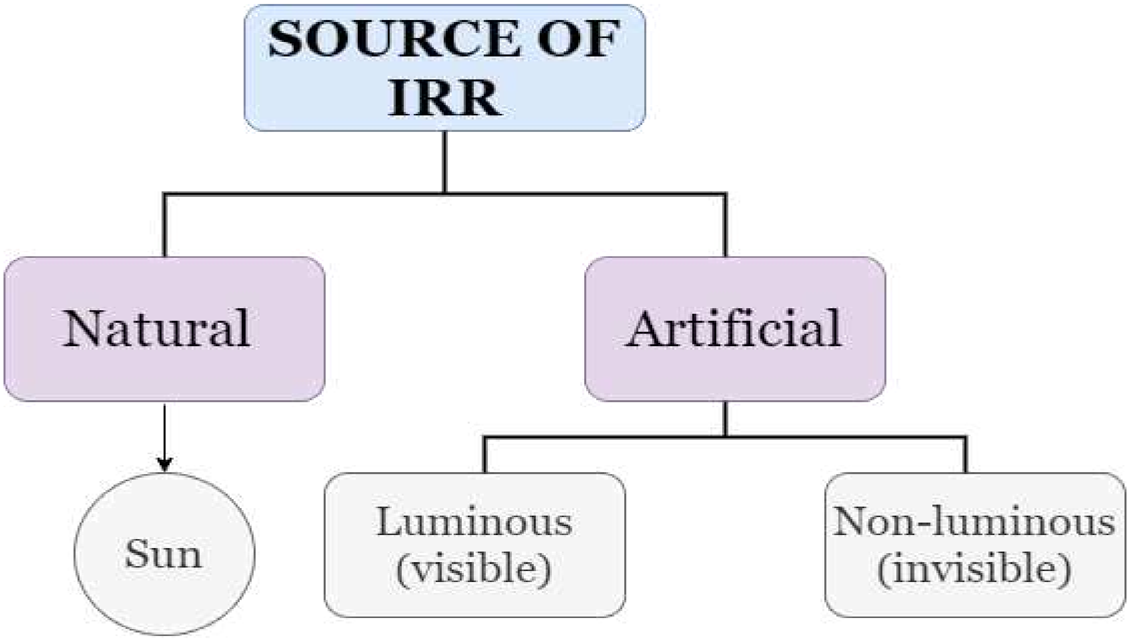


Fig. 2.1 Representing production of IRR

Non-luminous generators provide infrared rays only, while luminous generators emit visible and a few ultra-violet rays as well as infrared.

The spectral values of-

- **IRA vary from 760nm-1400nm.**
- **IRB vary from 1400nm-3000nm**
- **IRC vary from 3000nm-1mm**

2.2 Types of generators:

There are two types of infrared generators-

1. Luminous generator
2. Non-luminous generators

Luminous generators:

Fig. 2.2(a) Representing luminous generators

- Rays emitted from the luminous generators
- It is produced by one or more incandescent (Radiant) lamps.
- An incandescent lamp consists of a wire filament enclosed in a glass bulb, which may be evacuated or may contain an inert gas at low pressure.
- A part of the inside of the glass bulb is often silvered to provide a reflector.
- The filament is a coil of fine wire and is usually made of tungsten: as this material tolerates related heating and cooling.

- The passage of an electric current through the filament produces heat, infrared red, ultraviolet, **and visible radiation.**
- The ultraviolet produced is absorbed by the glass of the lamp, and therefore it's not emitted.
- These lamps generally available with a power level of between 250-1500W
- The lamp available at this time generally emits IRR, with wavelengths of between 780nm -1500nm with peak intensity at 1000nm.
- Penetration→ the dermis and subcutaneous tissue to a depth of 5-10mm.
- The luminous generator is sometimes called **radiant heat**.

Non-luminous generators:

Fig. 2.2(b) Representing non-luminous generator

These generators consist of a coiled resistance wire.

- Which is looped around or fixed in a ceramics insulated material and produces far infrared electromagnetic rays (1500-12000nm)

- Infrared radiation(IR) will be emitted, by both the wire and heated material surrounding it.
- These generators produce only infrared radiation and no other visible radiation.
- These are generally available with power levels of between **750-1000W**.
- The infrared emitter is placed at the focal point of a parabolic reflector, to reflect the radiation into an approximately uniform beam.
- The reflector has on its front a wire mesh.
- These generators produce radiation which peaks at a wavelength of around 4µm (4000nm) and penetrates the epidermis (2mm).

Though both the lamps require a warm-up period, non-luminous lamps take longer than luminous lamp to reach a peak level of heat emission, because of the thermal inertia of the considerable mass of metal and insulating material that has to be heated.

The small lamps may take 5 minutes, but larger ones may take up to 15 minutes to reach maximum emission**.**

2.3 Physical effects:

IRR obey the law of electromagnetic radiation such as:

- Reflection
- Refraction
- Transmitted
- Absorption

Like any other radiation, IR falling on the surface of the skin is partially reflected and partially absorbed through penetration.For therapeutic infrared, the amount of reflection is negligible.**Lambert's cosine law– close to 95% of the radiation applied perpendicular to the skin are absorbed, through transmission into**

body tissue and only a small amount is reflected. The transmitted energy is rapidly absorbed, so only a small amount of radiation penetrates the subcutaneous tissue and most of the energy is absorbed in the skin

Dangers:

- Burn
- Electric shock
- Gangrene
- Headache
- Faintness

3 INTERFERENTIAL THERAPY (IFT)

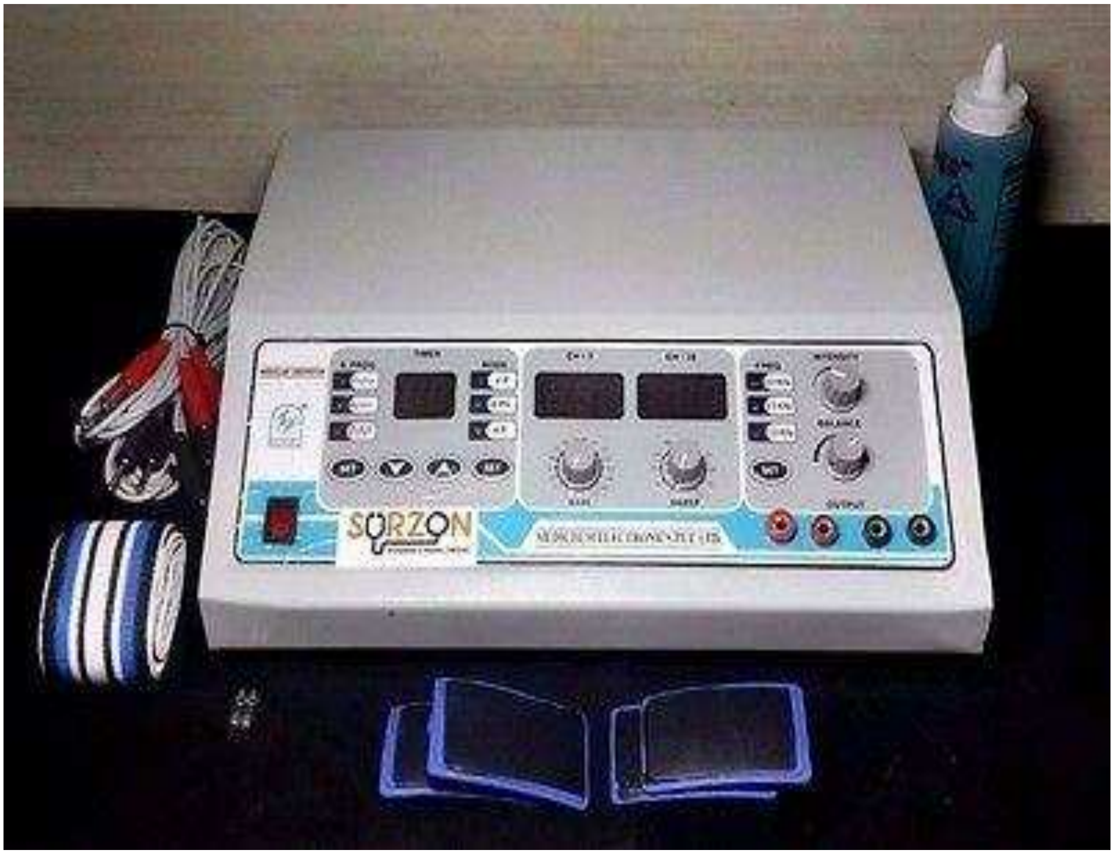


Fig. 3(a) Representing interferential therapy

Interferential therapy (IFT) is widely used in physiotherapy. It is developed by Dr. Hans Nemec of Vienna, Austria in the early 1950s. It is very helpful in relieving pain due to muscle spasm and various other kinds of painInterferential therapy is a form of electrical treatment in which we used interferential current.As the name suggests, there has to be two current that interferes with each other resulting in the production of interferential current.

Let me further explain it, when two medium frequency current interferes, they produce a beat frequency. This beat frequency is termed as Interferential current. The treatment process through this current is called as Interferential Therapy.

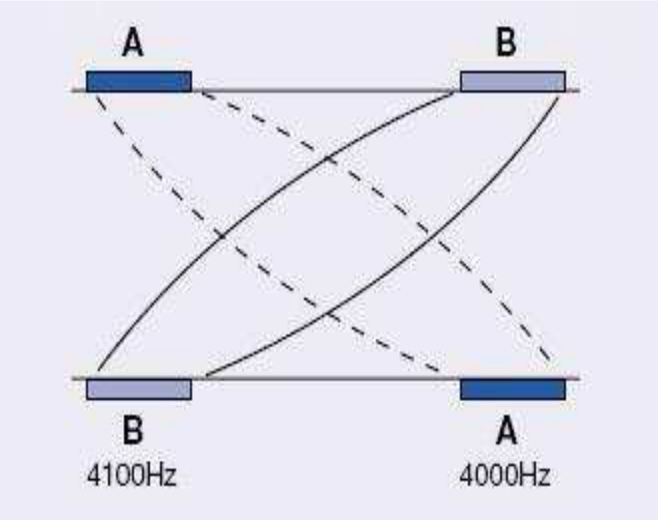


Fig. 3(b) Representing Beat frequency

The beat frequency is the difference between the two medium frequency currents. It is low frequency. This frequency gives soothing and pain-relieving effect on the part where it is applied.

3.1 Principle:

The basic principle of interferential therapy (IFT) is to use the important physiological effects of low-frequency electrical stimulation of nerve without the associated painful and somewhat unpleasant side effects.

- To produce low-frequency effects at sufficient intensity and sufficient depth, the patient can experience much discomfort in the superficial tissue (i.e. in the skin).
- This is due to the impedance of the skin.

- Interferential therapy utilizes two of these medium frequency currents, passed through the tissues simultaneously, where they interfere with each other.
- This interaction gives rise to an interference current (or beat frequency).
- Beat frequency controlled through input frequency
- for example- one current was at 4100Hz and it's associate current at 4000Hz, the resultant beat frequency, would be at 100Hz.

3.2 Treatment parameters :

Amplitude modulated frequency (beat frequency):

- The AMF frequencies are the same as used in low-frequency treatment.
- The sensation induced by interferential current stimulation changes with different AMF setting.
- Low AMFs for example obtain a beating or tapping sensation, while higher AMFs obtain a buzzing or tingling sensation.

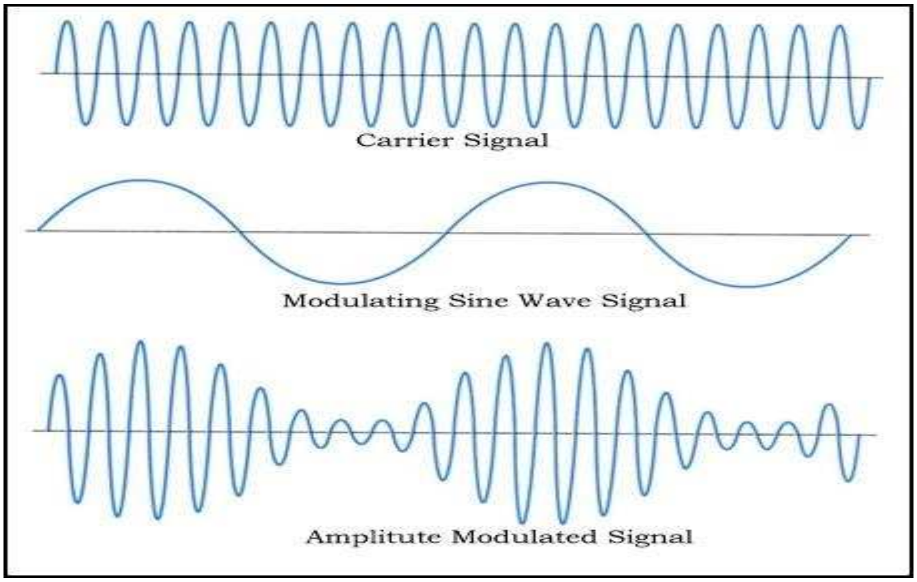


Fig. 3.2 Representing amplitude modulated frequency

Frequency:

- Frequency sweep means gradually changing frequency.
- It prevents the accommodation of nerves. because Nerves will accommodate to a constant signal.
- Frequency sweep is set in the machine automatically, using pre-set or user-set sweep range

Types of sweep patterns:

- Triangular sweep patterns
- Rectangular sweep pattern
- Trapezoidal sweep patterns

4 pole and 2 pole :

- In 4 pole and 2 pole, IFT produced with 4 or 2 electrode system.
- There is no known physiological difference between the effects of IFT produced with 2 pole or 4 pole.
- The key difference is that with 4 pole applications the interference is generated in the tissues and with a 2 pole treatment, the current is ‘pre modulated’ the interference is generated within the machine unit.

Vector mode:

The vector system should only be selected, if the site of a lesion can not be accurately localized. just like A patient who has a diffuse area of pathology, and the accuracy of the lesion, within the static interferential field is doubtful, the vector principle is used.It produces a scanning movement of the interferential field so that all parts of the field are subjected to the maximum interferential effect

Electrode:

- Suction electrode
- Flat carbon rubber suction electrode

has the advantage of allowing the application to large flat areas or patients who are relatively immobile.Flat carbon rubber electrodes may be easier to apply to the peripheral limbs, when they may be held in position by bandages or velcro straps.

Current density:

- Always turn the intensity dial to zero before beginning the treatment.
- The intensity should be slowly turned up until the patient signals that the required sensation has been reached.
- To neutralize adaptation, adjust intensity periodically.

Treatment duration has been reported by most clinicians to be between 10- 15 minutes.

3.3 Physiological effect of IFT:

This depend upon:

- Magnitude of current.
- Type of mode used i.e.rhythmic or constant.
- The frequency range used.
- Accuracy of electrode positioning

Dangers:

- Burns
- Increased pain
- General malaise
- Dizziness/ faintness

4 ULTRASOUND THERAPY

Fig. 4 Representing ultrasound therapy

Ultrasound is a mechanical pressure wave or mechanical vibration resonating at a high frequency beyond the upper limit of human hearing. Physiotherapist has been used it Since the 1940s. One of the greatest proposed benefits of ultrasound is that it increases the healing process of certain soft tissue injuries. This therapy is used for reducing pain, muscle spasm, and joint contractures.

ULTRASOUND =ULTRA+SOUND

- Ultra means-excessive or extreme.
- Sound means-something that can you hear.
- Sound is the periodic mechanical disturbance of one elastic medium.
- The normal human sound range is from 16Hz to something 20KHz (20,000 cycles per second).
- Ultrasound is mechanical vibration, beyond this upper limit

- Therapeutic frequencies of ultrasound being in the region of 1MHz or 3MHz.

Production of sound waves:

- Sound waves are mechanical vibration in an elastic medium. Sound waves are longitudinal in nature. A tuning fork (an oscillating source) is required for the production of sound waves. sound waves are traveling pressure waves in
- the medium which causes an alternate compression and rarefaction of the particles in the medium.

4.1 Factors related for waves:

Frequency is The number of times a particle undergoes a complete cycle (compression and rarefaction) in one second.

Wavelength is the distance between the two closest points on the waveform in the particular medium .

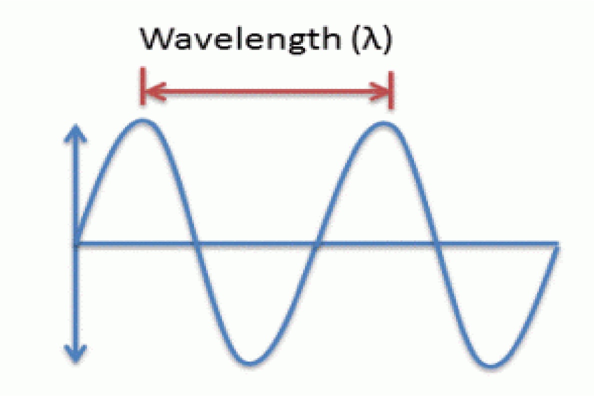


Fig. 4.1 Representing wavelength

Velocity of a wave is the speed at which the wave moves through the medium. It varies depending upon the physical nature of the medium.

4.2 Production of ultrasound:

- The Ultrasound instrument consists of a high-frequency generator. This is connected to a Piezoelectric crystal (treatment head or transducer circuit) by a co-axial cable. for the production of ultrasound waves.1 MHz or 3MHz frequency is needed When these varying potential difference or frequency
- applied on quartz crystal or barium titanate crystal, via a linking electrode, the crystal being fused to the metal front plate of the treatment head. Any changes in the shape of crystal(Compressed and Relaxed), produces an ultrasonic wave. it generates ultrasound waves by a Piezoelectric effect.
- Piezoelectric effect refers to the application of an electric field to a crystal, which causes a realignment of the internal dipole structure. This realignment results in crystal lengthening or contraction, converting electrical energy into kinetic or mechanical energy. This is how the ultrasound transducer produces sound waves

4.3 Continuous and pulsed ultrasound:

- Most ultrasound equipment can generate both continuous and pulsed ultrasound energy.
- In continuous mode, the treatment head continuously produces ultrasonic energy.
- In pulse mode, the period of ultrasound is separated by a period of silence.
- A pulsed ultrasound setting will be used, When a thermal effect is not desired, such as during acute inflammation or around a bony surface,
- Duty Cycle (Pulse Mark : Space Ratio)
- When ultrasound is applied in it is pulsed mode, the ratio of the time on to time off should be expressed. This is the mark: space ratio (M:S) or duty

cycle. Mark being the time ultrasound is on, space being the time silence. M : S Ratio have a variable range 1:1 , 1:2 , 1:3 , 1:4 , 1:7.

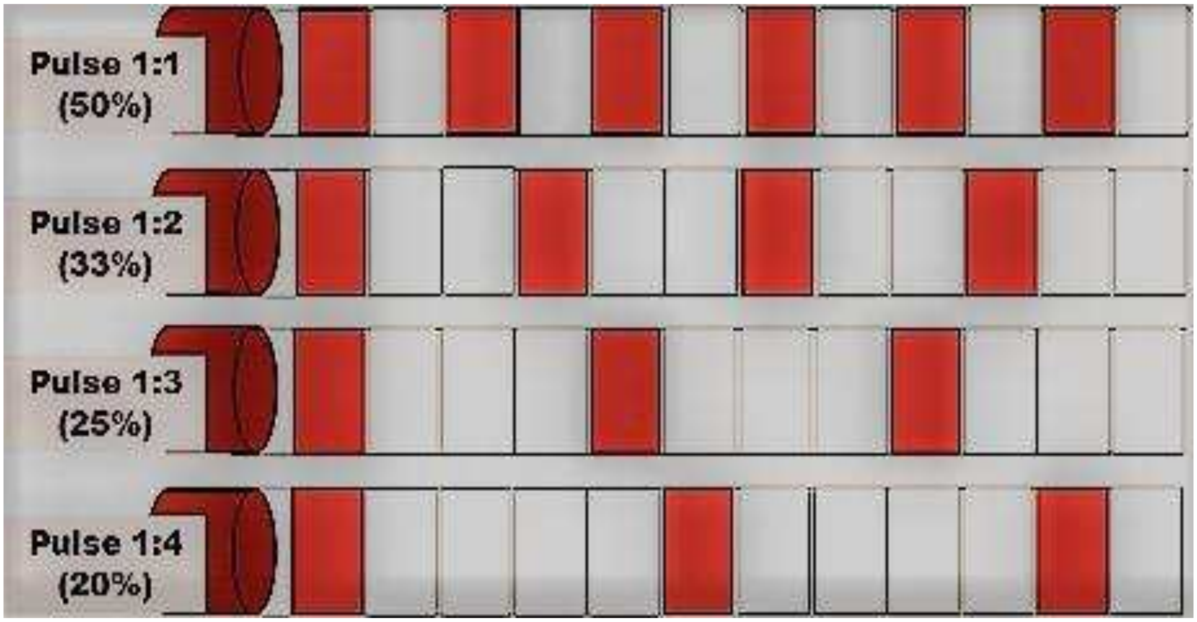


Fig. 4.3(a) Representing continues and pulsed ultrasound

- Ultrasound Beam, Far Field & Near Field
- The US beam is not uniform and changes in its nature with distance from the transducer.
- If it nearest the treatment head is called the near field, the Interference field or the Frenzel zone.
- If it's beyond the near field, away from the transducer head is called the far-field or the Fraunhofer zone.
- Near Field = r^2/λ.
- Here r = the radius of the ultrasound head and λ = the US wavelength
- Wavelength (λ) and Frequency (f) are inversely related.
- Near Field = $r^2 \times f$
- The depth of the near field varies with the frequency of ultrasound.

- For 1 MHz frequency, near field less than 3 MHz and vice versa.

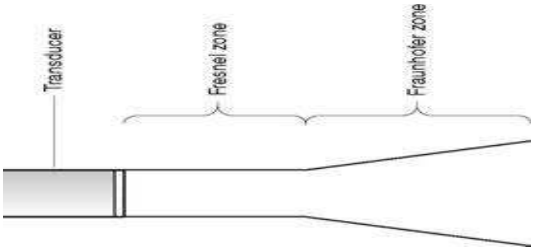


Fig. 4.3(b) Representing Ultrasound beam

4.4 Reflection of ultrasoud:

- Ultrasound follows the laws of optics. If an ultrasonic beam traveling through one medium encounters another medium which will not transmit it, reflection takes place.
- Air will not transmit ultrasonic waves, so in ultrasonic treatment great focus to avoid leaving air between the treatment head and patient, to minimize reflection.
- However, there will always be some reflection at each interface that the ultrasound beam encounters. this gives rise to the
  term ACOUSTIC IMPEDANCE(Z)
- Acoustic Impedance (Z) – It is the ratio between the reflected and transmitted ultrasound at an interface. If the acoustic impedance is low, the transmission is high and vice versa.

4.5 Attenuation of ultrasound:

The intensity of ultrasound waves decrease as they travel through tissue, it’s known as attenuation. it is the progressive loss of acoustic power. Two major factors contribute to attenuation absorption and scatter

Absorption:

Ultrasound is absorbed by the tissue and is converted to heat at the point. Absorption of ultrasound takes place at a molecular level. The tissues with the higher protein content will absorb the US to a greater extent

Scatter:

Scattering of ultrasound in the body occurs due to two phenomena, divergence in the far-field and reflection. Especially because of reflection, the ultrasound beam may spread in the body, so that effect can develop not only in the direction of the sound beam but also outside it. The ultrasonic beam is reduced in intensity the deeper it passes. this gives rise to the expression 'HALF VALUE DISTANCE' which is the depth of soft tissue that reduces the ultrasonic beam to half it's surface intensity.

Coupling media:

Ultrasonic waves are not transmitted by air. Some couplant used to improve contact and reduce friction between transducer and skin during ultrasound treatments. example- Aqua sonic gel.

Air is wholly unsuitable as a contact medium, because of the almost complete reflection of the ultrasound.

4.6 Uses :

- Relief of pain
- Muscle spasm
- Joint contracture
- Adhesive capsulitis
- Calcific bursitis
- Myositis
- Tendinopathy

- Ligament sprains
- Chronic indurated edema
- Iontophoresis
- Soft tissue injuries from sports or other causes

Dangers :

- Burn
- Cavitation
- Overdose (excessive treatment may cause an exacerbation of symptoms)
- Damage to equipment (when the treatment head is held in the air, while switched on)

5 PARAFFIN WAX BATH

Fig. 5 Representing paraffin wax bath

Paraffin wax has been used for many years, it is an effective medium for heat transfer to the skin and joint. It is a form of **deep heat therapy.**A paraffin treatment uses warm **oil-based (mineral oil) wax** to provide pain relief to hand, feet, and sore joints and muscles. Liquefied paraffin wax is very efficient at absorbing and retaining heat.The warm paraffin wax applied to the skin makes the blood vessels expand and therefore helps the circulation, bringing healing nutrients to the surface and flushing toxins out of the skin.

5.1 Paraffin wax bath unit:

Paraffin wax bath therapy is an application of the molten paraffin wax on the body part. The temperature of the paraffin wax is maintaining at **42-52°c,** whereas its melting point is 51-55°c.

If the molten wax at 51-55°c is poured on the body part, it's may cause burn over the body tissue, which is why some impurity is added to lower down its melting point such as liquid paraffin, mineral oil or petroleum jelly.

The combination of the paraffin and the mineral oil has low specific heat which enhancespatient's ability to tolerate heat from the paraffin better than from thwater of the same temperature.

The composition of the solid wax: liquid paraffin: petroleum jelly is 2:1:1 or Paraffin wax: or mineral oil is 7:1 or 6:1 ratio.

The mode of the transmission of heat from paraffin to the patient skin is through conduction.

5.2 Physiological response:

Heat production:

- There is a marked increase in skin temperature in the 1st two minutes, up to 12-13°c.
- This drop, while in the wax wrapping to an increase of about 8°c at the end of 30 minutes.
- In the subcutaneous fascia, there is an increase of 5°c at the end of the treatment.
- In the superficial muscles, then in only about 2-3°c rise in temperature at the end of the treatment

Circulating effect:

- Stimulation of superficial capillaries and arterioles causes local hyperemia and reflex vasodilatation.
- Hyperemia is due to the response of the skin to its function of heat regulation.
- Skin and subcutaneous tissue temperature drop after15-20 minute, reducing the vasodilatation
- Exercise after the wax is essential to increase the muscle circulation and sedative effect of heat to obtain more range of movement and muscle strength.

Analgesic effect:

- The most important effect of wax its marked sedative effect on the tissue.
- It is this effect that is used before the exercise, in the treatment of superficially placed joints.

Stretching effect:

- Wax leaves the skin moist, soft, and pliable.

5.3 Purification of wax bath:

After use, the wax needs to be purified periodically by transferring it into a purifier before it is reused.

Techniques for purification :

- The container with the wax is added with water and the mixture is heated till the wax is melted.
- After melting of the wax the mixture is left undisturbed and allowed to cool gradually.

- After cooling it will be found that, the dirty materials have been deposited at the bottom of the container whereas the wax has solidified at the top layerWith proper care the pure wax is removed into the wax tank, leaving the dirty material in the purifier
- This is useful for stretching scar and adhesion before applying mobilization techniques.

5.4 Uses:

- Arthritic condition (like rheumatoid arthritis and other poly or oligo arthritic conditions.)
- Pain (sprain, strain affecting the small distal joint)
- Stiff joints (following trauma or disease)
- Chronic inflammation

Danger :

- Open wound
- Skin infection
- Defective skin sensation
- Ischemic conditions
- Skin allergy

5.5 Advantage:

- Low specific heat allows for application at a higher temperature than water without the risk of a burn.
- Low thermal conductivity allows for the heating of tissues to occur more slowly, thus reducing the risk of overheating the tissues.
- Molten state allows for even distribution of heat to areas like fingers and toes.
- First dip traps air and moisture to create more even heat
- Oils used in the wax add moisture to the skin.

- Wax remains malleable, after removal, allowing for use as an exercise tool.
- Comfortable, moist heat.
- Relative inexpensive to replace wax

Disadvantage:

- Effective only for distal extremities in terms of ease of
- A most effective method of application is the bath method, which limits accessibility for other body parts to be treated effectively.
- No method of temperature controls once applied.
- Heating lasts only about 20 minutes

6 CONCLUSION

Physics plays major role in medical field. Physics principles are widely use to physiotherapy instruments. This field visit to AVM hospital was very useful for me to understand the basic principles of physics used in these instruments. and this concept, techniques, application are very clear and easy to understand. Physiotherapy is a unique treatment, which is generally used to cure people suffering from pain because of an illness, injury, or a disability. It also promotes good health and fitness. The most important of this therapy it helps to avoid surgery in most case they are proved successfully. Patient are getting fast recovery with the help of devices .

STUDIES ON DENTAL PROBES AND DENTAL X RAY

A field work report submitted by

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

J. DIANA ROSARY

Reg. No: 20SPPH03

Under the guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to verify that this field work report work entitled **"STUDIES ON DENTAL PROBES AND DENTAL X-RAY MACHINE"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 -2021** by **J.DIANA ROSARY** (Register No:20SPPH03)

Signature of the Staff – In – Charge

Padmavathi SP

Signature of the Co – Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Padmavathi SP
17/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, **"STUDIES ON DENTAL PROBES AND DENTAL X-RAY MACHINE"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree, Diploma or other similar titles.

J. Dia Rosary

Station: Thoothukudi
Signature of the Student

Date: 10.03.2021
(J.DIANA ROSARY)

ACKNOWLEDGEMENT

First of all, I thank the Lord Almighty for his blessing and grace to complete this Report work.

I am deeply indebted to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA. M.Phil., Ph.D., for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her support in my work.

It is my pleasure to extend my thanks to Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., HOD & Associate Professor for her inspirational work to complete this work.

I would like to express my special gratitude to Mrs. P. PADMAVADHI M.Sc., M.Phil., SET., Head of Department, for her inspirational words to complete this report work.

I would convey my heartfelt thanks to Ms. A. VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her efficient and encouragement in successful completion of this report.

I wish to record my sincere thanks to Dr. NANCY PASCALIN B.D.S., Nancy Dental Clinic, Eraiyur, Kallakurichi (Dist.) for her enthusiastic guidance and support for completion of this field work report.

CONTENT **Page. no**

1 INTRODUCTION

Dental instruments are an essential part of the dental practice to provide dental treatment. Dental professional including dentists, hygienists, and dental assistants use various types of instruments to clean, extract, examine, manipulate, treat, restore, remove teeth and surrounding oral structures. Mostly they are non-disposable items that are used by the dental team in discharging their duties. Dental hygienists use periodontal probe, which is a small measuring device that is gently used to evaluate the health of the bone and gingiva surrounding each tooth. The periodontal probing process is the most effective way to evaluate for areas of inflammation.

Some dental instruments are referred to by their use while others are referred to by their technical name. There are three basic groups of dental instruments used in general dentistry: general instruments that are used in a variety of procedures, extraction instruments, and those instruments used for reconstruction of the teeth.

2 HISTORY OF DENTAL PROBES

The early hand-operated instruments characterized by: Large, heavy handles and inferior metal alloys in the blades. Cumbersome, difficult to use, and ineffective in many situations. There was no uniformity of manufacture or nomenclature, many dentists made their own hand instruments in an effort to find a suitable instrument for a specific need effective sterilization was a problem. Designs of some early hand instruments Dental probe and its use was first described by F.V. Simonton of the University Of California, San Francisco in 1925.He proposed flat probes 1 mm wide, 10 mm long, and notched every 2 mm. Miller suggested probing of all pockets and recording their depth and putting this information on diagnostic chart. Orban (1958) described the periodontal probe as “the eye of the operator "beneath the gingival margin. Goldman et al. stated that "Clinical probing with suitable dental instruments such as the Williams calibrated probe is a prime necessity in delineating the depth, topography and character of the dental Pocket “. Glickman stated that "The probe is an instrument with a tapered rod- like blade which has a blunt and rounded tip. “The probes most commonly used today were developed by Ram fjord in 1959.He stated that the probes in use at that time were too thick to probe narrow clinical pockets and designed a round probe with a tip diameter of 0.4mm.

In 1967, Clavind and Leo reported the results of a research protocol in which they used a dental probe tip that was 0.8 mm in diameter with a 10 gm force. In 1992, B. L. Philtrum created a classification of dental probes. In 2000, Watts extended the classification system to include a fourth and fifth generation of probes. Rationale behind dental probing Detect and measure loss or gain of attachment level to determine the extent of previous or ongoing disease activity and assess the effect of ongoing treatment.

3 CLASSIFICATION OF DENTAL PROBES

General Instruments:

- Explorer
- Scaler
- Periodontal scaler
- Mouth mirror
- Dental syringes
- Dental Chairs
- Air/Water Tip
- Anesthetic

Extraction Instrument

- Wilson
- Elevator
- Dental drill

Surgical Instruments

- Forceps
- Chisel
- Root tip elevator
- Spoon excavator

Reconstructing Equipment

- Amalgam
- Carrier
- Plugger
- Carver
- Spatula
- Burnisher

3.1 General Instruments:

The use of general instruments is not limited to any particular part of the dental practice. These instruments can be used in both hygiene and operative procedures.

Explorer:

The explorer has a variety of uses. It can be used to prod the teeth in order to check for soft spots that indicate the presents of carries, to scrape plaque or tarter off the surfaces of teeth, or to help with the placement of amalgam during the filling process.

Scaler:

The scaler is primarily used to scrape solidified plaque and tarter off the surfaces of the teeth both above and below the gum line. Occasionally, the scalar is used to scrape off excessive glue from crowns or sealant material from the application of sealants.

Mouth Mirror:

A mouth mirror or dentist's mirror is an instrument used in dentistry. The head of the mirror is usually round, and the most common sizes used are the No. 4 (⌀ 18 mm) and No. 5 (⌀ 20 mm). A No. 2 is sometimes used when a smaller mirror is needed, such as when working on back teeth with a dental dam in place. The mouth mirror has a wide range of uses. Three of its most important functions are allowing indirect vision by the dentist, reflecting light onto desired surfaces, and retraction of soft tissues. There exists 2 different norms of the thread that are not compatible to each other. The US norm have a taper thread and is mostly used in the United States, Canada, Spain and South Korea.

Indirect vision is needed in certain locations of the mouth where visibility is difficult or impossible. The posterior (or lingual) surfaces of the anterior maxillary teeth is a notable area where mouth mirrors are often used. Other areas of the mouth can be viewed more readily with the mouth mirror, even though it would be possible to see them if the dentist or dental hygienist adjusted their body into a poor position. Without the mouth mirror, poor body positioning would occur daily and lead to chronic postural problems, especially of the back and neck. There are other areas of the mouth where lighting is difficult, even with overhead dentists' lights. In these instances, the mouth mirror is used to reflect light onto those surfaces. This is especially useful if the mirror is simultaneously being used for indirect vision of an obscure area.

Fig.3.1 Mouth Mirror

Additionally, the mouth mirror is used to retract tissues, such as the tongue or cheeks, to gain better visualization of the teeth. Dentist's mirrors are also commonly used by engineers to allow vision in tight spaces and around corners in equipment. They are a common tool in optics and laser labs as well

Dental Syringes:

A dental syringe is a syringe used by dentists for the injection of an anesthetic. It consists of a breech –loading syringes fitted with a sealed cartridge containing anesthetic solution. This type of instrument has multiple parts that allow the device to produce a thin stream of a numbing agent known as local anesthetic. Syringes can be dangerous if not handled correctly. A medical instrument used to numb the mouth prevents a patient from experiencing pain when undergoing a variety of dental procedures. For example, the anesthetic used in a dental syringe can numb the nerves in a tooth that must be given root canal therapy, which is a procedure that a dentist performs to save a tooth that has been infected.

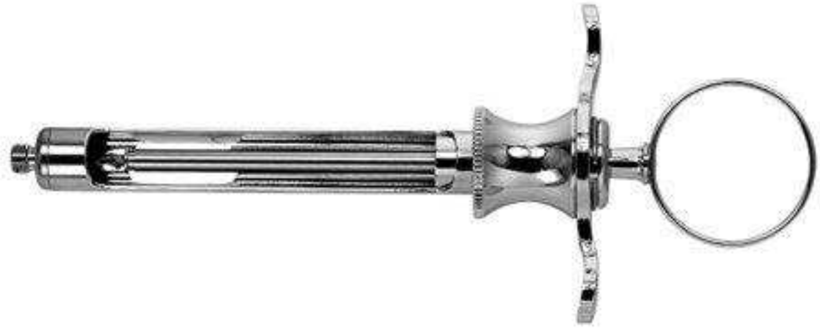


Fig.3.1.1 Dental Syringe

Dentists also use a dental syringe to locally anesthetize the gums prior to performing root planning and scaling, a treatment that involves scraping hard food deposits from the surfaces of the roots of teeth.

Periodontal Scalers:

Periodontal scalers are dental instruments used in the prophylactic and periodontal care of teeth (most often human teeth), including scaling and root planning. The working ends come in a variety of shapes and sizes, but they are always narrow at the tip, so as to allow for access to narrow embrasure spaces between teeth. They differ from periodontal curettes, which possess a blunt tip.

Uses:

Together with periodontal curettes, periodontal scalers are used to remove calculus from teeth. While curettes are often universal in that they can be used on both supra- and sub-gingival calculus removals, scalers are restricted to supra-gingival use. Use of a scaler below the gum line is likely to damage the gingiva (gums).

Fig.3.1.2 Periodontal Scaler

The anterior scaler (yellow ring) is straight, while the posterior scaler (orange ring) has an angled terminal shank (highlighted in red) to allow for easy access to the surfaces of posterior teeth.

Scalers have scraping edges on both sides of their blades and thus are fit for both mesial and distal surfaces of any tooth in the area in which they are being used. Scalers are best used when their terminal shank, namely, the last portion of the functional shank closest to the working end, is angled slightly toward the surface of the tooth.

There are two types of periodontal scaler designs:

- Anterior sickle scalers
- Posterior sickle scalers

Anterior sickle scalers:

Anterior sickle scalers are designed to be used on anterior teeth. Typically, they are constructed with one working-end and are categorized as single-ended instruments. As well, they may be combined to produce a double-ended instrument with two working ends on both sides.

Posterior sickle scaler:

Posterior sickle scalers may be used on both anterior and posterior teeth. The working ends are designed to be opposite images of one another, therefore, two posterior sickle scalers are combined to produce a double-ended instrument

Fig.3.1.3 Anterior and posterior Sickle scaler

Uses:

Together with periodontal curettes, periodontal scalers are used to remove calculus from teeth. While curettes are often universal in that they can be used on both supra- and sub-gingival calculus removals, scalers are restricted to supra-gingival use. Use of a scaler below the gum line is likely to damage the gingiva (gums).

The anterior scaler (yellow ring) is straight, while the posterior scaler (orange ring) has an angled terminal shank (highlighted in red) to allow for easy access to the surfaces of posterior teeth.

Dental Chairs:

A dental chair makes the dentist and the patient comfortable during treatment procedures. A dental chair equipped with modern technologies increases our productivity and builds confidence in patients. A dental chair should have an easily accessible control panel to adjust chair position and Programmable seat positions Backrest with soft cushion Powerful system for easy lifting up and down movements Foot control.

A compatible dental chair with all the facilities can easily be the best investment for any dental setup

Fig.3.1.4 Dental chairs

You should use the advised cleanser for dental chair disinfection. Use disposable barriers. They increase the longevity of the surface of the chair, and also aid in infection control. Be careful when using household cleaners that contain hydrogen peroxide and citric acid. They can harm the dental chair surface.

Air/Water tip:

The air/water tip is inserted into a valve that will allow the dental professional to blow air or squirt water on the desired area in the mouth. Air/water tips come in a stainless steel and disposable forms. Non-disposable syringe tips had significantly ($p < 0.05$) greater bacterial contamination than single-use disposable tips. There were no statistically different levels of contamination between flushed and non-flushed non-disposable syringes or between single-use and multiple-use non-disposable syringes. SEM and EDS analyses showed greater evidence of corrosion and contaminant build-up in multiple-use syringes compared to single-use non-disposable syringes.

Fig.3.1.5 Air/Water tip

Sterilization of non-disposable air/water syringes is not completely effective and rinsing, or the number of uses, does not affect the effectiveness of sterilization. There may be a lower risk of cross-infection from the use of disposable air/water syringe tips, instead of non-disposable ones. Due to its simplicity, a dentist orthodontist, and hygienist overlook the cross-contamination ramifications that can occur from not properly sterilizing their metal air water syringe tips.

Anesthetic:

General anesthesia is a state of unconsciousness produced by an anesthesiologist where the patient does not remember or feel anything during the procedure. In addition, the patient remains still and does not move. Novocain (local anesthesia) is used during most dental procedures. This medication is administered as an injection designed to temporarily prevent the teeth nerve fibers from transmitting impulses, thereby numbing the area. Within the rich local anesthetic drugs available in dentistry for the prevention and management of pain 4% articaine solutions achieve highest level of anesthetic potency and lowest systemic toxicity in all clinical situations, prior to its superlative physicochemical characteristics and the pharmacological profile. Ingestion of Lidocaine (also a local anesthetic, Lidocaine is a faster-acting and longer-lasting local anesthetic than procaine). Can cause numbness of the mouth and throat, which can lead to trouble swallowing and even choking. If a substantial amount is ingested, enough can be absorbed into the bloodstream to affect vital organs, primarily the brain and heart. With most local anesthetics, your tooth will be numb for 2-3 hours, while your lips and tongue will be numb for 3-5 hours after the time of injection. As the blood flow carries away the anesthetic from the injection site to be metabolized or broken down, the numb feeling will gradually fade away.

3.2 Extraction Instruments:

Extraction instruments allow the dentist to extract teeth from the mouth of the patient. These extractions can be based on the need to eliminate teeth that are too decayed to be crowned, primary teeth that need to be extracted in order to allow the permanent teeth to erupt, or to simply create space for orthodontic procedures.

Wilson:

The Wilson is the instrument that the dentist may use to pry back the gum tissue in performing an extraction. Wilsons come in many different shapes and sizes and are generally referred to as simply a small, medium, or large Wilson.

Fig.3.2 Wilson

Dental hand pieces:

Commonly known as the drill, the dentist uses the hand piece along with a variety of different bits to eliminate the decay, prepare a tooth for a crown, and to reconstruct the surface of a tooth after the bonding process. Dental Hand pieces are essential dental supplies of any practice. A hand piece is needed from the routine dental cleaning to complicated surgical procedures. Some hand pieces are specially designed to suit specific needs. Cleaning and lubricating the Hand piece as recommended by the manufacturer is a must for its better care. It also must be sterilized to avoid cross-contamination. Dental headpieces are required for most of the procedures hence you should understand these dental tools.

Fig.3.2.1 Dental Hand pieces

Types of hand pieces:

- High-speed hand pieces
- Low-speed hand pieces
- Specialist surgical hand pieces
- Laboratory hand pieces
- Hygiene hand pieces

3.3 Surgical Instruments:

User-friendly, high-quality instruments are a requisite for good dental and oral procedures. You need these instruments for extraction, implants, bone graft, and many others. These instruments help to make surgical procedures more efficient, safe and more successful.

Elevators:

Elevators (also known as luxators) are instruments used in dental extractions. They may be used to loosen teeth prior to forceps extraction, to remove roots or impacted teeth, when teeth are compromised and susceptible to fracture or when they are malpositioned and cannot be reached with forceps. During the extraction process, elevator instruments are used to pry back the gum tissue and dig underneath the tooth in order to thrust the tooth upward for extraction. These elevators also come in small, medium, and large sizes.

Forceps:

Dental forceps is another basic instrument used in dentistry for a multitude of tasks. They are used to separate tissues, hold them together, suture them, and to transport small objects to the oral cavity or out of it. Depending on the task to be performed, there are different types of forceps: surgical, ligatures, hemostatic etc... There are a variety of forceps used in extraction procedures. There are upper anterior, lower anterior, upper posterior, and lower posterior forceps. Each of these particular forceps also comes in pediatric sizes.

Fig.3.3 Forceps

Tissue Forceps:

Adson Forceps toothed at the tip used for handling dense tissue, in skin closures. Also called locking forceps, these are ratcheted instruments used to hold tissue or objects, or provide hemostasis.

Chisels:

This instrument is critical to the dental implant procedure as it is used to remove, smooth, and contour areas of bone so that implant hardware can be inserted.

Fig.3.3.1 Dental chisel

Root tip elevator:

Root tip picks, also known as root tip elevators, are delicate dental instruments used to remove root tips or fragments that may break away from the tooth during the extraction procedure and are in difficult-to-reach areas. When in use the sharp tip is placed into the periodontal ligament space and the root is teased from the socket. If the root is loose but will not elevate, a second Elevator can be placed on the opposite side of the root and lifted from the socket. Root tips can be left in place if the risks of surgery to remove the root tip outweigh the benefits of removing the root tip.

Fig.3.3.2 Root tip pick

To leave a fractured root tip in place, the root tip must be small, deep within the alveolus and must not be infected or have periapical lysis. Depending on the treatment have a range of surgical instruments to choose from. Surgical instruments must be cleaned and sterilized by using autoclave, dry heat or chemical vapor.

Spoon excavator:

Spoon excavator used for cutting and removing the carious dentine of a decayed tooth and then carving amalgam or direct wax patterns. Blades are slightly curved and cutting edges are either circular or claw like. Circular edge is known as a discoid, whereas the claw like blade is termed as cleoid Shanks may be bi-angled or triple-angled to facilitate accessibility. Spoon excavators are classified by their sizes. They are small. Medium and large The small spoon excavator has an approximate diameter of 1mm, used in smaller tooth cavities and for the cleaning the enamel dentine junction. The diameter of the medium spoon is about 1.5 mm which is used for removing soft caries from larger

Fig.3.3.3 Spoon excavator

cavities. Then the large spoon excavator is about 2mm which is used for tooth excavating and restoring procedures

3.4 Reconstruction Instruments:

Reconstruction of the teeth is done in many different ways and for numerous different reasons. Dental reconstruction includes amalgam and composite fillings, bonding, shaping, crowning, and root removal of the teeth.

Amalgam Carrier:

The amalgam carrier consists of a small tube on one end and a large tube on the other end. The dental assistant will load the ends with amalgam and hand it to the dentist who, in turn, fills the drilled out portion of the tooth with the amalgam.

Plugger:

After the amalgam is inserted into the tooth, the dentist uses the plugger to firmly pack the amalgam. This ensures all the air pockets are filled and allows the dentist to insert the maximum amount of amalgam.

Carver:

The amalgam, which is inserted into the drilled portion of the tooth, needs to have a smooth surface that will allow the upper and lower teeth to fit together when the patient bites down. The dentist uses the carver to create these crevices on the tooth's biting surface.

Spatula:

Whenever a tooth is capped, the crown, being either stainless steel or porcelain, will need to be glued to the remaining portion of the tooth. The assistant will use the spatula to mix the proper glue solution and powder to create the desired mixture. Then, the assistant will use the spatula to load the crown with the glue. Spatulas can also be used to mix temporary filling materials. While there are a countless number of dental instruments, the general, extraction, and reconstruction instruments listed above are the basic dental instruments that general dentists use.

Fig.3.4 Spatula

This is a basic list of instruments used in the field of dentistry, although; every dentist has his own preference and unique combination of dental instruments they use in their practice.

Burnisher:

Burnishers are dental hand instruments, normally used at the end of dental restoration procedures or operations. They are used for polishing and contouring amalgam fillings and to polish composite fillings. It is a process to emphasize grooves and to shave off surplus. The working end of a burnisher is smooth and rounded.

Fig.3.4.1 Burnisher

4 DENTAL INTRA ORAL CAMERAS

A dental intraoral camera is a pen-like video camera that is portable and can be connected to a screen wirelessly. It is equipped with LED and gives magnified images on the screen. These intraoral cameras save time and are the best tool when it comes to patient education.

4.1 Working of Intra Oral Cameras:

The camera wand has the lens & a light on one end & a cord leading back to the computer on the other. The light on the camera is a very important part. Even in a brightly lit dental office, it can be hard to see in the darkest parts of your mouth. The intraoral camera's brightly lit images help us get a better look at your teeth and gums.

Fig.4.1 Intra Oral Camera

Many dental professionals feel this process beats traditional tools alone, such as a headlamp & a mirror, when it comes to spotting & diagnosing abnormalities.

An intraoral camera allows us to take great “before & after” pictures. This is especially useful when replacing an old metal filling (called an “amalgam” filling) with a tooth-colored filling (called a “composite” filling). You’ll easily be able to see the huge aesthetic difference using white, natural-colored fillings can make.

Images of your teeth taken with an intraoral camera can be printed out if needed, but they primarily live in the digital realm. This makes it very easy to add photos to your digital dental record. We can easily send images to other specialists who might be involved in your care, to dental insurance companies or to dental lab technicians who are helping craft a custom tooth restoration, such as a crown.

4.2 Uses of Intraoral Cameras

- It helps in the early detection of dental problems
- Improved accuracy and better treatment
- Easy to explain the patient about the underlying problem and treatment procedure
- Images can be shared and saved for future reference.
- It is a revolutionary tool that gives live images and videos helping the patient to understand their oral situation better

5 STREILIZATION EQUIPMENT

Infection control is an important aspect of any dental practice. The dental sterilization equipment offers patient safety, avoiding any cross contamination.

Fig.5 Sterilization Equipment

Dental sterilizers are systems including autoclaves, chemical washers, or ultrasonic devices that are used clean to clean instruments and tools that require sterilizing. Short cycle time and large chamber volume are considered features of high end products.

To prevent accidental injury with the contaminated instruments, special handling should be used to transport the instruments to the cleaning and sterilization area. The Centers for Disease Control and Prevention (CDC) states that, “Contaminated instruments should be handled carefully to prevent exposure to sharp instruments that can cause percutaneous injury. Instruments should be placed in an appropriate container at the point of use to prevent percutaneous injuries during transport to the instrument processing area.” In addition, the Occupational Safety and Health Administration (OSHA) says, “The person handling the instruments through removal, cleaning, packaging and sterilization needs to use heavy-duty gloves to help prevent injury with sharp contaminated instruments." Although heavy-duty gloves (utility gloves) may feel more awkward than examination gloves, they provide extra protection while handling instruments during the cleaning, rinsing, drying, packaging and sorting procedures that take place during instrument reprocessing. The fine tactile sensitivity needed during dental procedures is not necessary during instrument cleaning and sterilization; therefore, heavy-duty gloves pose no problem in this regard. Additionally, nitrile utility gloves are available in a variety of sizes, allowing a more secure fit.

There are different types of sterilization to choose depending on our services and treatment options.

- Sterilizers or autoclaves
- Washers and dryers
- Dry heat sterilizers
- Chemical vapor sterilization

The autoclave is the most commonly used sterilization equipment. Dry heat is used to remove moisture.

6 ENDODONTIC EQUIPMENT

To provide root canal treatment, for cleaning and shaping of canals, you need endodontic equipment. Root canals are complex dental procedures that require a variety of specialized tools. Your endodontist may use some or all of the following during your root canal procedure.

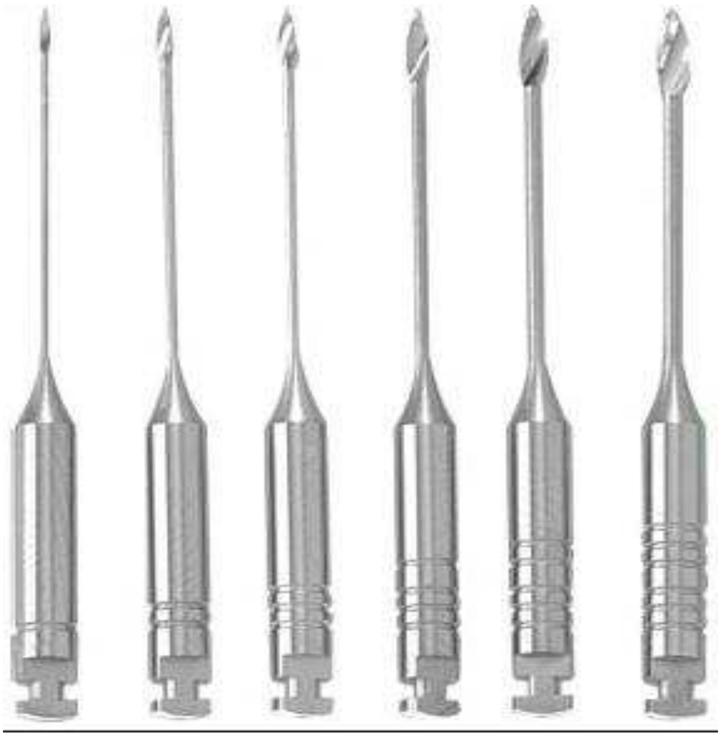


Fig.6 Endodontic Equipment

There is a variety of endodontic equipment available making it possible to achieve good results, no matter how narrow the canal is.

Endodontic Burs:

Burs are the first tools used during a root canal. They open the inside of the tooth so the canals can be reached. Burs come in different shapes and sizes depending on the type of tooth and treatment.

Root Canal Explorer:

This small, pointed tool is used to explore the inside of a tooth once it has been opened by burs so the endodontist can find orifices. Sometimes an explorer may be used to remove small amounts of calcification.

Barbed Broach:

The barbed broach is used to remove the majority of tissue from inside a tooth. It is inserted into the tissue so its barbs will grab the tissues when the tool is removed.

Files and Reamer Drills:

Like long, thin drill bits, these tools come in a variety of sizes. They are used gradually, the smallest first, to open and widen the canals so they can be accessed by the next appropriate tool.

Gates-Glidden drills:

This kind of drill bit helps to further open the canal, particular in molars. They are also used during root canal retreatment to remove gutta-percha, which is a putty-like material commonly used to fill root canals.

Piezo Reamer:

This tool is used exclusively to remove gutta-percha during retreatment.

Ultrasonic Instruments:

These tools can be used to uncover calcified canals and remove restorative and endodontic materials from the canal space within the tooth. These instruments operate through vibration and emit a high pitched sound that can be surprising when they are first turned on. Dental pulp testers help to test the pulp vitality. Apex locators measure the length of the root canal. More efficient Nickel-Titanium (Ni-Ti) endodontic shaping instruments. Endodontic hand pieces clean and shape the canal. Some procedures might need special equipment to achieve accurate root canal treatment

7 DENTAL RADIOGRAPHS

The role of exposing dental radiographs is an important one for the dental assistant and dental hygienist. Dental X-rays (radiographs) are images of your teeth that your dentist uses to evaluate your oral health. These X-rays are used with low levels of radiation to capture images of the interior of your teeth and gums. In our dental practice, diagnosis and treatment plan mainly depends on radiographic images. Digital radiography allows the dentist to view high-resolution images instantly on a computer screen. It also enables us to store to analyze the patient in time, and share the images with our colleagues. This latest technology provides added benefits to the dental imaging system with high accuracy.

7.1Types of dental X-Ray:

- Intraoral X-Ray (the X-ray film is inside the mouth)
- Extra oral X-Ray (the X-ray film is outside the mouth)

Intraoral X-rays:

These are the most common type of X-ray. There are several types of intraoral X-rays. Each shows different aspects of teeth.

Bitewing X-rays:

It show details of the upper and lower teeth in one area of the mouth. Each bitewing shows a tooth from its crown (the exposed surface) to the level of the supporting bone. Bitewing X-rays detect decay between teeth and changes in the thickness of bone caused by gum disease. Bitewing X-rays can also help determine the proper fit of a crown (a cap that completely encircles a tooth) or other restorations (such as bridges). It can also see any wear or breakdown of dental fillings.

Periapical X-rays:

It show the whole tooth from the crown, to beyond the root where the tooth attaches into the jaw. Each periapical X-ray shows all teeth in one portion of either the upper or lower jaw. Periapical X-rays detect any unusual changes in the root and surrounding bone structures.

Panoramic X-rays:

Specialized patient's full arch image and the entire mouth area (all the teeth in both the upper and lower jaws) on a single X-ray. This X-ray detects the position of fully emerged as well as emerging teeth, can see impacted teeth and helps diagnosis tumors.

Occlusal X-rays:

It track the development and placement of an entire arch of teeth in either the upper or lower jaw.

Extra oral X-rays:

These are used to detect dental problems in the jaw and skull. There are several types of extra oral X-rays.

Tomograms:

It show a particular layer or "slice" of the mouth and blur out of the layers. This X-ray examines structures that are difficult to clearly see because other nearby structures are blocking the view.

Cephalometric projections:

It show an entire side of the head. This X-ray looks at the teeth in relation to the jaw and profile of the individual. Orthodontists use this X-ray to develop each patient's specific teeth realignment approach.

Sialo gram:

It uses a dye, which is injected into the salivary glands so they can be seen on X-ray film. (Salivary glands are soft tissue that would not be seen with an X-ray.) Dentists might order this test to look for salivary gland problems, such as blockages, or Jorgen's syndrome (a disorder with symptoms including dry mouth and dry eyes. This disorder can play a role in tooth decay).

Cone beam system:

These are powerful 3D images help in dental implants, orthodontic treatment, and other clinical practices.

Digital Imaging Software:

Enhanced dental images help us to digitally plan the treatment and can be used for patient education.

Cone Beam Computerized Tomography (CBCT)

This shows 3D images, can be used for dental tumors, fractures, and facial bone related problems. This technique helps to avoid any complications during surgeries. These new options lead to better diagnosis, treatment plan, and patient education. Dental practice can reach new heights by adapting to digital radiography techniques.

MRI imaging:

It is an imaging method that takes a 3-D view of the oral cavity including jaw and teeth. (This is ideal for soft tissue evaluation.)

7.2 Dental X-ray Machine Components:

- Control panel with regulating devices.
- Extension arm or bracket enabling tube head to be positioned.
- Tube head containing x-ray tube from which x-rays are generated.
- X-rays help dentist to diagnose problems teeth and jaws.

7.3 Working principle of Dental X-Ray:

Most machine are designed to operate at 220 volts while some will work with 110 volts or 440 volts. The power company often cannot provide exactly 220 volts at all times. Because of variations in power distribution to the hospital and in power consumption by the various sections of the hospital, the voltage to the x-ray unit may vary by 5%, which will result in large variations in x-ray output. The power supplied to x-ray machine is delivered to a special transformer called an Autotransformer. It works on the principle of electromagnetic induction but is very different from conventional transformer.

Fig.7.2 Dental X-Ray Machine

7.4 Uses of Dental X-Ray:

In adults, X-rays show:

- Decay, especially small areas of decay between teeth.
- Decay beneath existing fillings.
- Bone loss in the jaw.
- Changes in the bone or root canal due to infection.
- Condition and position of teeth to help prepare for tooth implants, braces, dentures or other dental procedures.
- Abscesses (an infection at the root of a tooth or between the gum and a tooth).
- Cysts and some types of tumors.

In children, X-rays determine:

- If decay is developing.
- If there is enough space in the mouth to fit all incoming teeth.
- If wisdom teeth are developing.
- If teeth are impacted (unable to emerge through the gums).

8 CONCLUSION:

Complete set-ups have been included at the end of most sections for various procedures. The dental professional may have to modify these lists depending on operator preference. Each section is dedicated to a specific discipline or division of dentistry. Some instruments feature in many sections, and these have been included in the set-up subsections of the relevant sections. Infection control is a fundamental requirement in the dental surgery, and as such the first section is dedicated to this area. This section aim is to introduce the principles of health and safety, which must always be at the forefront of a dental professional's mind. Contact the legislative bodies for appropriate regulations and legislation relevant to your workplace.

MECHANISMS PRESENT IN THE PREPARATION OF PLASTER OF PARIS

A field work report submitted to

DEPARTMENT OF PHYSICS

ST MARY'S COLLEGE (AUTONOMOUS),THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirement for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

J.EMELDA AGNES FERNANDO

Reg. No : 20SPPH04

Under the Guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this field work entitled, " **MECHANISMS PRESENT IN THE PREPARATION OF PLASTER OF PARIS** " is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirement for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020-2021** by **J. EMELDA AGNES FERNANDO** (Register no: 20SPPH04)

Padmavathi S.I.P

Signature of Staff-In-Charge

Signature of the Co-Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Padmavathi S.I.P
17/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, " **MECHANISMS PRESENT IN THE PREPARATION OF PLASTER OF PARIS** " is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree , Diploma or other similar titles.

Emelda Agnes . J.

Station: Thoothukudi

Signature of the Student

Date: 10 . 04 . 2021

(J.EMELDA AGNES FERNADO)

ACKNOWLEDGEMENT

First and foremost, I feel obliged to our Almighty for his aid in the completion of this field project work successfully.

I am deeply indebted to our respected principal Rev. Dr. Sr. A.S.J. LUCIA ROSE M.Sc., M.Phil., Ph.D., PGDCA., for providing me this wonderful opportunity to spread my wings through this project.

I would like to extend my gratitude to our Director of SSC, Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., for her support and encouragement.

I would express my special gratitude to Dr. Sr. JESSIE FERNANDO M.Sc., M. Phil.,Ph.D., HOD and Associate Professor for her encouragement to perform this project.

I wish to extend my heartfelt gratitude to Mrs. P. PADMAVATHI M.Sc., M.Phil., SET., SSC Co-ordinator, Department of Physics , for her encouragement in completing our project.

I cordially extend my sincere gratitude to Ms. A. VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her guidance and support in the completion of the field work report.

I am extremely thankful to Mrs. B.CHELLATHAI (Proprietor), ANNAI PLASTERS, for giving me permission to enter their premises to complete this project successfully.

I sincerely acknowledge Mr. B. GUNASINGH (Co-Owner), ANNAI PLASTERS, for explaining and guiding throughout their factory for the successful completion of my field project.

I would also like to acknowledge my parents and friends for their succor throughout the fieldwork.

CONTENT **Page. no.**

1 INTRODUCTION:

ANNAI PLASTERS established in the year 2007, counted amongst leading companies for manufacturing, supplying and trading an extensive range of Plaster Of Paris, False Ceiling, Ceiling Tile, False Ceiling Accessories, False Ceiling Material and many more products. They are the sole proprietorship (Individual) based company which always provide superior quality products to their customers. Their offered products are made from high grade quality material that are specially procured from leading vendors of the market. The products they offer are used in construction, buildings, hotels, malls, decoration and many more uses.

Situated at Thoothukudi (Tamil Nadu, India), they are backed by huge infrastructure which is segregated into several segments. The departments of their infrastructure are handled accordingly by their team members who work in their specific department as per their knowledge and work allotted to them. The units in their infrastructure are production, testing, warehouse, quality control, packaging and many more. The team members work in cooperation with each other so as to handle work of each department in synchronization with each other. Under the guidance of Mrs. B. Chellathai (Proprietor) and Mr. B . Gunasingh (Co-Owner) ,the company is continuously growing to greater heights.

2 PLASTER OF PARIS:

Plaster of Paris, a quick setting gypsum plaster consisting of a fine white powder (calcium sulphate hemihydrates), which hardens when moistened and allowed to dry. It is also called as gypsum plaster or mentioned as POP (Plaster of Paris) because of its preparation from the abundant gypsum found near Paris, France. A large gypsum deposit at Montmartre in Paris led "calcined gypsum" (roasted gypsum or gypsum plaster) to be commonly known as "Plaster of Paris" .POP does not shrink or crack when dry making it an excellent medium. It is prepared from gypsum or calcium sulphate di-hydrate at high temperatures. It is in use since 15th century. The natural form of this compound is the mineral Bassanite. The chemical formula of Plaster of Paris is given as **$CaSO_4$. 1/2H_2O.**

Fig.2 Picture of Plaster of Paris (dry form)

The plaster is manufactured as a dry powder and is mixed with water to form a stiff but workable paste immediately before it is applied to the surface. The reaction with water liberates heat through crystallization and the hydrated plaster then hardens. Plaster can be relatively easily worked with metal tools or even sandpaper, and can be moulded, either on site or to make pre-formed sections in advance, which are put in place with adhesive. Plaster of Paris is non-flammable and non-combustible. Has generally low chemical reactivity but can act as an oxidizing agent under extreme conditions.

Fig.2.1 Picture of raw gypsum

3 TYPES OF PLASTER OF PARIS:

There are different types of POP and each has its own uses. They are discussed below:

3.1 Clay plaster:

Clay plaster is a mixture of clay, sand and water with the addition of plant fibres for tensile strength over wood lath. Clay plaster has been used since antiquity. Settlers in the American colonies used clay plaster on the interiors of their houses. The clay mixture is prone to shrinkage, crack and distort on drying. It will also probably drop off the wall. Sand and fine gravels were added to reduce the concentrations of fine clay particles which were the cause of the excessive shrinkage. Straw or grass was added sometimes with the addition of manure.

Clay plasters with their lack of tensile and compressive strength fell out of favor as industrial mining and technology advances in kiln production led to the exclusive use of lime and then gypsum in plaster applications. However, clay plasters still exist after hundreds of years clinging to split lath on rusty square nails. The wall variations and roughness reveal a hand-made and pleasing textured alternative to machine-made modern substrate finishes. But clay plaster finishes are rare and fleeting.

Fig.3.1 Picture of clay plaster in dry form

3.2 Gypsum plaster:

Gypsum plaster, gypsum powder or Plaster of Paris, or P.O.P. consists of white powder of calcium sulphate hemi-hydrate. It is mostly used in molding and casting. A large gypsum deposit at Montmartre in Paris led "calcined gypsum" (roasted gypsum or gypsum plaster) to be commonly known as "plaster of Paris".

Its chemical process , in producing the gypsum plaster, gypsum powder, or plaster of Paris, is obtained by heating gypsum to about 120–180 °C (248–356 °F) in a kiln:

$$\mathbf{CaSO_4.2H_2O + heat -CaSO_4.1/2H_2O + 1/2H_2O\ (released\ as\ steam).}$$

Plaster of Paris has a remarkable property of setting into a hard mass on wetting with water.Plaster of Paris is stored in moisture-proof containers, because the presence of moisture can cause slow setting of plaster of Paris by bringing about its hydration, which will make it useless after some time.

3.3 Lime plaster:

Lime plaster is a mixture of calcium hydroxide and sand (or other inert fillers). Carbon dioxide in the atmosphere causes the plaster to set by transforming the calcium hydroxide into calcium carbonate (limestone). Lime plaster was a common building material for wall surfaces in a process known as lath and plaster. A primary advantage of the material is that it is resistant to a fire within a room and so can assist in reducing or eliminating structural damage or destruction provided the fire is promptly extinguished. Lime plaster is used for frescoes, where pigments, diluted in water, are applied to the still wet plaster.

Fig.3.3 Picture of raw lime plaster

3.4 Cement plaster:

Cement plaster is a mixture of suitable plaster, sand, Portland cement and water which is normally applied to masonry interiors and exteriors to achieve a smooth surface. Interior surfaces sometimes receive a final layer of gypsum plaster. Walls constructed with stock bricks are normally plastered while face brick walls are not plastered. Various cement-based plasters are also used as proprietary spray fireproofing products.

Fig.3.4 Picture of cement and suitable plaster (gypsum plaster) on its process of mixing.

3.5 Heat-resistant plaster:

Heat-resistant plaster is a building material used for coating walls and chimney breasts and for use as a fire barrier in ceilings. Its purpose is to replace conventional gypsum plasters in cases where the temperature can get too high for gypsum plaster to stay on the wall or ceiling. The maximum working temperature of plaster is 1,200 °C (2,200 °F), so higher melting temperature materials would melt the plaster mold and decomposes at high temperature to generate toxic oxides of sulphur. Also, the sulphur produced reacts with iron, making it unsuitable for casting ferrous materials.

Fig.3.5 Picture of heat resistant plaster in dry form.

4 APPLICATIONS:

In decorative architecture:

Plaster may also be used to create complex detailing for use in room interiors. These may be geometric (simulating wood or stone) or naturalistic (simulating leaves, vines, and flowers). These are also often used to simulate wood or stone detailing found in more substantial buildings. In modern days this material is also used for False Ceiling. In this, the powder form is converted in a sheet form and the sheet is then attached to the basic ceiling with the help of fasteners. It is done in various designs containing various combinations of lights and colors. The common use of this plaster can be seen in the construction of houses.

Fig.4.1 Picture of false ceiling design made using POP

Art:

Products composed mainly of Plaster of Paris and a small amount of Portland cement are used for casting sculptures and other art objects as well as molds. Plaster is also commonly spread over an armature (form), made of wire mesh, cloth, or other materials. For these processes, limestone or acrylic based plaster may be employed, known as stucco. Plaster (often called stucco) is a far easier material for making reliefs than stone or wood.

Fig.4.2 Paintings made using POP

Funeral processes:

Plaster is used by many morticians and funeral home directors to recreate destroyed tissue, reconnect severed limbs to corpses, and to fill wounds sustained during the incident that caused the death.

Medicine:

Plaster is widely used as a support for broken bones as a bandage impregnated with plaster is moistened and then wrapped around the damaged limb, setting into a close-fitting yet easily removed tube, known as an orthopedic cast. Plaster is also used in preparation for radiotherapy when fabricating individualized immobilization shells for patients. In dentistry, plaster is used for mounting casts or models of oral tissues. These diagnostic and working models are usually made from dental stone, a stronger, harder and denser derivative of plaster which is manufactured from gypsum under pressure. Plaster is also used to invest and flask wax dentures.

Fig.4.3 Hand mold used in the bone repairment.

3D printing:

Powder bed and inkjet head 3D printing is commonly based on the reaction of gypsum plaster with water, where the water is selectively applied by the inkjet head.

Fig.4.4 A 3D Painting made with the help of POP

Fire protection:

Plasters have been in use in passive fire protection, as fireproofing products, for many decades. The finished plaster releases water vapor when exposed to flame, acting to slow the spread of the fire, for as much as an hour or two depending on thickness. It also provides some insulation to retard heat flow into structural steel elements, that would otherwise lose their strength and collapse in a fire. Fireproofing plasters are closely related to firestop mortars. Most firestop mortars can be sprayed and tooled very well, due to the fine detail work that is required of firestopping, which leads their mix designers to utilise concrete admixtures, that enable easier tooling than common mortars. Plaster of Paris is generally fire resistant and heat resistant so they can kept at high temperatures but at very high temperatures , they lose their resistive power and start to melt.

Other uses:

- It is used in making toys, decorative materials, cheap ornaments, cosmetics, black-board, chalk and casts for statue.
- It is used in chemical laboratory for sealing air-gaps in apparatus when air-tight arrangement is required.
- It is used to make historical monuments and structures.
- Used to fill small gaps on walls & roofs.

5 ADVANTAGES AND DISADVANTAGES:

Advantages:

- It is light-weighted and more durable.
- It has low thermal conductivity.
- It is quite resistant to heat naturally. So it makes good heat resisting material.
- It has good adhesion.
- It is difficult to remove once fixed.
- It has a thick surface to knock off normal cracks that occur on drying of the Plaster of Paris application on walls , roofs , etc.
- It does not cause alkali attack and is less reactive with paints so it is safe when paint is coated on it.
- It can be easily molded into any shape of desire with ease.

Disadvantages:

- It is very expensive.
- If the false ceiling made using POP is not maintained well, could become home to insects .
- It is not suitable at all environments.
- It is not suitable for exterior furnishes.
- It cannot be used in moist situations.

6 SAFETY ISSUES:

The chemical reaction that occurs when plaster is mixed with water is exothermic. When plaster sets, it can reach temperatures of more than 60 °C (140°F) and, in large volumes, can burn the skin causing upto 3rd degree burns. Some variations of plaster that contain powdered silica or asbestos may present health hazards if inhaled. People can be exposed to Plaster of Paris in the workplace by breathing it in, swallowing it, skin contact, and eye contact.

Fig.6.1 Picture of symptoms caused when POP is inhaled.

The Occupational Safety and Health Administration (OSHA) has set the legal limit (permissible exposure limit) for plaster of Paris exposure in the workplace as 15 mg/m3 total exposure and 5 mg/m3 respiratory exposure over an 8-hour workday. The National Institute for Occupational Safety and Health (NIOSH) has set a Recommended Exposure Limit (REL) of 10 mg/m3 total exposure and 5 mg/m3 respiratory exposure over an 8-hour workday.

Fig.6.2 Picture of the burns caused while POP was in exothermic reaction with water.

Exposure to high dust levels may irritate the skin, eyes, nose, throat, or upper respiratory tract. Inhalation Exposure to dust generated during the handling or sanding of the product may cause temporary irritation to eyes, skin, nose, throat, and upper respiratory tract.

Fig.6.3 Picture of things to be worn when entering the POP facility.

So it is mandatory to wear gloves to protect your skin , mask to protect your lungs , googles to protect your eyes, a sensor to detect the percentage of Plaster of Paris dust surrounding you and a laboratory coat to cover any visible parts of skin. If not properly protected we maybe entangled to symptoms which are like:

- sneezing and an itchy, runny or blocked nose (allergic rhinitis)
- itchy, red, watering eyes (conjunctivitis)
- wheezing, chest tightness, shortness of breath and a cough.
- a raised, itchy, red rash (hives)
- swollen lips, tongue, eyes or face.
- tummy pain, feeling sick, vomiting or diarrhoea.

7 MACHINERY AND THE PREPARATION PROCESS :

In the preparation of POP, the pure quality of raw gypsum is used as the source . The machinery used in the production of POP and the process is described below:

Pulverizer:

The raw gypsum is given as the input inside the pulverizer, which is a mechanical machine used for grinding large particles. It converts large pieces of gypsum into smaller sized particles mostly by crushing. A single pulverizer which is mostly used has 60HP motor which produces 1440 RPM (Revolutions per minute). The small particles are now elevated using an elevator.

Elevator:

The elevator is used to lift up the small particles to the boiler using a motor (probably 3HP motor). It has an attached filter which is inbuilt which filters out the particles, if the particle size exceeds the desired required size then the particles are pushed down again to the pulverizer for further crushing. Then the particles which are fine are considered and the ones which do not satisfy go back to the pulverizer. This process keeps on repeating itself throughout the day.

Fig.7.1Picture consisting of a pulverizer, filter and an elevator.

Boiler:

The particles entering the boiler is gypsum (calcium sulphate di-hydrate) in smaller size. Inside the boiler, there is a calcinator which under the phenomenon of calcination at high temperature (about 125^{o}C) removes 3\4th water content from gypsum and converts it into Plaster of Paris in fine size particles range and of high quality.

Calcination is a process in which the ore is heated to a high temperature below the melting point of metal in absence of air or limited supply of air. The change that takes place during calcination with reactions are moisture and water from hydrated ores, volatile impurities and organic matter are removed.

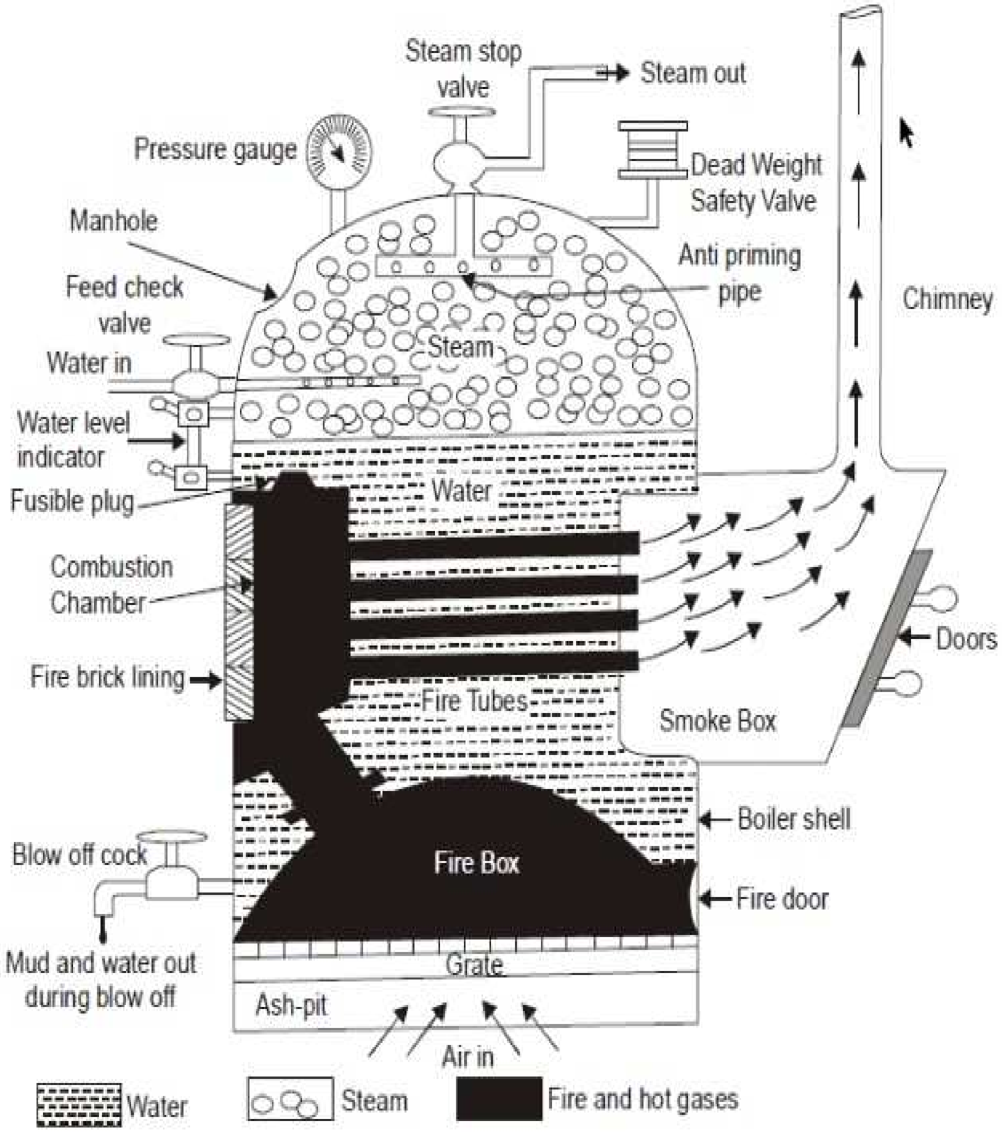


Fig.7.2 Schematic diagram of the boiler

A normal boiler has 2.5 ton capacity with the calcinator having 25HP motor with 960 RPM. The required high temperature about 125°C is achieved using the traditional method of burning firewood at the bottom layer of the boiler which has a small opening for the firewood input.

Fig.7.3 Picture of boiler containing an opening for firewood input.

The product which comes out is the required POP in pure and dry form which is packed and ready for trade and other uses. All these machinery are controlled by gear box .It is also called gypsum boiler calcinator. Calcination is also called process of purification.

Gear box:

The gear box is the control panel which controls the working of the machinery system. It converts the horizontal form of input to downward vertical form of output. The output is first given to the pulverizer to be activated, which inturn activates the elevator, which inturn activates the boiler atlast.

Fig.7.4 Picture of Gear box

It converts input to output in the ratio 6:1 for a stable supply of current for the long lasting life of the machinery used.

Generator:

To supply a steady current to the machinery with the help of gear box through motherboard, a generator is used. An engine-generator is the combination of an electrical generator and an engine (prime mover) mounted together to form a single piece of equipment. This combination is also called an engine-generator set or a gen-set.

The engine generator works on diesel with frequency 50Hz and standby power rating as 25kW. It gives 440V as output with its own air cooling system. It is connected to the motherboard.

A diesel generator (DG) (also known as diesel genset) is the combination of a diesel engine with an electric generator (often an alternator) to generate electrical energy. This is a specific case of engine-generator. A diesel compression-ignition engine is usually designed to run on diesel fuel, but some types are adapted for other liquid fuels or natural gas.

Diesel generating sets are used in places without connection to a power grid, or as emergency power-supply if the grid fails, as well as for more complex applications such as peak-lopping, grid support and export to the power grid.

Proper sizing of diesel generators is critical to avoid low-load or a shortage of power. Sizing is complicated by the characteristics of modern electronics, specifically non-linear loads.

Fig.7.5 Picture of an engine generator or genset running on diesel.

Motherboard:

The motherboard receives the current from the generator and it amplifies and supplies a steady flow of current to the gear box which inturn operates the machinery. It consists of capacitor, amplifier, regulator, etc. A capacitor is a device that stores electric charge in an electric field. It is a passive electronic component with two terminals. The effect of a capacitor is known as capacitance. An amplifier, electronic amplifier or amp is an electronic device that can increase the power of a signal.

Fig.7.6 Picture of the Motherboard connecting between genset and gear box.

A regulator is a device which has the function of maintaining a designated characteristic. It performs the activity of managing or maintaining a range of values in a machine.

Packaging:

The final stage in this process is the packaging of Plaster of Paris coming out from the boiler. They are weighed and packed in an airtight package by wearing gloves and mask inorder to preserve its purity. There are packages of different weights as per the client’s demand.

Fig.7.7 Picture of sealing machine.

The weighing is done by the electronic weighing machine manually by hand and sealing of ends is done by the sealer machine. After packaging it is ready to use for various purposes.

Fig.7.8 Picture of Packaged Plaster of Paris ready to use.

8 CONCLUSION

Based on this report, the use of PLASTER OF PARIS has led to increased economic and trade welfare in the country. Plaster of Paris is used mainly in buildings, molds and casting. The Plaster of Paris preparation from gypsum is only performed by a very few government verified companies.

In this study, we have found that Plaster of Paris made out of gypsum has more advantages compared to other types when compared with their strength, durability, usage, etc.

Thus, the preparation of molds using Plaster of Paris is also used in aircraft parts making and also in making ship parts. These are also commonly used in the sculptures and paintings.

The recent debate and research is about whether or not the usage of the Plaster of Paris in rockets to carry satellites as they are heat resistant is profitable or not. Plaster is not a strong material so it is suitable for coating rather than load-bearing, and when thickly applied it may require a hidden supporting framework, supposedly a metal.

In Physics, the usage of Plaster of Paris has not yet fully branched nor succeded but there are few traces where it has been used in basic physics applicable areas.

STUDY ON LATHE MACHINE

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

W. JENSLIN DIVONA

Reg. No: 20SPPH05

Under the guidance of

Ms. A.VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to verify that this field work report entitled "**STUDY ON LATHE MACHINE**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfillment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 -2021** by **W. JENSLIN DIVONA** (Register No.20SPPH05)

Signature of the Staff – in – Charge

Signature of the Co-Ordinator

Joyce
Signature of the Director
Director
Self Supporting Courses
St. Mary's College (Autonomous,
Thoothukudi - 628 001.

Lucia Rose
Signature of the Principal
Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21
Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, "**STUDY ON LATHE MACHINE**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree, Diploma or other similar titles.

W. Jenslin Divona

Station : Thoothukudi

Date : 10.04.2021

Signature of the student

(W. JENSLIN DIVONA)

ACKNOWLEDGEMENT

First of all I thank the Lord Almighty for his blessing and grace to complete this Report work.

I am deeply indebted to our Principal Rev. Dr. Sr. A.S.J.LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, Rev. Sr. F.MARY JOYCE BABY for her support in my work.

I would like to express my special gratitude to Rev.Dr. Sr. JESSIE FERNANDO M.Sc.,M.Phil.,Ph.D – HOD and Associate Professor for her inspirational words to complete this report work.

I would convey my heartfelt thanks to Mrs. P. PADMAVADHI M.Sc., M.Phil., SET., SSC Co-Ordinator, Department of Physics for her efficient and encouragement in successful completion of this report.

I wish to record my sincere thanks to Ms.A.VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her enthusiastic guidance and support for completion of this field work report.

And most importantly it's my pleasure to extend my thanks to Mr.BALA (MD) for his help and support to complete my field work at "KPS AUTOMATION".

I would like to record my sincere thanks to my parents and teachers for their guidance and support.

CONTENTS:

1.Lathe Machine Introduction:

Lathe machine is probably the oldest machine tool know to mankind. Its first use date back to 1300 BC in Egypt. The first lathe was a simple Lathe which is now called a two-person lathe. In this one person would turn the wood work piece using rope and the other person would shape the work piece using a sharp tool.

This design was further improved by the Ancient Romans who added the turning bow and lather the paddle (as there in the sewing machine) was added. Further during the industrial revolution Steam Engines and water wheel were attached to the Lathe to turn the work piece to a higher speed which made the work faster and easier. Then, in 1950 servo mechanism was used to control the lathe machine. From this crude begging and over a period of more than two centuries, the modern engine lathe has evolved. Now we have the most advanced form of the Lathe which is the CNC Lathe. HENRY MAUDSLAY, a British Engineer is considered as the inventor of a lathe.

2. Lathe Machine Definition:

A lathe machine is a machine tool that removes the undesired material from a rotating work piece in the form of chips with the help of a tool that is traversed across the work and can be feed deep into the work.

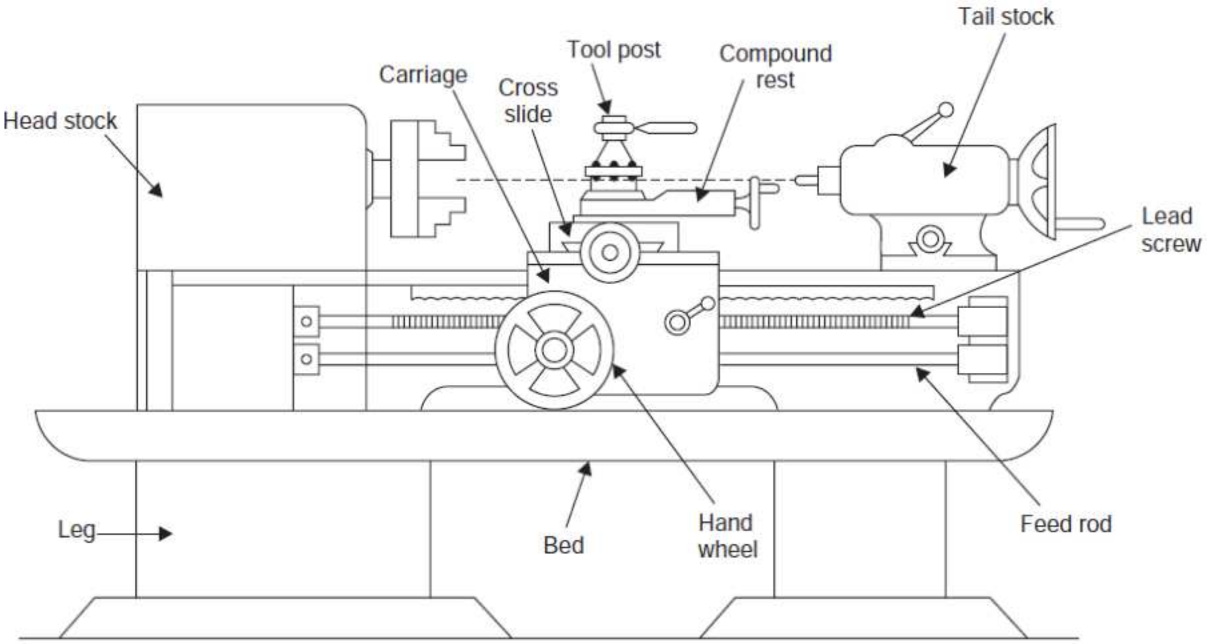
It one of the most versatile and widely used machine tools all over the world.

Pictorial Representation of lathe machine (Fig.2)

This is also known as the ‘Mother of all Machines’. Nowadays, Lathe Machine has become a general-purpose machine tool, employed in production and repair work, because it permits a large variety of operations to be performed on it.

3. Machinery Parts:

- The Lathe Machine consists of following Main Parts:
- Bed
- Headstock
- Tail stock
- Carriage
    - Saddle
    - Cross Slide
    - Compound rest
    - Tool Post
    - Apron
- Chuck
- Feed rod
- Lead Screw
- Spindle



Schematic Representation of Lathe Machine (Fig 3)

Bed: The bed of the lathe machine is the base on which all the other parts of the lathe are mounted. The bed is made from Cast iron or nickel cast iron alloy and is supported on broad box-section columns.

Its upper surface is either scraped or grounded and the guiding and the sliding surfaces are provided.

The bed consists of heavy metal slides running lengthwise. It is rigidly supported by cross griths.

The **three major units** mounted on a bed are:

1. Headstock.
2. Tailstock.
3. Carriage.

The scrapped or the ground guiding along with the sliding surfaces on the lathe bed ensure the accuracy of the alignment of these three units.

Headstock: The headstock is present on the left end of the bed. The main function of the headstock is to transmit power to the different parts of the lathe.

It supports the main spindle in the bearing and aligns it properly. It also houses a necessary transmission mechanism with speed changing levers to obtain different speeds.

Accessories mounted on the headstock spindle are:

1. Three jaw chuck.
2. Four jaw chuck.
3. Lathe center and lathe dog.
4. Collet chuck.
5. Face Plate.
6. Magnetic chuck.

Tailstock: The tailstock is a movable casting located opposite to the headstock on the way of the bed.

The **basic function of the tailstock** is:

1. To support the other end of the work when being machined.
2. To hold a tool for performing operations like drilling, reaming, tapping, etc.

It consists of the dead centers, the adjusting screws, and the hand wheel. The body of the tailstock is adjustable on the base which is mounted on the guide ways of the bed and can be moved.

Carriage: Carriage is located between headstock and tailstock. The basic function of the carriage is to support, guide, and feed the tool against the job during operation.

It consists of 5 main parts:

- Saddle
- Cross Slide
- Compound rest
- Tool Post
- Apron

Saddle: It is an H-shaped casting mounted on the top of the lathe ways. It provides support to cross-slide, compound rest, and tool post.

Cross Slide: Cross slide is provided with a female dovetail on one side and assembled on the top of the saddle with its male dovetail.

The top surface of the cross slide is provided with T slots to enable fixing of rear tool post or coolant attachment. Carriage basically provides a mounted or automatic cross-movement for the cutting tool.

Compound Rest: Compound rest is present on the top of the cross slide. It supports the tool post and cutting tool in its various positions. Compound rest is necessary for turning angles and boring short tapers and forms on forming tools.

Tool Post: The tool post is mounted on the compound rest. It is used to hold various cutting tool holders. The holders rest on a wedge which is shaped on the bottom to fit into a concave-shaped ring (segmental type),

Which permits the height of the cutting edge to be adjusted by tilting the tool. It is fixed on the top slide. It gets its movement by the movement of the saddle, cross slide, and top slide.

The three types of tool post which are commonly used are:

- Ring and rocker tool post: It consists of a circular tool post with a slot for accommodating the tool or tool holder.
- Quick change tool post
- Squarehead tool post.

Apron: The Apron is fastened to the saddle and hangs over the front of the bed. Apron consists of the gears and clutches for transmitting motion from the feed rod to the carriage, and the split nut which engages with the lead screw during cutting threads.

Two types of Apron are extensively used:

- Incorporating drop worm mechanism.
- Friction or dog clutches.

Chuck: Chuck is basically used to hold the work piece, particularly of short length and large diameter or of irregular shape which can’t be conveniently mounted between centers. It can be attached to the lathe by screwing on the spindle nose.

Four different types of chucks are most commonly used in Lathe:

- Independent or four-jaw chuck
- Three jaw or universal chuck
- Collect chuck and
- Magnetic Chuck

Independent or four-jaw chuck: It is used for irregular shapes, rough castings of square or octagonal in such jobs, where a hole is to be positioned off the center. It consists of four jaws and each jaw is independently actuated and adjusted by a key for holding the job.

Three jaw or universal chuck: It consists of three jaws that move simultaneously by turning a key and the workpiece automatically remains in the center of the chuck opening. It is used for holding a round, hexagonal bar or other symmetric work.

Collet chuck: It is mostly used in the places where production work is required such as in Capstan Lathe or automats. It is used for holding the bars of small sizes (below 63mm).

Magnetic chuck: They are of permanent magnet type or electrically operated. In Lathe, it does not have widespread use.

Feed Rod: Feed rod is a power transmission mechanism used for precise linear movement of the carriage along the longitudinal axis of the lathe. In some lathe machines instead of feed rod lead screws are used.

Lead screw: The lead screw is used mostly in the case when the threading operation is to be performed on a lathe. As we know for threading operation requires rotational movement of the job (work piece) and the linear movement of the tool (tool post).

So rotation of the job is obtained by the chuck and the desired linear motion of the tool-post (as the lead screw drives the saddle when it is engaged) is provided with the help of a lead screw.

Spindle : In machine tools, a spindle is a rotating axis of the machine, which often has a shaft at its heart. The shaft itself is called a spindle, but also, in shop-floor practice, the word often is used metonymically to refer to the entire rotary unit, including not only the shaft itself, but its bearings and anything attached to it (chuck, etc.).

A machine tool may have several spindles, such as the headstock and tailstock spindles on a bench lathe. The main spindle is usually the biggest one. References to "the spindle" without further qualification imply the main spindle.

4. Lathe Machine Working Principle:

A Lathe works on the principle of rotating the work piece and a fixed cutting tool.

The work piece is held between two rigid and strong supports called a center or in a chuck or in faceplate which revolves.

Lathe removes the undesired material from a rotating work piece in the form of chips with the help of a tool that is transverse across the work and can be fed deep in the work.

The main function of the lathe is to remove the metal from a job to give it the required shape and size.

The normal cutting operations are performed with the cutting tool fed either parallel or at right angles to the axis of the work.

The cutting tool can be fed at an angle relative to the axis of the work for machining tapers and angles.

5. Products made by Lathe Machine:

A variety of products can be made from the lathe machine and that are Nuts, bolts, piston, ram, pump part, electric motor parts, sleeves, Aircraft parts, gun barrels, candlesticks, train parts, cue sticks, wooden bowls, baseball bat, crankshaft and many more things.

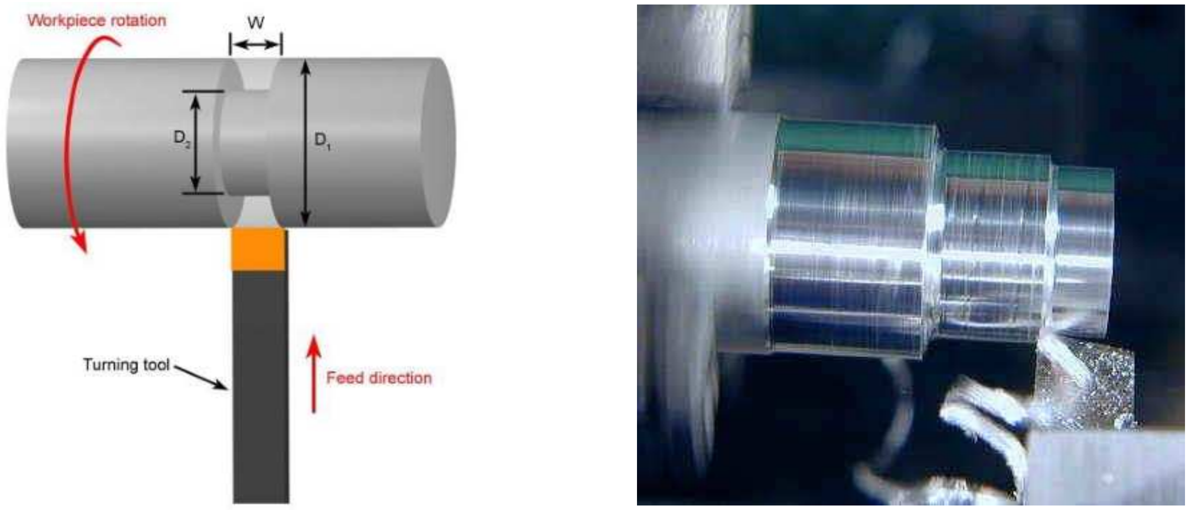
Pictorial Representation of Products (Fig 5)

6. Different Operation Performed on Lathe Machine:

The following different types of Lathe Machine Operation are:

- Turning Operation
- Tapered Turning
- Shoulder Turning
- Facing Operation
- Thread cutting operation
- Parting Operation
- Chamfering Operation
- Knurling Operation
- Drilling Operation
- Boring Operation
    - Counter Boring Operation
    - Countersinking Operation
- Reaming Operation

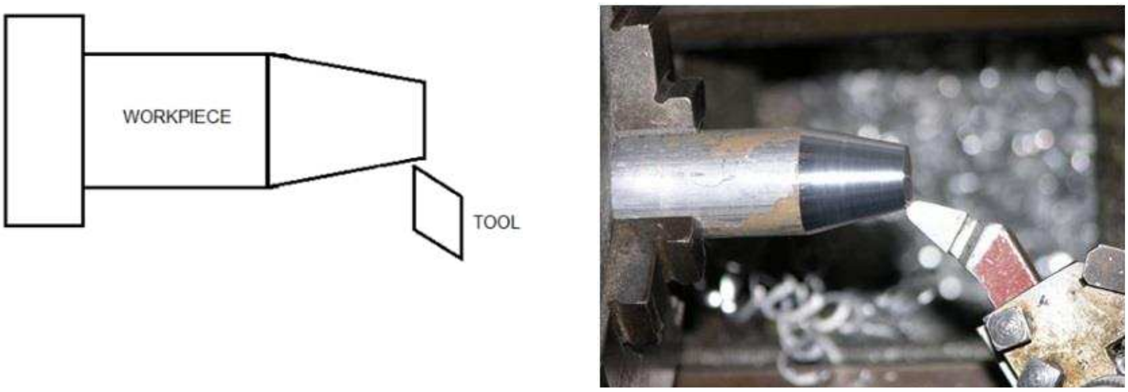
6.1. **Turning Operation**: Turning is the most common operation performed on the lathe. Turning is a machining operation in which the diameter of the work piece is being reduced by removing the excess material from the outer diameter of the job (work piece) which is mostly cylindrical or conical in shape. Turning operation results in the good surface finish of the metal.



Pictorial Representation of Turning Operation (Fig 6.1)

The various type of turning operation are:

6.2 Tapered Turning Operation: Tapered Turning is a machining process in which the cylindrical jobs are being machined to produce a conical surface. In taper Turning the tapered component will be produced.



Pictorial Representation of Tapered Turning Operation (Fig 6.2)

The various methods used for Taper Turning are:

- Compound Rest Method
- Tailstock Method.
- Taper Turning Attachment method
- Form tool Method.

Let’s discuss each method in brief:

FEATURES:

1. It can be used for both internal, external operations.
2. Up to 0.1degree accuracy can be produced.
3. Maximum taper angle which can be produced is 8 degree.
4. The maximum taper length of the component in one sitting is 235mm.

Compound Rest Method: In compound Rest Method the compound rest is swiveled by an angle equal to the required taper angle on the component. Any taper angle can be produced by this method and both internal and external taper turning operations can be performed by this method.

Tailstock method: The method is used for producing only external tapers. In this method, the tailstock is moved from its middle position to one side of the bed, which makes the work piece tilted with respect to the lathe axis and feed.

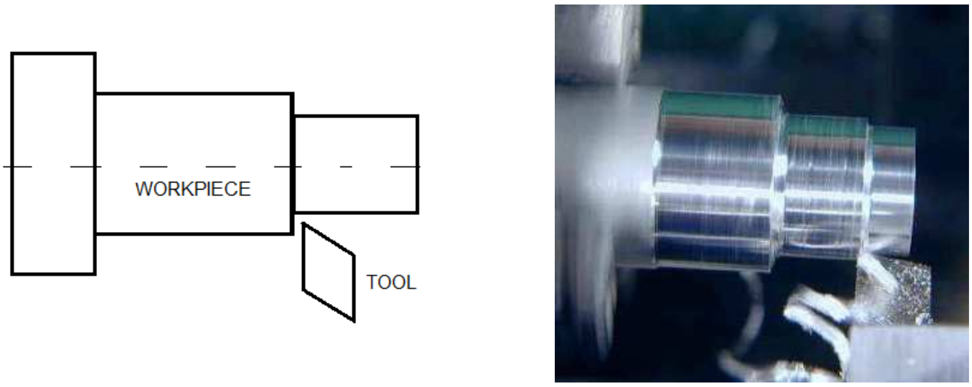
Thus, when the tool moves it cuts the work piece at an angle to the axis creating a taper.

Taper Turning Attachment Method: In taper turning attachment method the slideways are tilted by an angle equal to the taper angle of the component so that the saddle is automatically tilted and when the saddle is moving on the slideways it produces a tapered component

Form Tool method: The form tool method is used for producing external tapers only. The form tool method is a type of method in which the shape of the tool is the same as that of the shape of the component to be produced. Whatever the angle on the tool that can be produced on the component.

Accuracy produced on the component depends upon the accuracy present on the tool. It is mostly used in the chamfering operation.

6.3 Shoulder Turning Operation: Shoulder Turning is used in the case where several diameters are to be turned on the work piece. The surface forming the step from one diameter to the other is called the shoulder.



Pictorial Representation of Shoulder Turning Operation (Fig 6.3)

SHOULDER TURNING Operation

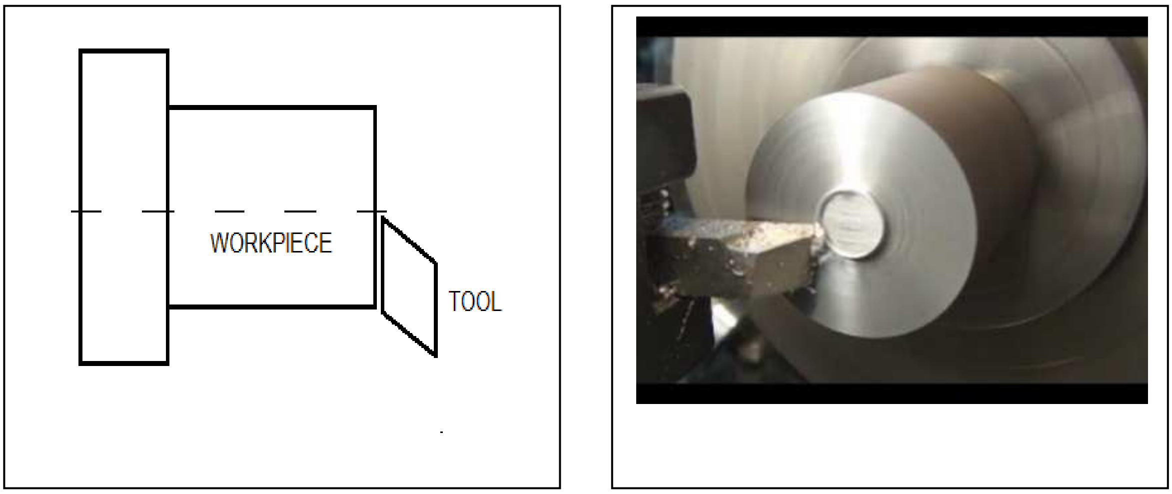
There are four types of shoulder:

1. Square
2. Beveled
3. Radius and
4. Undercut.

A right-cut tool is used to make the square shoulder.

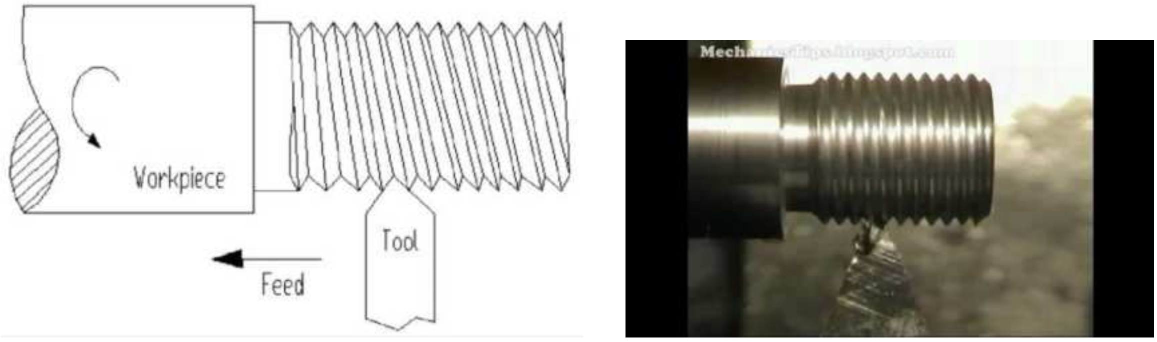
6.4 Facing operation: Facing is a process in which the end of the work piece is being machined by the tool which is at a right angle to the axis of the rotation of the work piece.

Facing is frequently the first operation performed in the production of the work piece and often the last. We can relate it to the phrase" ending-up", which will help us in remembering its sequence.



Pictorial Representation of Facing Operation (Fig 6.4)

6.5 Thread cutting operation: Thread cutting is a type of operation in which the threads are being cut on the internal and the outer surface of the workpiece as per the requirement.



Pictorial representation of Thread cutting operation (Fig 6.5)

In the thread cutting operation, only the automatic feed is given.

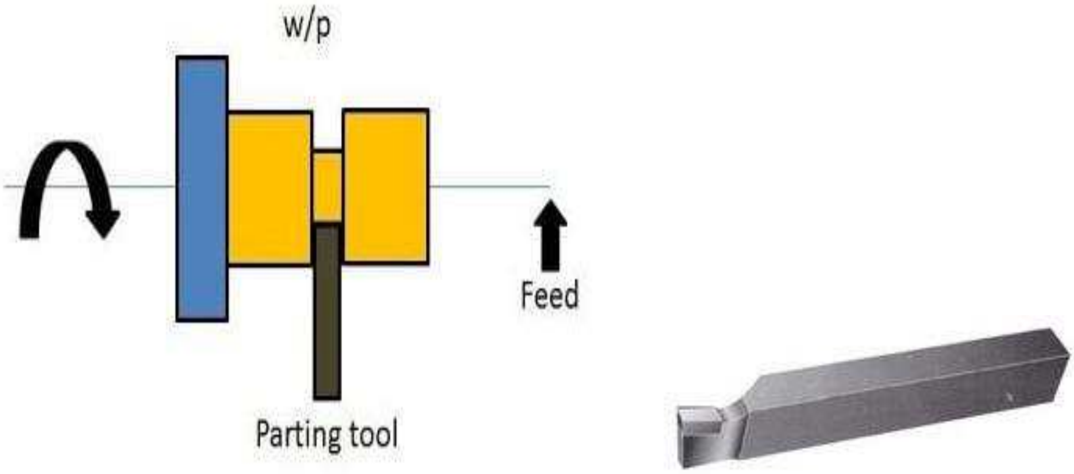
The automatic feed required for the thread cutting operation is given by using a lead screw and the feed gearbox.

127 toothed gear is used for producing Metric threads on engine Lathe.

The feed of the lead screw has to be changed in order to get the different pitch of thread on the job.

Job speed: Job speed during threading is up to 1/4th of the job speed during turning.

6.6 Parting Operation: Parting is an operation in which the deep groves are being made on the parent material to remove the specific portion from the parent material resulting in dividing the work piece into two or more parts.

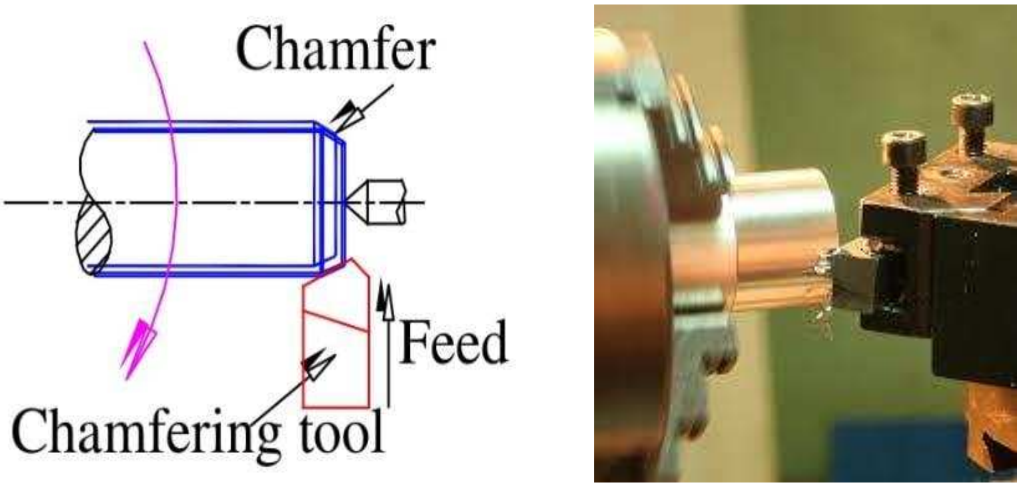


Pictorial representation of Parting Operation (Fig 6.6)

6.7 Chamfering Operation: Chamfering is the operation of beveling the extreme end of a workpiece. Chamfering is provided for:

1. Better look.
2. To enable the nut to pass freely on the threaded workpiece.
3. Remove burrs and
4. Protect the end of the workpiece from being damaged.

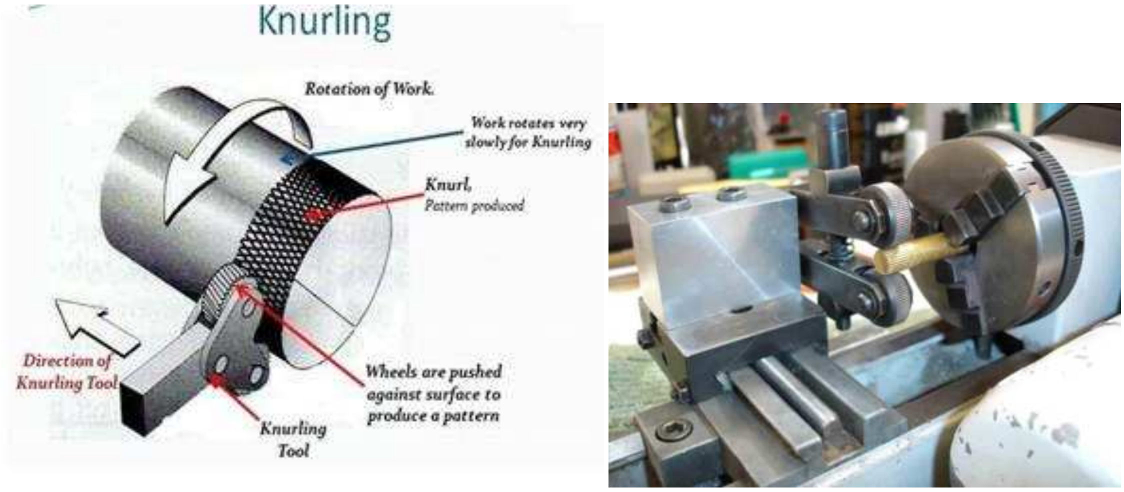
Chamfering is done usually after knurling, thread cutting, etc…



Pictorial representation of Chamfering Tool (Fig 6.7)

6.8 Knurling Operation: The process of making the surface of the work piece rough by embossing (impressing) a diamond-shaped regular pattern on the surface by making use of a knurling tool is called a knurling operation.

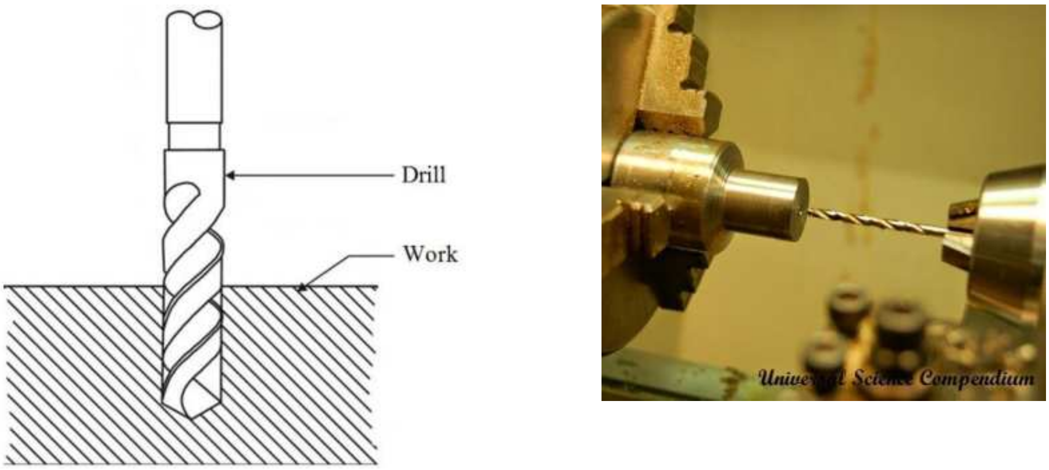
Knurling is done at a lower speed and plenty of oil is used. Knurling provides an effective gripping surface on a work piece to prevent it from slipping when operated with hand.



Pictorial representation of Knurling Operation (Fig 6.8)

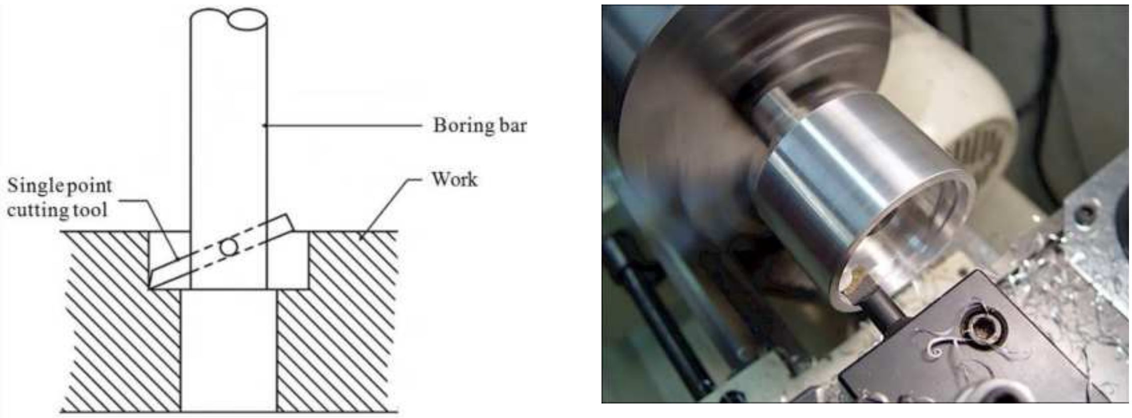
6.9 Drilling Operation: Drilling operation is a type of machining operation which is used to remove the material from the work piece by making use of a drill bit, which is held stationary in the Tailstock. Finally creating a hole in the work piece.

Drill bits are generally made up of high-speed steels and carbon steels.



Pictorial representation of Drilling Operation (Fig 6.9)

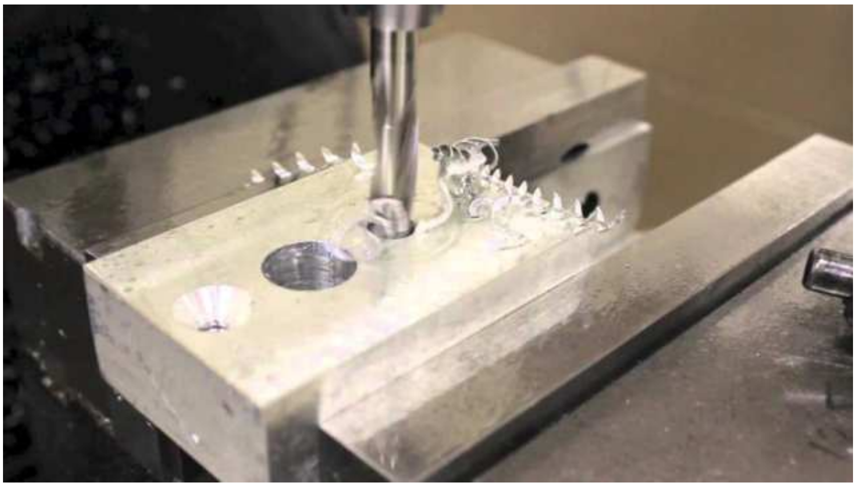
6.10 Boring Operation: Boring is an internal turning operation used for enlarging the existing holes by some amount.



Pictorial Representation of Boring Operation (Fig 6.10)

Boring Operation : It can further be divided as:

- **6.10.1 Counter boring Operation**: Counter boring is an internal turning operation used for enlarging the end of the holes.

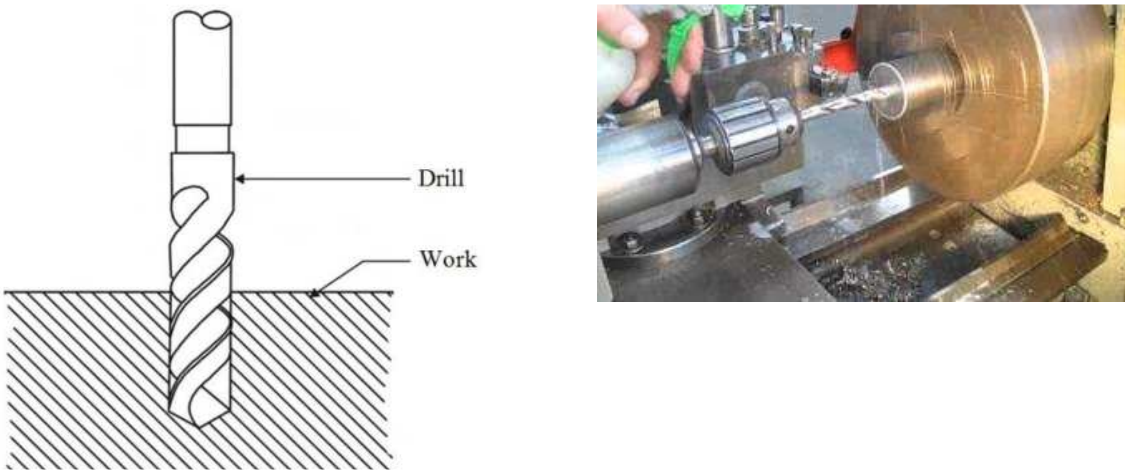


Pictorial Representation of Counter Boring Operation (Fig 6.10.1)

- **6.10.2 Countersinking Operation:** Counter Sinking is the operation of the conical enlargement of the end of the hole. It requires a large size drill bit then that required for the hole.

Pictorial Representation of Counter Sinking Operation (Fig 6.10.2)

6.11 Reaming Operation: It is a machining process that is done after drilling to make internal holes of a very accurate diameter. This operation helps to remove a very small amount of material from the holes which are already drilled.

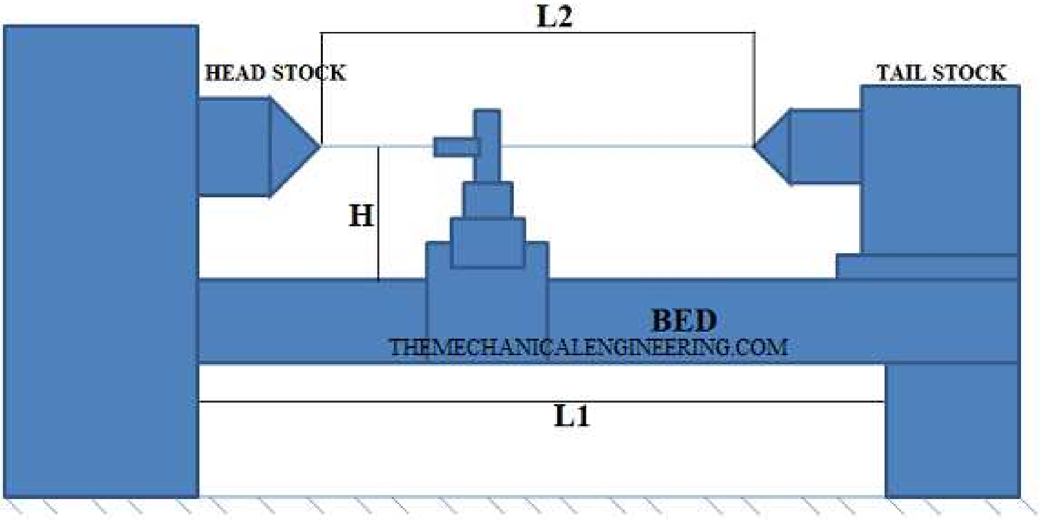


Pictorial Representation of Reaming Operation (Fig 6.11)

7. Lathe Machine Specification:

In order to specify the lathe Machine completely the following parameter should be included:

- The length between the two centers
- Height of the center
- Swing Diameter over the bed
- Maximum bar diameter
- Tailstock sleeve travel
- Metric thread pitches
- Lead screw Pitch
- Motor horsepower and RPM
- Shipping dimension: (length x width x height x weight).



Specification Diagram (Fig 7)

Lathe Machine Specification

a) The length between the two centers:

It is the measure of the maximum length of the work piece that can be fixed between the lathe center.

b) Height of the center:

The distance between the lathe axis and the lathe bed is called the height of the center.

c) Swing Diameter over the bed:

It is the maximum diameter of the work piece that can we turned on a lathe without hitting the lathe bed.

d) Maximum bar diameter:

It is the maximum diameter of the work piece that can be passed through the hole in the headstock.

Other factors for the lathe specification are:

- Tailstock sleeve travel.
- Metric thread pitches.
- Lead screw Pitch.
- Motor horsepower and RPM.
- Shipping dimension: (length x width x height x weight).

8. Application of Lathe Machine:

The following application of Lathe Machine are:

- Metalworking operations,
- Metal spinning,
- Thermal spraying,
- In the automobile industry mainly in the crankshaft, woodturning, Glass turning operation, for forming screw threads, also used for reclamation of the parts, and many more.

A CNC lathe finds extensive use in the several tasks being performed by it in various industries like:

- Textile
- Power Generation
- Defense
- Medical
- Plastic
- Aerospace
- Automotive
- Automobile industries.

9. Advantages of the Lathe machine:

Lathe Machine has numerous advantages, some of them are:

- The lathe is a High-quality product.
- It has a high speed.
- It also Saves time and
- Saves Money

a) **High-Quality Products**: Lathe machine, especially the CNC Lathe machine, produce final products with high quality.

b) **High Speed**: The machining in the lathe can be done at a very high speed especially in automatic and CNC lathe machines.

c) **Saves time:** Lathe machine because of its extensive high speed and high accuracy saves a lot of time, resulting in the increased production.

d) **Saves Money**: Lathe machine helps in reducing the cost of machining because fewer operators are required for machining.

10. Disadvantages of Lathe Machine:

Lathe Machine has some disadvantages too, some of them are:

- The Initial cost is very high.
- The high skilled worker required for the initial setup.

11. Conclusion

In conclusion the final outcome of products were precise and accurate thus leading to the success of study. Although a few random and systematic errors were observed in the dimension of the pieces the workshop was overall a success and enabled us to learn more about the working process of a lathe machine. The experiment is better performed by or in presence of certified individual.

STUDY ON MANUFACTURING OF MACHINES

A field work report submitted to
DEPARTMENT OF PHYSICS
ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI
Affiliated to
MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI
In partial fulfilment of the requirements for the award of
MASTER OF SCIENCE IN PHYSICS
Submitted by
J. KAROLIN ANGEL
Reg. No : 20SPPH06
Under the guidance of
Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS
ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI
(Re-accredited with 'A+' Grade by NAAC)
2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled **"STUDY ON MANUFACTURING OF MACHINES"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020-2021** by **J.KAROLIN ANGEL** (Register No: 20SPPH06)

Signature of the staff-in-charge

Signature of the co-ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled **"STUDY ON MANUFACTURING OF MACHINES"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field work report has been submitted for any Degree , Diploma or other similar titles.

Station: Thoothukudi

Date: 10 /04/2021

Signature of the student

(J.KAROLIN ANGEL)

ACKNOWLEDGEMENT

First of all, I thank the Lord Almighty for his blessing and grace to complete this report work.

I am deeply indebted to our principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her support in my work.

I would like to express my special gratitude to Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., Head of Department, for her inspirational words to complete this report work.

I would convey my heartfelt thanks to Mrs. P. PADMAVADHI M.Sc., M.Phil., SET., SSC Co-ordinator, Department of physics for her efficient and encouragement in successful completion of this report.

I wish to record my sincere thanks to Ms. A. VALENTINA M.Sc., M.Phil., Assistant professor, Department of Physics for her enthusiastic guidance and support for completion of this field work report.

It is my pleasure thanks J.M.J.ENGINEERING WORKS, Thoothukudi for help and support to complete my field work.

CONTENT **Page. no.**

1 INTRODUCTION

The first known painting showing a lathe dates to the 3^{rd} century BC in ancient EGYPT. The Lathe was very important to the industrial revolution. It is known as the mother of machine tools, as it was the first machine tool that led to the invention of other machine tools.

During the Iron Age the Egyptians and people in the eastern Mediterranean area learned to weld pieces of iron together.

The cutting process was one of the earliest processes to be discovered, which used a laser beam, with several types being invented at the same time.. This is also the same year as the crystal laser process for cutting was developed, which was also founded at Bell Labs in 1964, albeit by a different engineer named J.E.

The first new drilling technology came in 1683, when Henning proposed a new drill system that used on vertical holes and the drill steel would be pounded into the rock to start.

2 LATHE MACHINE

Lathe Machine is one of the oldest machine tools in the production machine. This Machine is also known as the "MOTHER OF ALL MACHINES". Lathe machine is probably the oldest machine tool know to mankind. The first lathe was a simple Lathe which is now called a two-person lathe. In this one person would turn the wood workpiece using rope and the other person would shape the workpiece using a sharp tool. This design was further improved by the Ancient Romans who added the turning bow and lather the paddle (as there in the machine) was added. Further during the industrial revolution Steam Engines and water wheel were attached to the Lathe to turn the workpiece to a higher speed which made the work faster and easier.

Then, in 1950 servo mechanism_was used to control the lathe machine. From this crude begging and over a period of more than two centuries, the modern engine lathe has evolved. Now we have the most advanced form of the Lathe which is the CNC Lathe. **HENRY MAUDSLAY,** a British Engineer is considered as the inventor of a lathe.

2.1 Definition:

A lathe machine is a machine tool that removes the undesired material from a rotating the workpiece in form of chips with the help of a tool that is traversed across the work and can be feed deep into the work. It one of the most versatile and widely used machine tools all over the world.

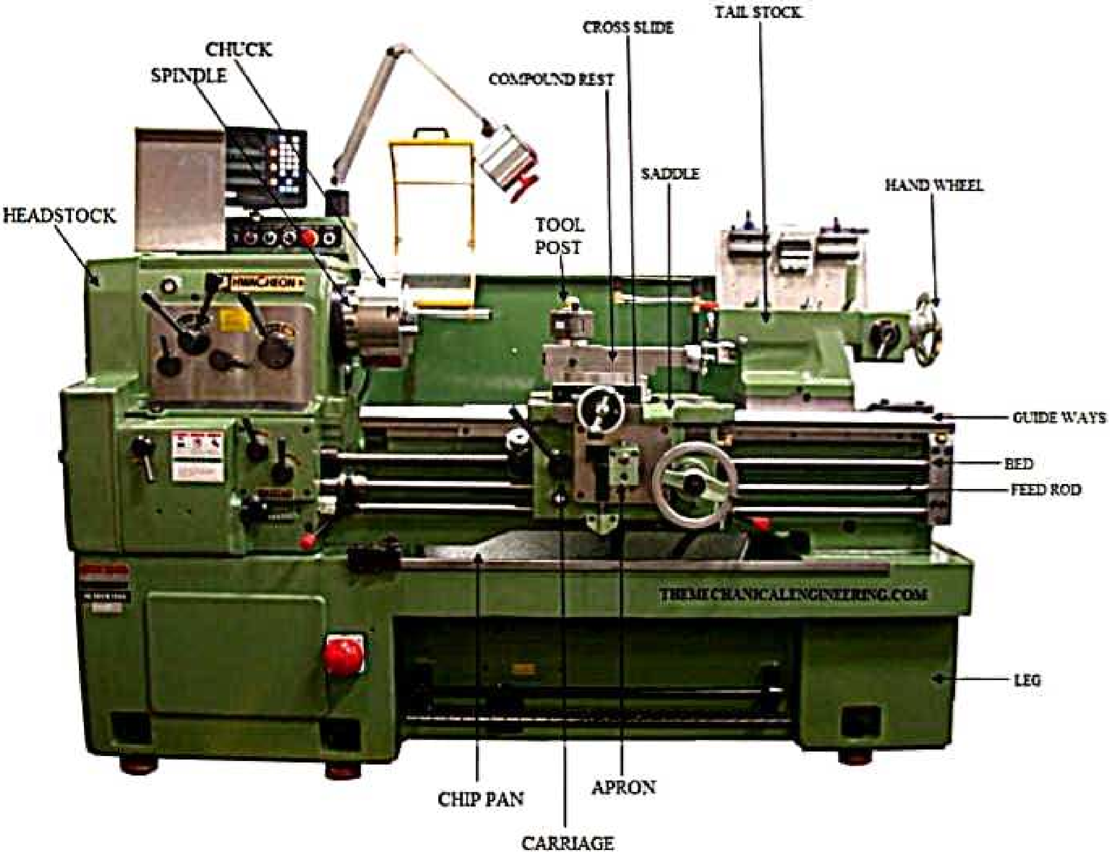


Fig. 2.1 Lathe Machine

This is also known as the '**Mother of all Machines**'. Nowadays, Lathe Machine has become a general-purpose machine tool, employed in production and repair work, because it permits a large variety of operations to be performed on it.

2.2 Parts:

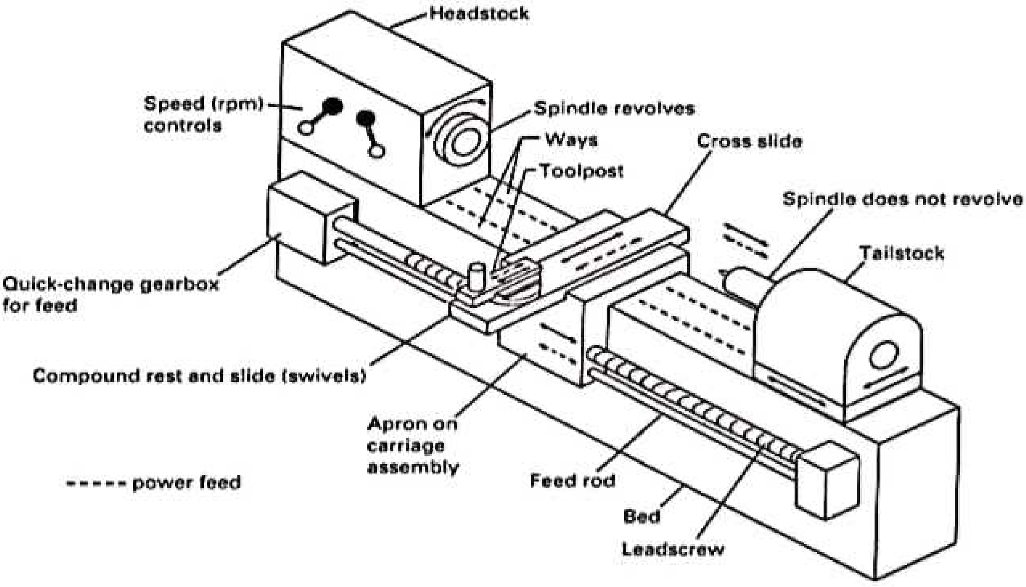


Fig. 2.2 lathe machine parts

- Bed
- Headstock
- Tail stock
- Carriage
- Saddle
- Cross Slide
- Compound rest
- Tool post
- Apron
- Chuck
- Feed rod
- Lead Screw
- Spindle

2.3 Working Principle:

A Lathe works on the principle of rotating the workpiece and a fixed cutting tool. The workpiece is held between two rigid and strong supports called a center or in a chuck or in faceplate which revolves. Lathe removes the undesired material from a rotating workpiece in the form of chips with the help of a tool that is transverse across the work and can be fed deep in the work. The main function of the lathe is to remove the metal from a job to give it the required shape and size. The normal cutting operations are performed with the cutting tool fed either parallel or at right angles to the axis of the work. The cutting tool can be fed at an angle relative to the axis of the work for machining tapers and angles.

2.3.1 Products made by Lathe Machine:

A variety of products can be made from the lathe machine and that are Nuts, bolts, piston, ram, pump part, electric motor parts, sleeves, Aircraft parts, gun barrels, candlesticks, train parts, cue sticks, wooden bowls, baseball bat, crankshaft and many more things.

2.4 Types:

There are **10 different types of Lathe Machine** and those are:

- Engine Lathe or Center Lathe
- Speed Lathe
- Turret Lathe
- Capstan Lathe
- Tool room Lathe
- Bench Lathe
- Gap bed lathe
- Hollow spindle lathe
- Vertical Turret Lathe
- CNC Lathe Machine.

2.5 Different Operation:

- Turning Operation
- Tapered Turning
- Shoulder Turning
- Facing Operation
- Thread cutting operation
- Parting Operation
- Chamfering Operation
- Knurling Operation
- Drilling Operation
- Boring Operation
- Counter Boring Operation
- Countersinking Operation and
- Reaming Operation

Feature:

- It can be used for both internal, external operations.
- Up to 0.1degree accuracy can be produced.
- Maximum taper angle which can be produced is 8 degree.
- The maximum taper length of the component in one sitting is 235mm.

2.6 Application:

- Metalworking operations,
- Metal spinning,
- Thermal spraying,
- In the automobile industry mainly in the crankshaft, woodturning, Glass turning operation, for forming screw threads, also used for reclamation of the parts, and many more.

2.7 Advantages:

Lathe Machine has numerous advantages, some of them are:

- The lathe is a High-quality product.
- It has a high speed.
- It also Saves time and
- Saves Money

High-Quality Products: Lathe machine, especially the CNC Lathe machine, produce final products with **high quality**.

High Speed: The machining in the lathe can be done at a very high speed especially in automatic and CNC lathe machines.

Saves time: Lathe machine because of its extensive high speed and high accuracy saves a lot of time, resulting in the increased production.

Saves Money: Lathe machine helps in reducing the cost of machining because **fewer operators** are required for machining.

2.8 Disadvantages:

Lathe Machine has some disadvantages too, some of them are:

- The Initial cost is very high.
- The high skilled worker required for the initial setup.
- CNC machines can not use for small production.

3 ELECTRIC WELDING MACHINE

The electric welding machine uses the high-temperature arc generated when the positive and negative poles are instantaneously short circuited to melt the solder on the electrode and the material to be welded, and the purpose of combining the objects to be contacted. Its structure is very simple, it is a high-power transformer.

Fig. 3(a) Electric Welding

Electric welding machines can generally be divided into two types according to the output power source, one is AC power and the other is DC. They use the principle of inductance, the inductance will produce a huge voltage change when the inductance is turned on and off, and the high voltage arc generated when the positive and negative poles are short-circuited instantaneously is used to melt the solder on the electrode to achive the purpose of atomic bonding.

Fig. 3(b) Welding Machine

3.1 Principle

It uses the high-temperature arc generated when the positive and negative poles are short-circuited instantaneously to melt the solder and the material to be welded on the electrode to achieve the purpose of combining them. The structure of the electric welding machine is very Simple. To put it bluntly, it is a high-power transformer, which converts 220/380V AC into a low-voltage, high-current power supply, which can be DC or AC. Welding transformers have their own characteristics, that is, they have a sharp drop in voltage. After the electrode is ignited, the voltage drops. In the adjustment of the working voltage of the welding machine, in addition to the primary 220/380V voltage conversion, the secondary coil also has a tapped voltage conversion, and at the same time, it is adjusted by an iron core. The adjustable iron core welding machine is generally It is a high-power transformer, which is made by using the principle of inductance. The inductance will produce huge voltage changes when it is switched on and off. The high voltage arc generated by the instantaneous short circuit of the positive and negative poles is used to melt the welding rod. Solder to achieve the purpose of combining them. A voltage is applied between the electrode and the workpiece, and the arc is ignited by scratching or contacting, and the energy of the arc is used to melt the electrode and heat the base material.

3.2 Advantages:

Electric welding machine uses electric energy to convert electric energy into heat energy instantly. Electricity is very common. The electric welding machine is suitable for working in a dry environment and does not require too many requirements. Because of its small size, simple operation, convenient use, and fast speed, after welding, the advantages of strong welds are widely used in various fields, especially for parts requiring high strength. It can instantly connect the same metal materials permanently. Afterheat treatment, the welds will have the same strength as the base metal. The sealing is very good, which solves the problems of sealing and strength for the manufacture of storage gas and liquid containers.

3.3 Disadvantages:

During the use of the electric welding machine, a certain magnetic field will be generated around the welding machine. When the arc burns, radiation will be generated to the surroundings. The arc light contains infrared rays, ultraviolet rays, and other light species, as well as metal vapor and smoke, and other harmful substances. Therefore, adequate protective measures must be taken during operation. Welding is not suitable for high-carbon steel welding. Due to the process of crystallization, segregation, and oxidation of weld metal, the welding performance of high-carbon steel is poor, and it is easy to crack after welding, resulting in hot and cold cracks. Low carbon steel has good welding performance, but the process must be handled properly. Dusting and cleaning are more cumbersome. Sometimes the weld will have defects such as slag inclusion, cracks, pores, and undercuts, but the proper operation will reduce the occurrence of defects.

4 CUTTING

Cutting is the separation or opening of a physical object, into two or more portions, through the application of an acutely directed force.

Implements commonly used for cutting are the knife and saw, or in medicine and science the scalpel and microtome. However, any sufficiently sharp object is capable of cutting if it has a hardness sufficiently larger than the object being cut, and if it is applied with sufficient force. Even liquids can be used to cut things when applied with sufficient force.

Cutting is a compressive and shearing phenomenon, and occurs only when the total stress generated by the cutting implement exceeds the ultimate strength of the material of the object being cut. The simplest applicable equation is:

Stress = force/area or $T=F/A$

The stress generated by a cutting implement is directly proportional to the force with which it is applied, and inversely proportional to the area of contact.[1] Hence, the smaller the area (i.e., the sharper the cutting implement), the less force is needed to cut something. It is generally seen that cutting edges are thinner for cutting soft materials and thicker for harder materials. This progression is seen from kitchen knife, to cleaver, to axe, and is a balance between the easy cutting action of a thin blade vs strength and edge durability of a thicker blade.

4.1 Movement:

Broadly defined, two movements-cutting and feeding are required in machining. Cutting is the movement that cut off parts from the workpiece, and generally is achieved by a cutting tool moving in a straight line.

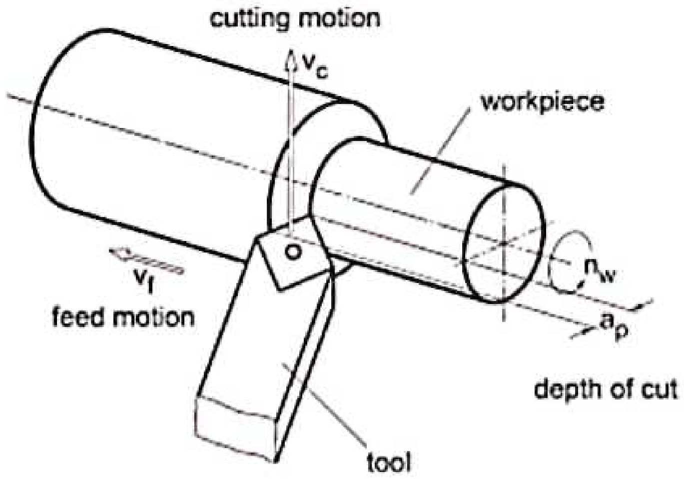


Fig. 4.1 Movements

An Introduction to Machine Tools

Machine refers to using machines to process materials according to the specifications based on the pieces of equipment essential to achive this. Machine tools are useful as machines that produce not only machine tools themselves.

With the progression of the digitization of machine tools, high-performance Manufacturing may see within reach for any manufacturer through the introduction of machine tools, but this is not always the case. In addition to simply introducing machine tools, manufacturers have employed creative use of machine tools, making their own tools and jigs, including tool bits (cutting tools), and developing original techniques. These efforts are still crucial today even with drastic increases and improvement in NC (numerical control) and CNC (computerized numerical control). It is often said on the work floors that even the most advanced machine tools "have a uniqueness in each model." Operators fine-tune the parameters according to the individual characteristics of the machine tool to constantly achieve precision cutting. In conclusion, when using machine tools, it is crucial to be versed in the characteristics of the machines and to be creative in order to fully utilize the machines' potential based on the understanding of the individual qualities. Moreover, knowing about machine tool on their own does not make one an excellent engineer. The knowledge of the origin of machine tools—how line marking, cutting, bending, and filing are done manually—also leads to work excellence.

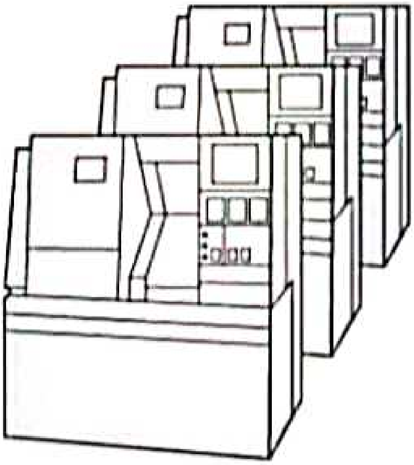


Fig. 4.1.1 Cutting machine

Knowing and understanding an individual machine tool's peculiarities well, in addition to knowing its functions and performance, produces good machining.

4.2 Precision Factors:

Stiffness

When an object is subjected to a force, the shape attempts to change while also generating a force to resist this change. This property is called stiffness. For machine tools, the stiffness is the key to successful machining with the desired accuracy. While today's machine tools are capable of progressively meeting stiffness requirements, in cases where micron-order precision is necessary, operators need a deeper understanding of stiffness.

Stiffness can be categorized into two types, static stiffness and dynamic stiffness. Static stiffness, explained as simply as possible, is stiffness when the direction and magnitude of the force are constant. With machine tools, the moving part is not moving on the table. Strictly speaking, the table is deformed by the weight of the moving part. While the actual impact is extremely small, in some cases the machining precision may decrease.

Thermal deformation

Objects expand with increases in temperature. Metals are no exception to this law, and to accurately measure length, the measuring room must be completely temperature-regulated. In machining, operators need to take particular care to prevent thermal deformation in workpieces. This is because machine tool components generate heat when the machine tool is in operation, increasing the temperature of the workpieces being cut. Thermal deformation becomes a greater consideration as the machine tool continues to operate. Therefore, it is important to know the temperatures at different points of an operation in order to ensure precision machining. Machine tools must be designed to prevent vibrations and heat that can affect machining precision.

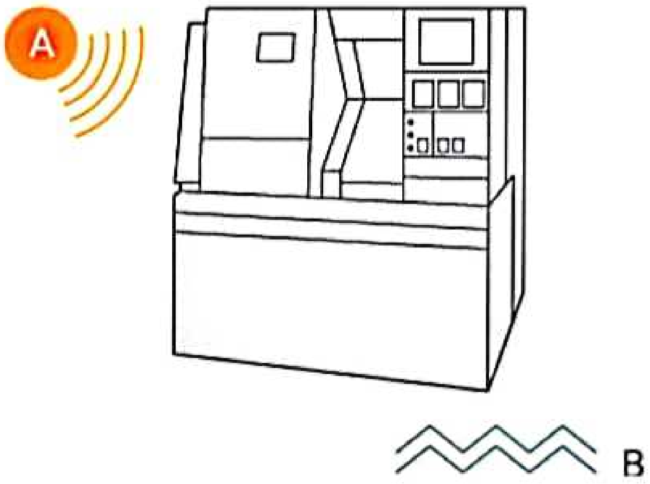


Fig. 4.2 Thermal deformation

A: Heat B: Vibration

4.3 Basics:

Cutting means to cut off parts from workpieces using a tool. Broadly defined, two movements—cutting and feeding—are required in machining. Cutting is the movement that cuts off parts from the workpiece, and generally is achieved by a cutting tool moving in a straight line. Feeding, on the other hand, is the movement that enables cutting of other parts by moving the cutting tool. For example, after cutting on one line, by feeding the cutting tool perpendicularly to the cutting direction, a new surface can be cut. Repeating this can create a plane.

Machining and deflection

When machining, the tool and workpiece come into contact and their forces interfere with each other, generating deflection. It must be noted that the generated deflection varies according to the tool being used. For example, when using a cutting tool, the deflection depends on such factors as the material of the workpiece, the area of the cut end, and the type of cutting tool being used. In particular, the area of the cut end affects deflection significantly, which should be noted when machining. When it comes to drilling, the operator must also consider deflection for torque and feeding. Torque is the strength of torsion and is also called the torsional moment. On the other hand, feed is the movement in the direction of moving the drill forward. In drilling, the value of deflection varies depending on the material of the workpiece, drill type (shape of the blade), rotational speed of the drill, and feed speed. The quality, efficiency, and durability of tools can be improved by planning machining on the work floor with influences of deflection in mind.

Machining and speed

On the machining work floor, work efficiency is another key element alongside quality control. Speeding up machining improves efficiency. However, increasing the speed of the machine requires additional planning due to the risk of increased deflection and thermal deformation caused by higher speeds. Increasing machining speed can also shorten the life of tool bits. This can shorten the replacement cycle of tool bits and consequently increase the cost per machining unit. Therefore, it is important to consider the speed, precision, and the life of tools when machining.

5 DRILLING MACHINE

It is a machine which is used to drill the holes on the components or workpiece with the help of drill bits. The drill bits are also called as Multi-point cutting tools which can have their rapid impact on the Material Removal Rate (MRR) i.e. a single-point cutting tool (like the one used in a lathe machine) can remove the material slowly whereas, a multi-point cutting tool removes the material at a faster rate and thereby increases MRR.

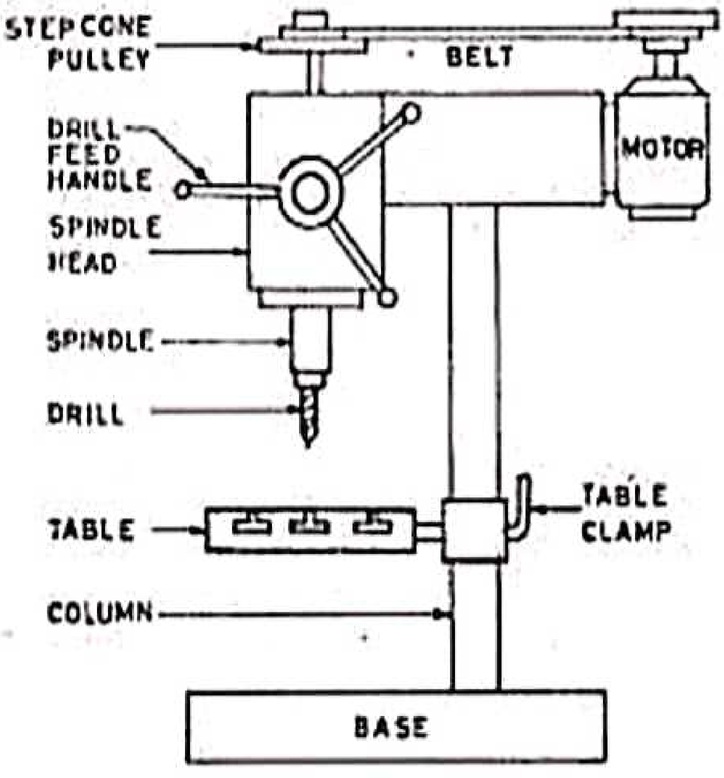


Fig. 5 Drilling Machine

5.1 Parts:

- Base
- Vertical Column
- Swivel Table
- Power Transmission system (Stepped Cone Pulley)
- Drill Feed Handle (Hand Wheel)
- Chuck
- Table Clamp
- Drill bit
- Spindle

5.2 Working Principle:

When the power is given to the motor, the spindle rotates, and thereby the stepped pulley attached to it also rotates. On the other end, one more stepped pulley is attached and that is inverted to increase or decrease the speed of the rotational motion.

Now, a V-belt is placed in between the stepped pulleys so as to drive the power transmission. Here a V-belt is used instead of a flat belt, in order to increase the power efficiency.

Now the drill bit also rotates which was placed in the chuck and which was in connection with the spindle. As the Pulleys rotates, the spindle also rotates which can rotate the drill bit.

Now, by the rotation of hand-wheel, the spindle moves up and down in the vertical direction in order to give the necessary amount of feed to the work and this drill bit is used to make the holes on the component placed in the machine vice.

5.3 Types:

Below is the list of drilling machines which are used in the industries for the production of the materials.

- Radial drilling machine
- Upright drilling machine
- Multiple Spindle drilling machine
- Deep hole drilling machine
- Sensitive drilling machine
- Portable drilling machine
- Gang drilling machine

5.4 Operations:

- Drilling
- Boring
- Reaming
- Tapping
- Spot facing
- Trepanning
- Honing
- Counter boring
- Counter Sinking

An Explanation for the Operations to be performed on Drilling Machines:

The explanation is as follows.

Drilling Operation:

The operation of making holes on the surface of the workpiece by the use of drill bit is called Drilling Operation.

Boring Operation:

The operation of enlarging an existing hole is called the Boring Operation. The existing hole was created by the drilling operation.

Reaming Operation:

The operation of sizing and finishing an existing hole with the help of a reamer is called Reaming Operation.

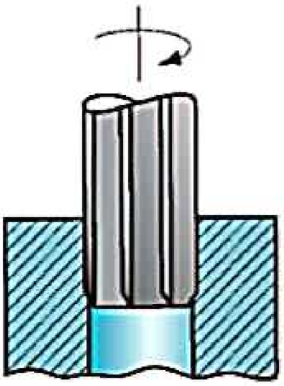


Fig. 5.4. Reaming

Reamer is a multipoint cutting tool having several cutting edges to finish the surface.

Tapping Operation:

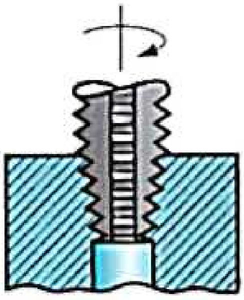


Fig. 5.4.1 Tapping

It is the operation of creating internal threads by means of a cutting tool called Tap and the operation is called Tapping Operation.

Spot Facing Operation:

Fig. 5.4.2 spot spacing

This is an operation of removing the chips from the surface of the hole such that proper seating of bolts takes place and this removal can be done through end mill cutter using a drilling machine.

Trepanning Operation:

Without drilling, a Trepanning operation is used for producing a large-size hole of more than 50mm in diameter. This Trepanning operation cannot be used for blind holes.

Honing Operation:

In this operation, the tool will rotate and reciprocate about its axis for producing very smooth holes.

This honing operation is mainly used for finishing the holes in the IC Engine cylinder.

Counterboring Operation:

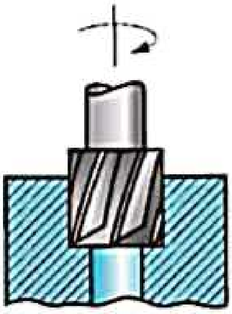


Fig. 5.4.3 Counterboring

The Counter boring operation is used to enlarge a particular portion of the hole.

Countersinking Operation:

The Countersinking operation is used to enlarge the end of the hole to give it a conical shape for a shorter distance.

Fig. 5.4.4 countersinking

These are the various operations that are performed on Drilling machines.

5.5 Advantages and Disadvantages of the Drilling Machine along with its applications.

Advantages:

- It requires less labor.
- High precision and accuracy will be maintained by the operator in Bench Drilling Machine whereas, in the case of Automatic drilling machine, high accuracy is maintained by the machine itself.
- It is easy to operate
- The maintenance is low.

Disadvantages:

- As it makes rough holes during the drilling operation. Therefore, a medium surface finish can be expected but not a high surface finish.
- A small size workpiece that can fit on the worktable is machined whereas large size components cannot be machined.
- If there is an improper clamping between the drill and the workpiece, there will be a probability of breaking the drill bit.

Applications:

- Surface mining
- Counter boring
- Countersinking
- Underground mining
- Tapping etc.

These are the different types of Drilling machines. Let's find its Advantages, disadvantages and applications in a detailed way.

6 CONCLUSION

I have learnt about the types of machines and how they are working mechanically in the Industry. I dent to know the same basic techniques like welding, cutting and drilling. I have studied about Lathe machine and got the knowledge of about the machine. We had repaired the machine and remove the faulty parts from it and did the maintenance chart. If welding in a confined space, additional training is necessary to ensure your safety. Do not underestimate the role of welding in safe operations. Many disadvantages of single point cutting tool are reduced by multi point cutting tool. Drilling machine is the most important in workshop. Primarily designed to originate hole. Holes may be drilled quickly and at a low cost.

STUDIES ON FLUID MECHANISM AND PUMPS

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY
TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE PHYSICS

Submitted by

M.KOHILA

Reg. No : 20SPPH07

Under the guidance of

Ms. A.VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled **"STUDIES ON FLUID MECHANISM AND PUMPS"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirement for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 – 2021** by **M.KOHILA** (Register Number : 20SPPH07)

Signature of the Staff – in – Charge

Signature of the Co-Ordinator

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonom
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/09/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, **"STUDIES ON FLUID MECHANISM AND PUMPS"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree, Diploma or other similar titles.

M. Kohila

Signature of the Student

(M.KOHILA)

Station : Thoothukudi

Date : 10/04/2021

STUDIES ON LASER- EYE SURGERY AND ITS OPERATION

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

M. MAFRIN FERNANDO

Reg. No: 20SPPH08

Under the guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled, " **STUDIES ON LASER-EYE SURGERY AND ITS OPERATION**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020-2021** by **M.MAFRIN FERNANDO** (Register No:20SPPH08)

Signature of the Staff-in-charge

Signature of the Co-Ordinator

Joyce
Signature of the Director
Director
Self Supporting Courses
St. Mary's College (Autonomous,
Thoothukudi - 628 001.

Lucia Rose
Signature of the Principal
Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/9/21
Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, "**STUDIES ON LASER –EYE SURGERY AND ITS OPERATIONS**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS),THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree, Diploma or other similar titles.

Mafrin fdo. M

Station: Thoothukudi

Signature of the student

Date: 10-04-2021

(M.MAFRIN FERNANDO)

ACKNOWLEDGEMENT

First of all, I thank the Lord Almighty for his blessing and grace to complete this Report work.

I am deeply indebted to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, Rev.Dr. Sr. F.MARY JOYCE BABY for her support in my work.

I would like to express my special gratitude to Rev.Dr.Sr.JESSIE FERNANDO M.Sc., M.Phil., Ph.D. HOD, for her inspirational words to complete this report work.

I would convey my heartfelt thanks to Mrs. P. PADMAVADHI M.Sc., M.Phil. SET., SSC Co-ordinator, Department of Physics for her efficient and encouragement in successful completion of this report.

I wish to record my sincere thanks to Ms. A. VALENTINA M.Sc., M.PHIL., Assistant Professor, Department of Physics for her enthusiastic guidance and support for completion of this field work report.

It is my pleasure to extend my thanks to DR.V. RAMALAKSHMI M.B.B.S., M.S., Consultant – General Ophthalmology, Vasan Eye Care, Thoothukudi for her help and support to complete my Field work.

I am deeply grateful to all staff members of Department Of Physics (SSC) for supporting us in all aspects.

CONTENT Page.no

1. Introduction

"I shut my eyes and all the world drops dead;

I lift my eyes and all is born again,"

-Sylvia Plath.

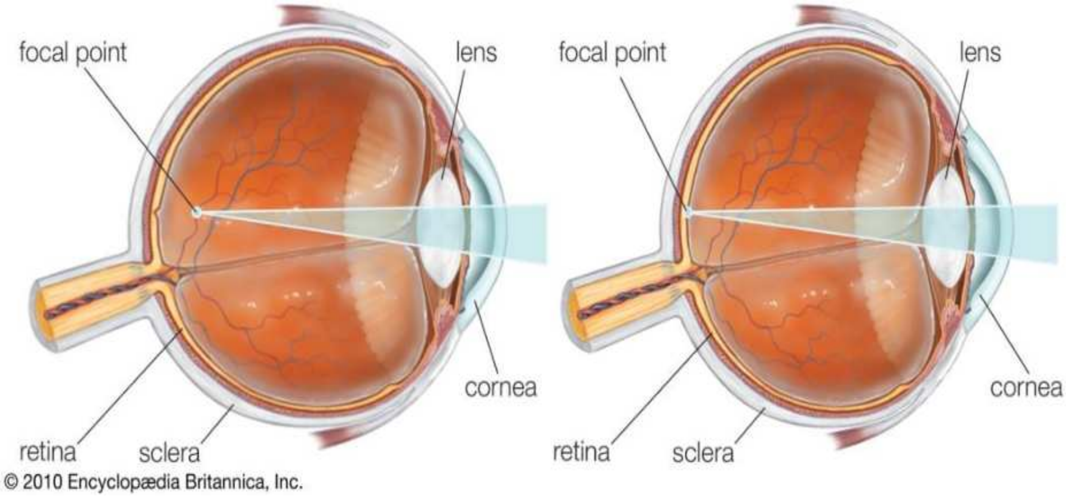
Fig: 1

In 1948 Spanish ophthalmologist Jose Ignacio Barraquer Moner was feed up with glasses. He wanted a solution for blurry vision fixed the eye itself, without relying on external aids .But the surgery he eventually devised was not for the faint of heart. Barraquer began by slicing off the front of the patient's cornea and dunking it in liquid nitrogen. Using a miniature lathe, he ground the frozen cornea into the precise shape necessary to focus the patient's vision .Then he thawed the disc, and sewed it back on. Barraquer called this procedure Keratomileusis, from the Greek word for "carving" and cornea". And although it might sound grisly, his technique produced reliable results.

1.1 How did Barraquer's surgery work?

Keratomileusis corrects what are called refractive errors: imperfections in the way eye focuses incoming light. Ideally, the cornea work together to focus light on the surface of retina, but several kinds of refractive errors can impair this delicate system.

In people with **myopia**, or **short-sightedness**, a steep cornea focuses light just short of the retina.



© 2010 Encyclopædia Britannica, Inc.

Fig 1.1 Myopia (nearsightedness) and Normal eye

Those with **hyperopia**, or **far-sightedness** have the opposite problem, light is focused too far beyond the retina. And in people with **astigmatism**, the cornea has two different curvatures which focus light at two distances and produce blurry vision.

Fig 1.1.1 Normal Vision and Hyperopia

- Normal Vision: Near object is clear
- Hyperopia: Near object is blurry eyeball is too short.

Even those with perfect vision will eventually suffer from presbyopia, or "aging eyes".

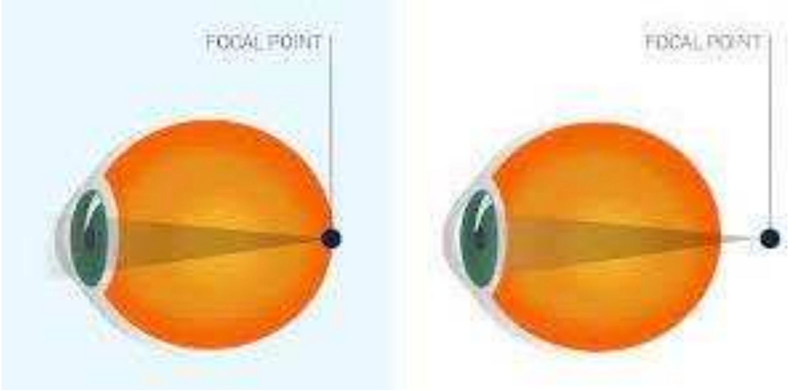


Fig 1.1.2 Normal vision and Presbyopia

As the Proteins in lens age, they slowly increase its size. By an adult's mid-40's, the lens is too large to easily change shape and shift focus. Glasses and contact lenses bend light to compensate for these refractive errors But, as Barraquer's procedure shows, we can also alter the shape of the cornea itself; moving the focal point backwards, forwards, or pulling a divided image together. And thankfully, modern eye surgeons can sculpt the cornea with far less invasive tools. In corrective laser eye surgery, surgeons rely on excimer lasers. These tools are accurate enough to each word into a human hair. To safely accomplish this ultra-fine incision, they use a technique called **photoablation**. This allows the laser to essentially evaporate organic tissue without overheating surrounding eye tissue

Fig 1.1.3 Photoablation

The human eye is constructed like a camera with a clear lens in the front and light sensitive tissue at the rear this tissue makes up the retina which acts like a photographic film.
If an eye that has a perfect vision, light rays passing through the pupil is focused by the lens to fall precisely at the centre of the retina .there are many common problems that affect the eye and prevent light rays from focusing properly on the retina

Three of these problems are

- Myopia or nearsightedness
- Hyperopia or shortsightedness
- Astigmatism

1.2 Myopia or nearsightedness

Myopia occurs when the shape of the eye is too long or the curve is too extreme .in this case light rays are focused on the point in front of the retina (instead of retina itself).

1.3 Hyperopia or shortsightedness

Hyperopia occurs when the shape of the eye is too short .in this case the light rays are focused behind the retina.

1.4 Astigmatism

Astigmatism occurs when the cornea is unevenly curved causing the light to fall of center or not to focus properly at all.

In either case, PRK laser surgery can be used to flatten all or part of the cornea allowing your doctor to cause the focal point of light entering the eye to fall more closely to the centre of the surface of the retina.

2. PRK Laser

- Simple and non-constructive
- Designed to reduce or eliminate the need for glasses or contact lenses
- PRK (photorefractive keratectomy) is a type of laser refractive surgery to correct myopia (nearsightedness), hyperopia (farsightedness) and astigmatism. PRK was the first type of laser eye surgery for vision correction and has been performed longer than LASIK, which has surpassed PRK in popularity.

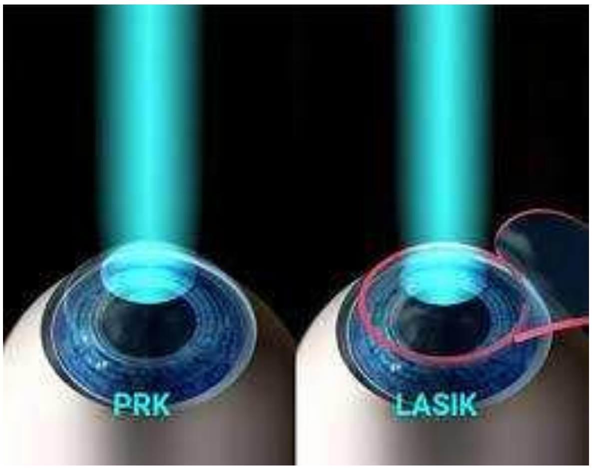


Fig 2 PRK and LASIK

- PRK Laser does not have effect on patients overall health and there are no risk in choosing not to have the surgery.

2.1 Procedure (on the day of operation)

- You will be asked to put on the surgical gown.
- You may receive a sedative by mouth and an intravenous line may be put in.
- You will then be transferred to the operating table.
- You will be given an anesthetic in the form of eye drops and an eye lid holder will be placed around the eye to prevent blinking.
- When the operative field is numb the doctor will carefully remove the epithelium, or top layer of cells, exposing the stroma –the non-cellular portion of the cornea.
- Next, your doctor will use the computer to control pulses of cool laser. These pulses will delicately remove microscopically thin layers of cells from the stroma.

- By removing tissue in this manner, your doctor will take the new shape of the cornea according to the exact vision problem.
- The entire procedure usually will take about 5 minutes and is painless
- Following surgery ,you’ll be given protective contact lenses to wear for a few days while the outer layer of cells grow back

2.2 How does laser eye surgery actually work?

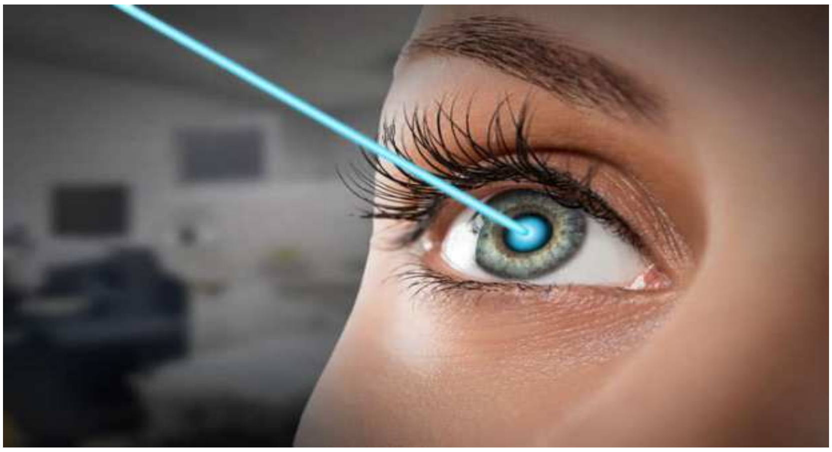


Fig 2.2 Laser eye surgery

The first step to separate a thin layer from the front of the cornea. This can be done with either a flat, wide blade, or a femto-second laser that produces millions of tiny plasma bubbles to create a plane beneath the corneal surface. Surgeons then lift the flap to expose the inside of the cornea. Guided by the refractive error and the shape of the cornea, the excimer laser robotically sculpt the exposed corneal bed into the correct shape This process usually takes less than 30 seconds for each eye. Finally, the flap is closed, and its edges reseal themselves in just a few hours. Because the lasering is done on the eyeball itself, it’s described as ‘’in situ’’, or’’ on site’’. Its complete name is ‘’laser in situ keratomileusis’’-but you probably know as Lasik. Essentially this technique carves a patient’s contact lens prescription onto their cornea. Like any surgical procedure, LASIK comes with certain risk. Some patients experience slightly blurred vision that can’t be corrected by glasses .But the technique is currently about as likely to damage your eyes as wearing daily disposable contact lenses for one year. Today a technique called SMILE enables surgeons to sculpt the cornea through even smaller incisions-further reducing the recovery time. And lasers are just correcting the three types of refractive errors-this technology can also restore aging eyes. In a technique called Laser Blended Vision, surgeons adjust one eye to be slightly better at distance vision and the other at better at close range vision The difference between the two eyes is small enough that most patient can merge their vision, allowing both eyes to work together at all distance. Advances in laser technology continue to make vision correction surgery more effective and accessible.one day soon, Barraquer’s vision of a world without glasses may finally come true

2.3 Cautions for Vision Surgery

Illnesses that affect healing may make vision surgery a poor choice. If you have diabetes, HIV, lupus, or rheumatoid arthritis, talk with an ophthalmologist about your best options. Other conditions that need careful evaluation and could make you a poor candidate for surgery include:

- Dry eye
- Large pupils
- Thin cornea

3. Visual activity

3.1 Definition

Acuity of vision is defined as the power of the eye to see a smallest object or letter clearly and distinguishably at specified distances.

Visual acuity is the medical terms for sharpness of vision .It deals with the sharpness or discrimination of central vision, rather than the extent or clarity of peripheral vision.

3.2 Standard of visual activity

Vision should be tested with and without glasses on a standard chart in **figure(4.1)**

Each eye should be tested independently. A normal eye can easily distinguish two points separated by an angle of one minute to the eye. This is the standard of normal vision acuity. This is the standard of normal vision acuity. Perfect acuity of vision requires two other basic factors the light sense and color sense .The acuity of vision is tested by the standard chart known as Snellen’s chart.

The Snellen’s chart is used almost universally in testing the acuity of vision .The chart consist of Snellen’s optotypes specially formed letters of the alphabet arranged inn rows of decreasing letter size. The size of the letter is standardized so that letters in each row will be clearly legible at a designated distance to a person with a normal vision.

4. Snellen's Chart

4.1 Principles of Snellen's chart

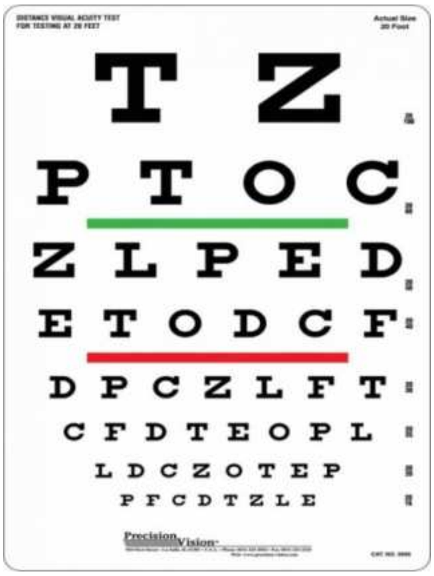


Fig 4.1 Snellen's chart

The chart consists of series of letters of diminishing size. Each letter is of such a shape that it can be enclosed in a square. The size of the square ids five times the thickness of lines composing the letter .The square subtends an angle of five minutes at a specified distance. The Snell's chart should be at a distance of six meters of twenty feet. The rays of light from that distance ar3 parallel for particular purpose half this distance may also be used, but in that case the test types should be seen reflected through a plane mirror, kept at a distance of three meters or ten feet from the patient. This could be carried out in a room with a length of three meters and a breadth of minimum one and a half meters. If six and a half meters of length is available, the chart could be fastened at eye level on a light, uncluttered wall that has no windows nearby. The general illumination of the room should not be less than one-fifth the illumination of the chart.

The chart should be placed above the patient’s head. The patient looks at a mirror hung on the opposite wall. The light from the chart travels to the mirror and then reflects from the mirror to the patient’s eyes, and thus an available room space of 3 meters can be converted into one of 6 meters.

The letters are so constructed that the angle of one minute is formed when

- First letter is at 60 meters distance
- Second line is at 36 meters distance
- Third line is at 24 meters distance
- Fourth line is at 18 meters distance
- Fifth line is at 12 meters distance
- Sixth line is at 9 meters distance
- Seventh line is at 6 meters distance
- Eight line is at 5 meters distance

The right eye is tested conventionally first, expect where the patient's complaint is particularly of defective left eye vision, in which case the left eye is assessed first. The patient reads down the chart as far as he can and then this is repeated with the other eye. Lastly both the eye is tested together. If the visual acuities of 2 eyes are about equal it is usually found that they reinforce each other so that the binocular vision is slightly better than the uniocular**.**

4.2 Types of visual acuity

- Distant visual acuity
- Near visual acuity
- Pinhole visual acuity

4.3 Distant visual acuity

It is the visual ability of a person to distinguish an object or letter whose rays are parallel and where no accommodation is required.

Various distant visual acuity charts are:

In adults

- Snelling's chart
- EDTRS Chart (log MAR chart

In illiterates

- E-chart / pictures chart
- Sandlot's broken ring chart
- Multiple pictures chart

In children

- Cake decoration
- Teller acuity cards
- Allen picture cards
- Sheridan Gardiner testing
- Keeler's preferential looking tests
- Cardiff's charts

Things required for the test

- Snelling’s chart with rows of letters
- (for those who can read)
- E chart (for illiterates)
- Trial set

Trial set consist of

- Trial frame
- Retinascopy mirror
- Convex(+) spherical and cylindrical lenses
- Concave(-) spherical and cylindrical lenses
- Pinhole
- Occluder
- Red and green glasses
- Prism
- Slit and Maddox Rod
- Cross cylinder

4.4 Retinascope

Retinascope is one of the most common essential tool for determining ‘the patients’ refractive status objectively. Retinascope is the only device to estimate the refractive errors of those who are unable to co-operate particularly children and mentally retarded persons.

Fig 4.4 Retinascope

Retinascope is basically available in two types. They are spot retinascope and streak retinascope. In the early days, the spot retinascope was used widely and now the streak retinascope is popular among the practitioners because of its simple and easy principles.

4.5 Phoropter

Fig 4.5 Phoropter

Phoropter or refractor is exclusively designed for refraction. It is comprised of spherical lens, cylindrical lens, prism and all types of auxiliary lenses. It is also equipped with Jackson cross cylinder. Although the trial lens/frame is used widely a phoropter is capable of doing the entire test such as JCC test, duochrome test, measurement of phoria and tropia and the binocular vision test.

4.6 Auto refractometer

Auto refractometer represents the most advance technology of measuring the most advance technology of measuring the refractive power of the eye. It is easily operated even by nontechnical persons. It provides a quick reliable guideline for the objective refraction.

Fig 4.6 Auto refractometer

5. Pre-Operative Instructions

Before coming to eye surgery you are advised to put total castle plus or directing eye drops in your eye an hour before the surgery.

- If you are any particular meditations for your diabetes or blood pressure to continue to take all these meditations as per the schedule as your normally following.

Fig 5.1

- If you have any allergies to any particular medicines to inform to us before you come in for the surgery.
- Certain do’s is to have a hair wash before you come for the surgery because you’ll be asked to avoid water going in to you for a couple of days after your surgery
- Wear light clothing and have a light meal before you come for the surgery.
- Always bring a responsible adult who can drive you back home after your surgery.
- Do not use any fragrance or perfumes before you come in for your surgery like Lasik surgery.
- Do not skip your meditations and do stick to the timings that have been allotted to you for the surgery.
- Do not use any eye makeup or any eye liner on the day of surgery.

6. Keratometer

Fig 6 Keratometer

6.1 Introduction

- Kerato = cornea, metry = measurement.
- It is the measurement of the anterior surface of the cornea across a fixed chord length, usually 2 – 3 mm which lies within the optical spherical zone of the cornea.
- It is based on the assumption that the anterior surface of the cornea acts as a perfect spherical convex mirror and the size of the image varies with the curvature of the cornea.
- It is also known as ophthalmometer, is diagnostic equipment, particularly for accessing the extent and the axis of astigmatism.

6.2 History

- It was invented by the German physiologist Hermann Von Helmhotz in 1851.
- Although an earlier model was developed in 1796 by Jesse Ramsden and Everard Home.

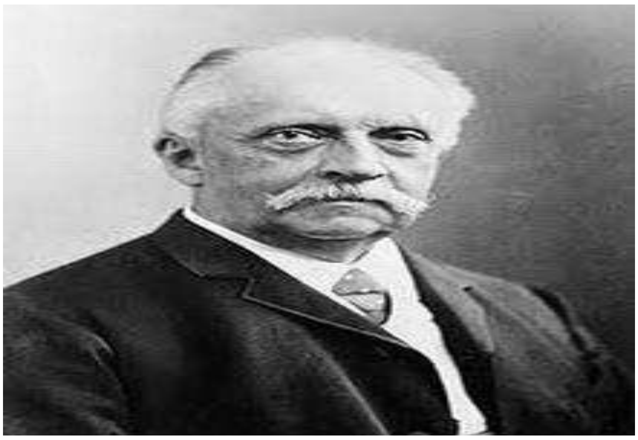


Fig 6.2 Physiologist Hermann Von Helmhotz

- Development of auto – Keratometer in 1980's.

6.3 Principle

- It basically works on the principle of measuring the image that gets reflected from a known object in our case it going to be the cornea.
- Radius of the curvature / dioptric power of cornea ,

$$\boxed{D = n-1/r}$$

where,

D – diopter power of cornea

n - index of refraction of cornea (1.3375)

r – radius of cornea in meters

- The cornea acts like a convex spherical lens.
- If the curvature increases the image decreases in **fig 6.3.1.**
- As the curvature decreases the image increases in **fig 6.3.2**.
- So knowing the image size we can actually calculate the size of the cornea.

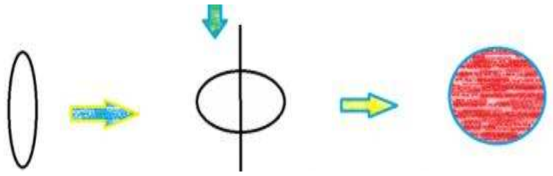


Fig 6.3.1 Curvature increases the image decreases

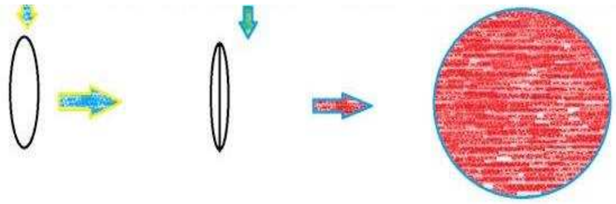


Fig 6.3.2 Curvature decreases the image increases

6.4 Types of Keratometer

Manual Keratometer	Automated Keratometer
• Baush and Lomb Keratometer • Javal – Schiotz Keratometer • Zeiss (Oberkochen) Ophthalmometer	• Topcon AK • IOL Master • Pentacam • Orbscan • Corneal Topography • The Humphrey Auto Keratometer

6.5 Types of Optical system

Baush and Lomb Keratometer:

- It is the most commonly used keratometer
- Variable doubling
- One position
- Fixed mires

Fig 6.5.1 Baush and Lomb Keratometer

Javal – Schiotz type Keratometer:

Fig 6.5.2 Javal – Schiotz type

Telecentric:

- IOL – Master 700

6.6 Doubling principle

- Minimal involuntary movements during fixation of eye
- Image formed by anterior curvature of eye also moves
- Based on biprisms : 2 image formed

1. Depending upon position of prism
2. If Distance increases, Doubling decreases.

FIXED DOUBLING	VARIABLE DOUBLING
• Variable – image size and mire separation. • Fixed: Object Height and doubling device distance. • BAUSH AND LOMB ,TOPCON	• Fixed – Image size and mire separation. • Variable – Object height and doubling device distance. • HAAG STREIT , JAVAL SCHIOTZ

6.7 POSTIONS:

ONE POSITION	TWO POSITION
• Double images are produced side by side as well as 90° from each other. • Principle meridians are assumed to be at right angles to each other.	• Require rotation about the axis to measure each of principle meridians.

6.8 HOW TO USE A KERATOMETER?

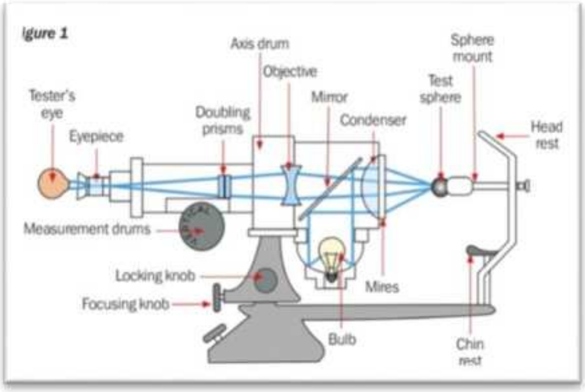


Fig 6.8 Parts of Keratometer

- When the lamb illuminates the mires by means of a diagonally placed mirror.
- Light from the mirror strikes the patient's cornea forming the object.
- The objective lens focuses the light from the image, along the central axis there is a four aperture diaphragm near the objective lens and beyond the diaphragm there are two doubling prism.
- Light passing through the left and the right aperture along the left and the right part of the central axis
- Deviate by means of base-up and base –down of prisms the light passing through the upper and lower aperture passes along the central axis.
- The total area of the upper and lower aperture is equal to the area of each of the other two apertures thus the brightness of the image is deviated.

6.9 Usage of manual Keratometer

Fig 6.9.1 Manual Keratometer

- The above figure is a manual kertometer.
- Here the eye piece is used for focusing.
- The chin height knob and the head height knob.
- The chin rest and the height rest knob where the patient’s aligns himself.
- The keratometer height knob right at the bottom to adjust the mires over the patient‘s cornea.
- The focusing knob to exactly align the mires and thereafter the horizontal and the vertical knob to align the axis in both the meridian.
- Along with the anterior posterior rotation axis scale for oblique astigmatism or irregular astigmatism.
- Before we use a keratometer on any patient it is important that we calibrate the keratometer machine by mounting a 5/8 inch steel ball ring at position closed to that normally of patient eye.

- We align the three mires as shown in the picture. After aligning the mires we check for the vertical and horizontal drum which is around 45 in this case which comes upto zero.
- Steel ball has a known radius of curvature which of proper calibration of keratometer can be correctly read.
- Focus the eye piece of the keratometer for the examiner's eye, set the adjustable eye piece as far counter clockwise as possible.
- Turn the eye piece clock wise until the vertical plus sign is first seen as sharp focus.
- Adjust height of patient‘s chair and instrument to a comfortable position for both patient and examiner.
- Instruct patient to place chin on the chin rest and fore head against fore head rest and adjust for patient.
- Raise or lower chin rest until the patient's outer canthes or lateral canthes is aligning with mark on upright support of instrument.
- Now from outside instrument roughly align the barrel with patient's eye raising or lowering the instrument or by moving it to left or right until the reflection of mire is seen on patient's cornea.
- One more easier way is to shine torch light through the eye piece and see the light reflecting on the patient and there by adjusting the height knob and seeing the light falling on to the cornea.

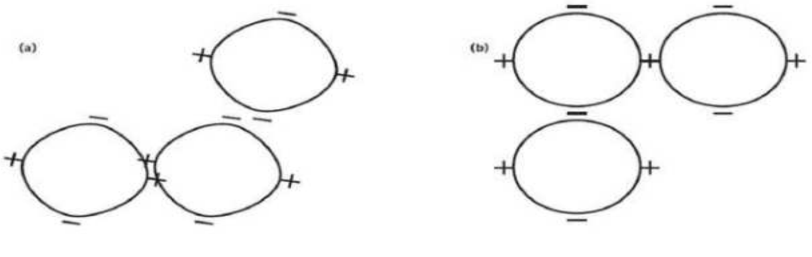


Fig 6.9.2 Patient's Cornea

- Look into the keratometer and refine the alignment of the image of the mires that is 3 circles on patient's cornea during this time instruct the patient to keep their eyes wide open and oclude the other eye and tell the patients blink normally.
- During focusing the mires the most crucial is to focus the mires and adjust the instrument so that the plus sign is centered on the lower right circle.
- After centration of the plus sign of the lower right hand circle adjust the horizontal power wheel until the horizontal mires enclose the position.
- Once the horizontal mires sign encloses the position adjust the vertical drum until the vertical mires enclose the position thereby getting super imposition of plus and minus of all three mires align to each other.
- After the mires are aligned each of vertical slash horizontal drum mires yields a meridional reading in diopters or mms
- With a rule astigmatism 42/44 @90 degree
- Against the rule astigmatism 42/44@180 degree

6.10 Advantages

- Determine base curve of lens (steep vs. flat)
- Detect abnormalities on the lenses
- Measurement of the pre and post-surgical astigmatism
- IOL power calculation (cataract surgery)
- Detection of tear film abnormalities
- Rough estimate of refractive errors in cases of hazy media or uncooperative patient
- Detection of irregular astigmatism (keratoconus, pterygium,scarring)

6.11 Measurements

Record both horizontal and vertical measurements (in eights of diopters)

- Record flatter/steeper@steeper meridian
- Record clarity of mires : clear or distorted

Always record findings to 2decimals (total of 4 digit)

Range -36.00D to 52.00D

To increase the range:

- Place +1.25 D lens in front of the aperture to extend range to 61D (ADD 9 D)
- Place -1.00 D lens in front of the aperture to extent range to 30 D(SUBTRACT 6 D)

6.12 Errors

- Improper calibration of the instrument
- Faulty positioning of the patient
- Lack of proper fixation by patient
- Improper eye piece focusing
- Misalignment of mires
- Reduced visual acuity or uncorrected refractive error of the examiner
- Accommodation fluctuation by examiner
- Localized corneal distortions or opacities, poor tear exchange, abnormal lid position.

6.13 Feedback

- MK is the most widely used keratometer because of low cost and ease of use
- Despite latest advanced in optical biometers for keratometer readings, still used as a second instrument for confirmation of K readings.
- Despite certain limitations, MK still remains part of the armamentarium in the preop settings for various corneal and cataract surgery.

7. Do’s and don’ts (after your surgery)

- It is important that you put in the eye drops exactly as prescribed to promote quick recovery.
- Do wear the protective glasses that have been provided to you and continue wearing them indoors and outdoors till your doctor instruct them to stop.
- Avoid rubbing your eyes for atleast 6 days.
- Report your doctor immediately if you have any excessive pain watering or irritation in the eyes.
- Avoid any water going into your eye for the first few days after your surgery
- Avoid hair wash for four to five days after your surgery
- You can watch television or read books if you’re comfortable to do so on the same day of your surgery
- There is no restriction in terms of light activities such as cooking, walking around and moving out for your routine activities however, it is advisable to lifting heavy weights for the first few days of your surgery.
- If you need to rub your eyes use style gauze piece or tissue paper to wipe any tears or to wipe excessive drops that is there in your eyes

8. Conclusion

The need for laser eye surgeries arises from vision problems. The dependency on corrective eyewear can get cumbersome for some people hence the need for LASIK eye surgery.

Right from the correcting blurred vision to recurring pain in the eye due to refractive error , this type of laser eye surgery offers benefits that allow you to see better without causing any hassles in your day-to-day life .As a result of LASIK surgery ,millions of individuals worldwide have reduced their dependency on spectacles and contact lenses .Improvements in laser design ,eye-tracking ,and laser algorithms can all be great improvements in the future laser refractive surgeries, Using a excimer laser for corneal tissue removal has been consistently successful .

“Let your eyes change someone’s life, Let’s donate eyes”

STUDIES ON BIOMEDICAL INSTUMENTATION

A field work report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

A. MALAI MATHU ABITHA

Reg. No: 20SPPH09

Under the Guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to certify that this field work report entitled, **"STUDIES ON BIOMEDICAL INSTRUMENTATION"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirement for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020-2021** by **A. MALAI MATHU ABITHA** (Register No: 20SPPH09)

Signature of the Staff-in-Charge

Signature of the Co-Ordinator

Joyce
Signature of the Director
Director
Self Supporting Courses
St. Mary's College (Autonomous,
Thoothukudi - 628 001.

Lucia Rose
Signature of the Principal
Principal
St. Mary's College (Autonomous,
Thoothukudi - 628 001.

17/4/21
Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, **"STUDIES ON BIOMEDICAL INSTRUMENTATION "** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree , Diploma or other similar titles.

A. Malai Mathu Abitha

Station: Thoothukudi **Signature of the Student**

Date: 10.04.2021 (A. Malai Mathu Abitha)

ACKNOWLEDGEMENT

First and foremost, I feel obliged to our Almighty for his aid in the completion of this field project work successfully.

I am deeply indebted to our respected principal Rev. Dr. Sr. A.S.J. LUCIA ROSE M.Sc., M.Phil., Ph.D., PDGCA., for providing me this wonderful opportunity to spread my wings through this project.

I would like to extend my gratitude to our Director of SSC, Rev. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her support and encouragement.

I would express my special gratitude to Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M. Phil., Ph.D., HOD and Associate Professor for her encouragement to perform this project.

I wish to extend my heartfelt gratitude to Mrs. P. PADMAVATHI M.Sc., M.Phil., SET., SSC Co-ordinator, Department of Physics, for her encouragement in completing our project.

I cordially extend my sincere gratitude to Ms. A. VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her guidance and support in the completion of the field work report.

I am extremely thankful to Mr. RAMESH BABU (Dean), AVM Hospital, for giving me permission to enter their premises to complete this project successfully.

I would also like to acknowledge my parents and friends for their succor throughout the field work.

CONTENT **Page. no.**

1 INTRODUCTION

Biomedical instrumentation is the field of creating such instruments that helps us to measure, record and transmit data to or from the body.it helps physicians to diagnose the problem and provide treatment. It involves measurement of biological signals like ECG, EMG, or any electrical signals generated in the human body. Bioinstrumentation is an application of biomedical engineering, which focuses on the devices and mechanics used to measure evaluate and treat biological systems. It focuses on the use of multiple sensors to monitor physiological characteristics of human or animal.

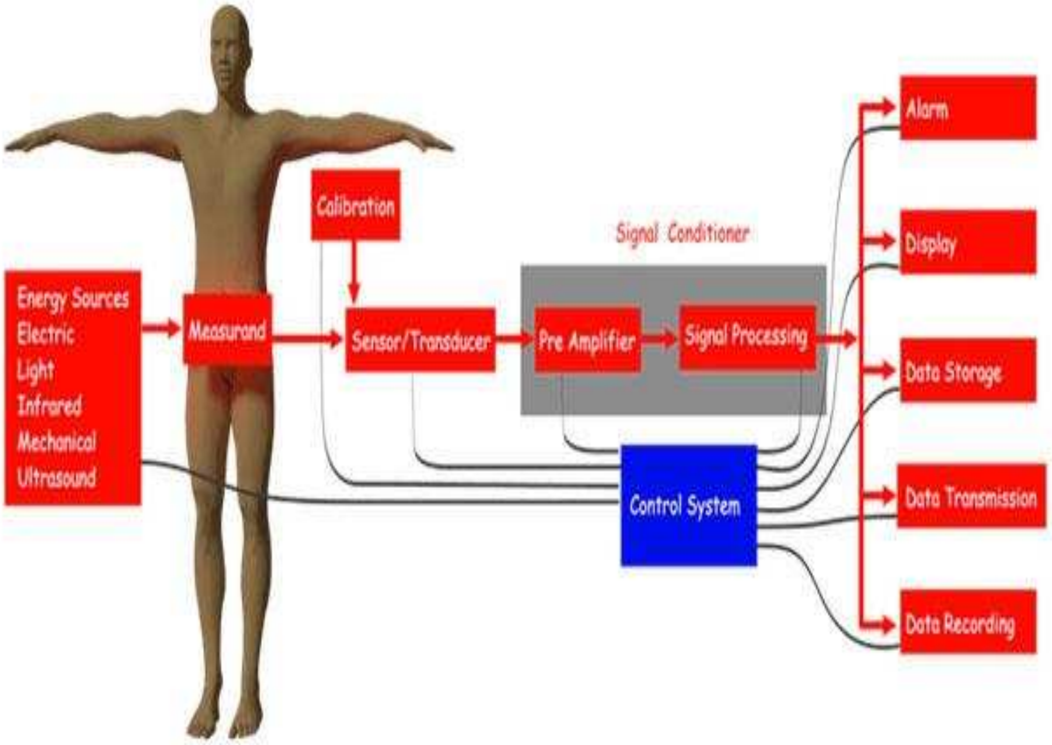


Fig. 1 Biomedical instrumentation processing

1.1 Types of measurands

- Internal- Blood pressure
- Body surface-ECG or EEG potentials
- Peripheral-Infrared radiation
- Offline-Extract tissue sample, blood analysis, or biopsy

1.2 Measurand quantities

- Biopotential
- Pressure
- Dimensions(imaging)
- Displacement (velocity, acceleration, force)
- Impedance
- Temperature
- Chemical concentration

Fig.1.2 Basic medical instrument

1.3 Basic functional parts

Any medical instrument consists of the following functional basic parts:

- Measurand: The measurand is the physical quantity, and the instrumentation systems measure it. Human body acts as source for measurand, and it generates bio-signals. Eg: body surface or blood pressure in the heart.
- Sensor/Transducer: The transducer converts one form of energy to another form usually electrical energy. For example, the piezoelectric signal which converts mechanical vibration into the electrical signal. The sensor is used to sense the signal from the source.
- Signal conditioner: Signal conditioning circuits are used to convert the output from the transducer into an electrical value. The instrument system sends this quantity to the display or recording system. Generally, signal conditioning process includes amplification, filtering, analogue to digital and digital to analogue conversions. Signal conditioning improves the sensitivity of instruments.
- Display: it is used to provide a visual representation of the measured parameter or quantity. Example: chart recorder, Cathode Ray Oscilloscope. Sometimes alarms are used to hear the audio signals. Example: signals generated in Doppler Ultrasound Scanner used for fetal monitoring.
- Data Storage and Data Transmission: data storage is used to store the data and can be used for future reference. Recent days electronic health records are utilized in hospitals. Data transmission is used in Telemetric systems, where data can be transmitted from one location to another remotely.

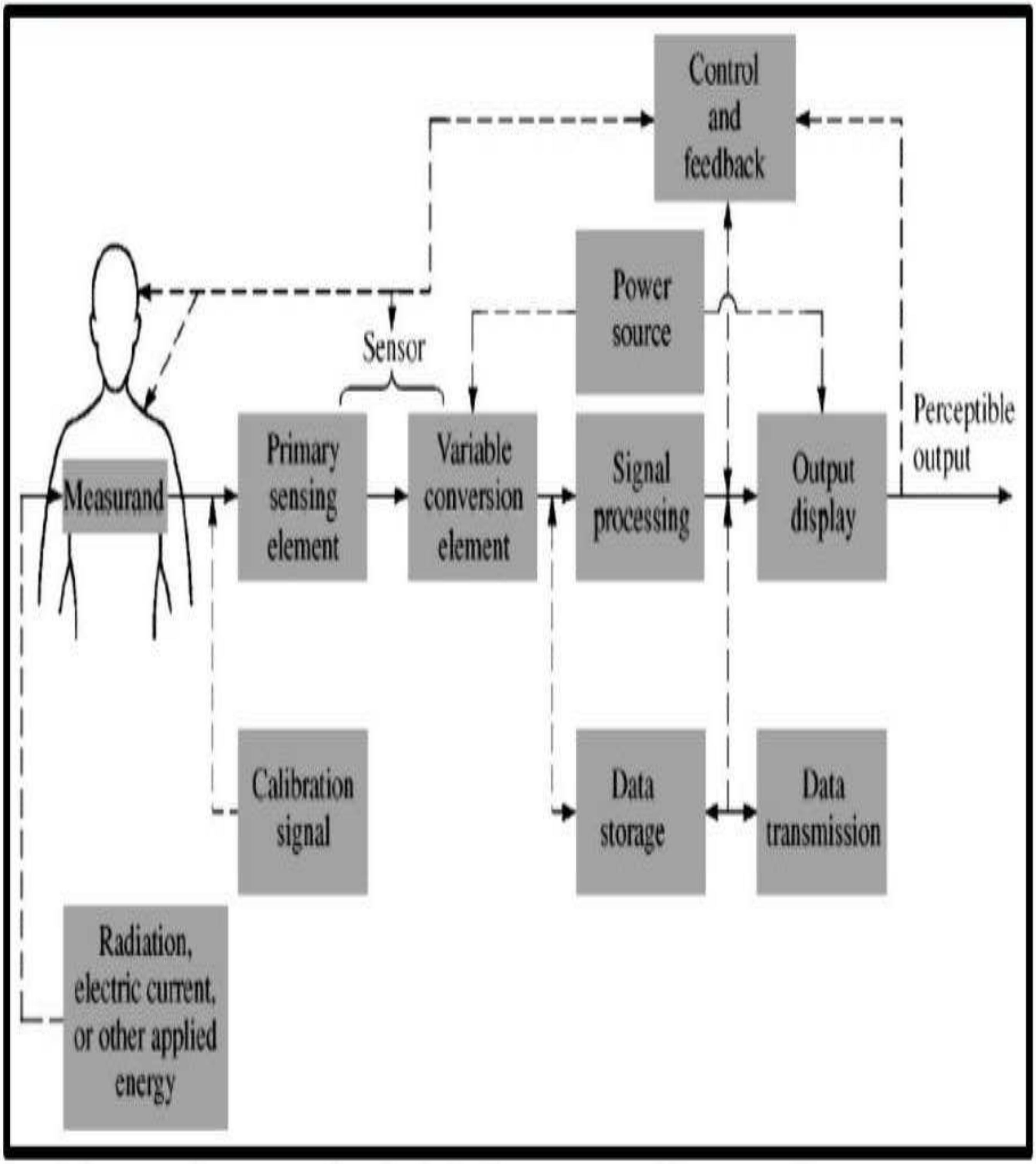


Fig.1.3 Generalized medical instrumentation system

2 MAGNETIC RESONANCE IMAGING(MRI)

Magnetic resonance imaging system provide highly detailed images of tissue in the body. The systems detect and process the signals generated when hydrogen atoms, which are abundant in tissue, are placed in strong magnetic field and excited by resonant magnetic excitation pulse.

Fig.2 Magnetic resonance imaging

Hydrogen atoms have an inherent magnetic moment as a result of their nuclear spin. when placed in magnetic field, the magnetic moments of these hydrogen nuclei tend to align. The nuclei have an resonant or “Lamor” frequency determined by their localized magnetic field strength just as a string has a resonant frequency determined by the tension on it. For hydrogen nuclei in a typical 1.5T MRI field, the resonant frequency is approximately 64MHz.RF field at resonant frequency of the hydrogen nuclei can force the magnetic moment of the nuclei to partially, or completely, tip in to a plane perpendicular to the applied field. When the applied RF excitation field is removed, the magnetic moment of the nuclei precess in the static field as they realign. This realignment generates an RF signal at a resonant frequency determined by the magnitude of the applied field. This signal is detected by the MRI imaging and used to generate an image. MRIs are a superior imaging modality for viewing soft tissues. MRI scans are more expensive.

In simpler terms, an MRI scanner consist of large powerful magnet in which the patient lies. A radio wave antenna is used to send signals to the body and then a radio frequency receiver detects the emitted signals. These returning signals are converted in to images by a computer attached to both scanner. The signal emitted is allowing the identification of various tissues, including bones, joints, muscle and cartilage.

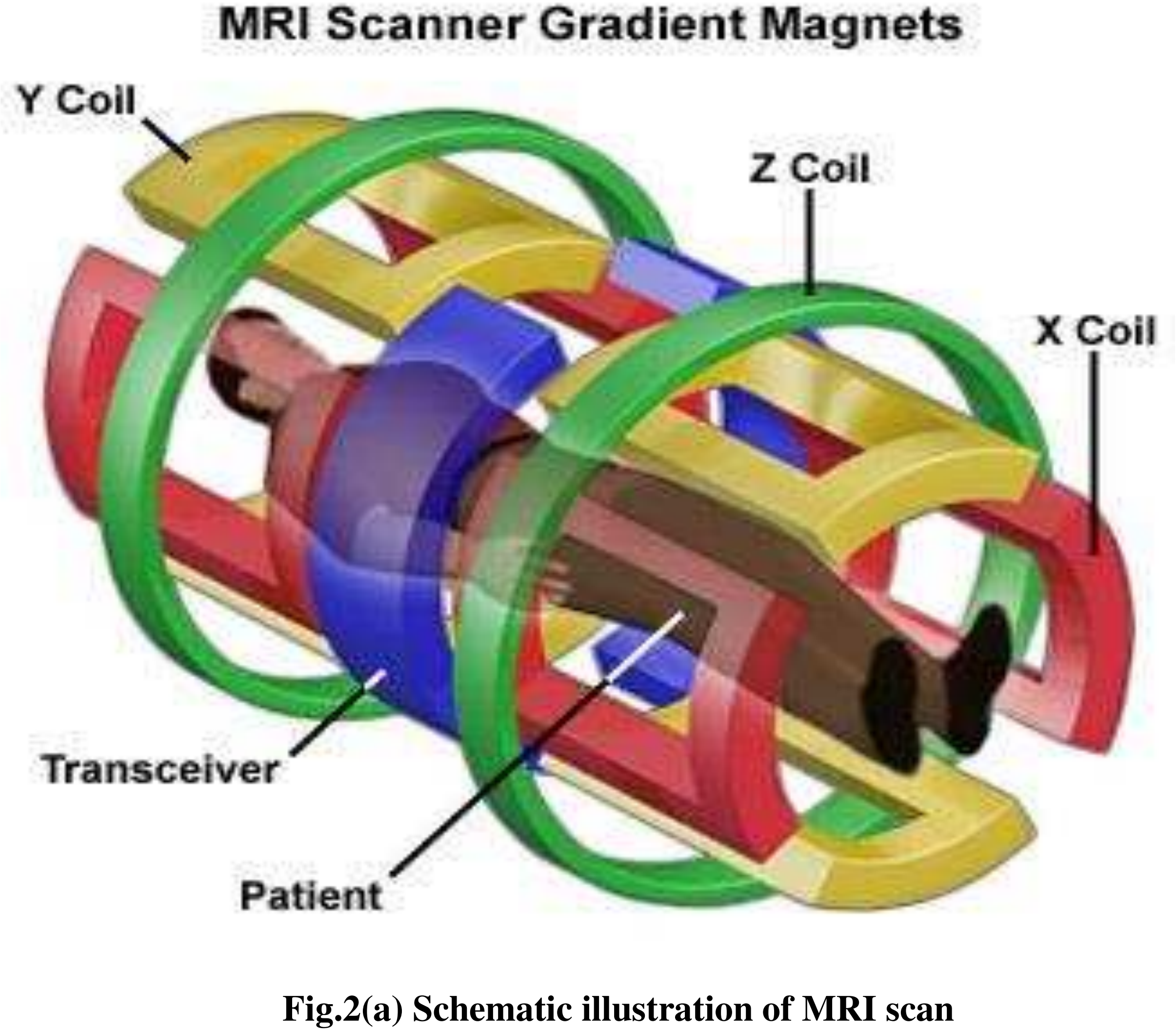


Fig.2(a) Schematic illustration of MRI scan

2.1. Uses

- MRI has wide range of application in medical diagnosis
- Neuro imaging: MRI is the investigative tool for neurological cancers.
- FMRI: Functional magnetic resonance imaging same as MRI can detect brain problems such as the effects of stroke, or tumors or epilepsy.
- Cardiac MRI: Complementary to other imaging techniques such as echocardiography, cardiac CT and nuclear medicine, vascular diseases and congenital heart disease.
- MRA: Magnetic resonance angiography is an alternative to conventional angiography and CT angiography.
- Musculoskeletal: Includes spinal imaging, assessment of joint disease and soft tissue tumors.
- Oncology MRI: investigation of choice in the preoperative staging of colorectal and has a role in diagnosis, staging, and follow up of other tumors.
- Liver and gastrointestinal MRI: Hepatobiliary MRI is used to detect and characterize lesions of the liver, pancreas, and bile ducts.
- MRI images demonstrate superior soft tissue and plain radiographs making it the ideal examination of brain, spine, joints, and other soft tissue body parts.
- Ability to image without ionizing x rays.
- Images can be acquired in multiple planes without repositioning the patients.

2.2 Computed Tomography

The term “Computed Tomography”, or CT, refers to a computerized x-ray imaging procedure in which a narrow beam of x-rays is aimed at a patient and quickly rotated around the body, producing signals that are processed by the machine’s computer to generate cross -sectional images- or “slices”- of the body. These slices are called tomographic images and contain more detailed information than conventional x-rays. Once a number of successive slices are collected by the machine’s computer, they can be digitally “stacked” together to form a three-dimensional image of the patient that allows for easier identification and location of basic structures as well as possible tumors or abnormalities. CT scanner uses a motorized x ray source that rotates around the circular opening of a donut shaped structure called gantry. The thickness of the tissue represented in each image slice can vary depending on the CT machine but usually ranges from 1-10 mm. when full slice is completed, the image is stored and the motorized bed is moved forward incrementally in to the gantry. The x ray scanning process is then repeated to produce another image slice. This process continues until the desired number of slices is collected.

Fig.2.2 Computed Tomography

2.3 Uses

- CT can diagnose muscle and bone disorders, such as bone tumors.
- Pinpoint the location of tumor, infection or blood clot.
- Guide procedures such as surgery, biopsy, and radiation therapy.
- Detect and monitor diseases and conditions such as cancer, heart disease, lung nodules and liver masses.
- Monitor the effectiveness of certain treatments, such as cancer treatment.
- Detect internal injuries and internal bleeding.

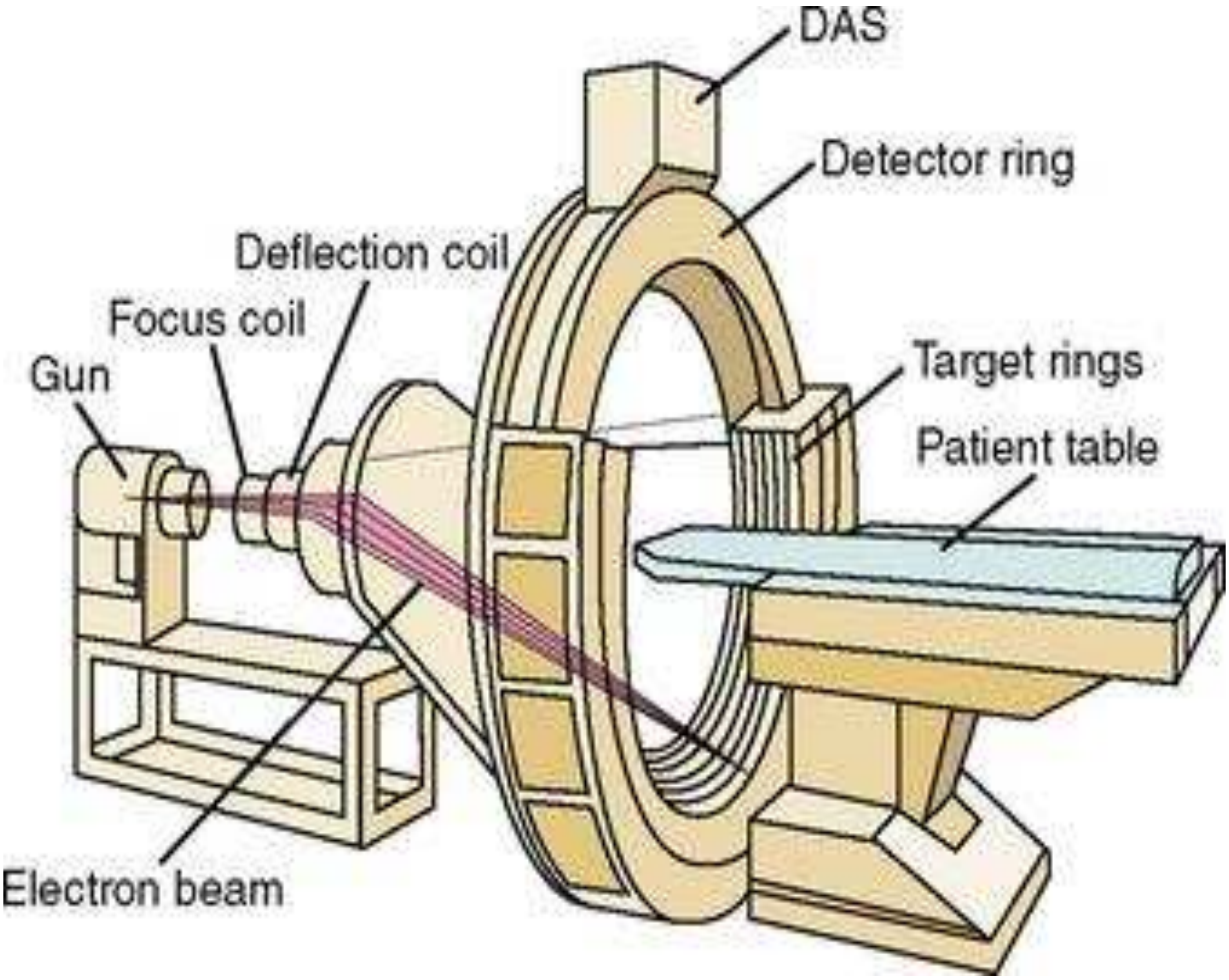


Fig.2.3 Circuitry of CT scan

3 ELECTROCARDIOGRAM(ECG)

The electrocardiogram, also referred to as ECG, or EKG, or 12-lead ECG, is a non-invasive diagnostic test that evaluates the heart's electrical system to assess for hearts disease. It uses flat metal electrodes placed on the chest to detect electrical charges generated by the heart as it beats, which are then graphed. The doctor can analyze the patterns to get a better understanding of our heart rate and heart rhythm, identify some types of structural heart diseases, and evaluate cardiac efficiency. An ECG detects the heart's electrical rhythm and produces tracing, which looks like squiggly lines. The tracing consists of representations of several waves that recur with each heartbeat, about 60-100 times per minute. The wave pattern should have a consistent shape. If the waves are not consistent, or if they do not appear as standard waves, this is indicative of heart disease. An ECG is recommended if we have signs or symptoms of heart disease, such as chest pain, shortness of breath, lightheadedness, dizziness, or fainting spells. An ECG is required prior to any type of surgery, including surgery for pacemaker placement.

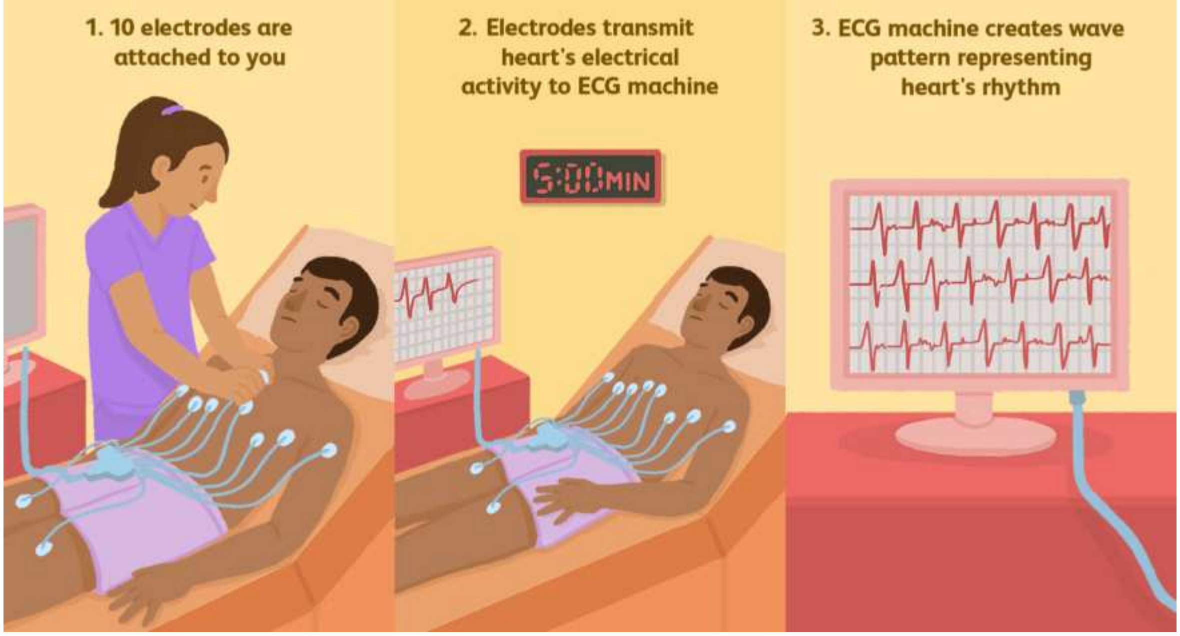


Fig.3 Electrocardiogram (ECG)

3.1 Uses

- An ECG is often used alongside other tests to help diagnose and monitor conditions affecting the heart.
- It can be used to investigate symptoms of a possible heart problem such as chest pain, palpitations, dizziness and shortness of breath.
- Detect arrhythmias where the heart beats too solely, too quickly, or irregularly.
- Detect coronary heart diseases where the heart's blood supply is blocked or interrupted by a build-up of fatty substances.
- Detects heart attacks where the supply of blood to the heart is suddenly blocked.
- Detects cardiomyopathy where the heart walls become thickened or enlarged.

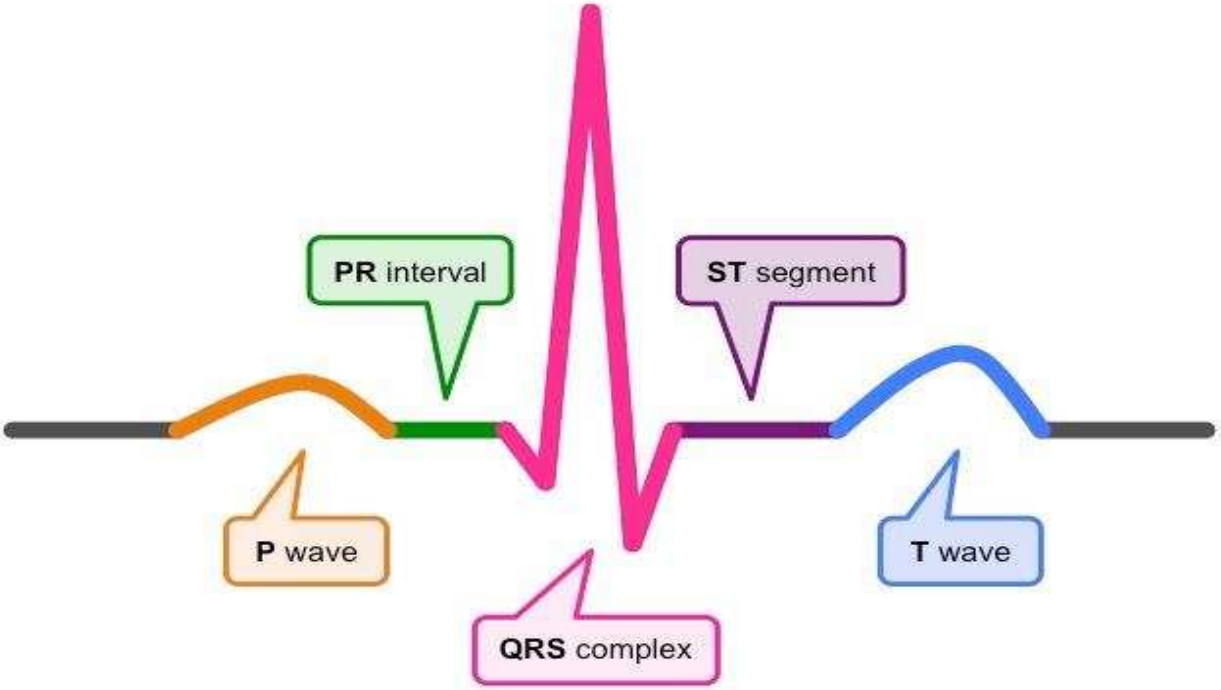


Fig.3.1 ECG Graph results

3.2 Electroencephalogram (EEG)

The electroencephalogram is a recording of the electrical activity of the brain from the scalp. The waveforms recorded are thought to reflect the activity of the surface of the brain, the cortex. This activity is influenced by the electrical activity from the brain structures underneath the cortex. The nerve cells in the brain produce signals that are called action potentials. these action potentials move from one cell to another across a gap called synapse. Special chemicals called neurotransmitters help the signals to move across the gap. ECG activity is quite small, measured in microvolts with the main frequencies of interest up to approximately 30 hertz. Small metal discs called electrodes are placed on the scalp in special positions. The electrodes are placed 10% and 20% of these distances. Each electrode site is labelled with a letter and a number. The letter refers to the area of the brain underlying the electrode.

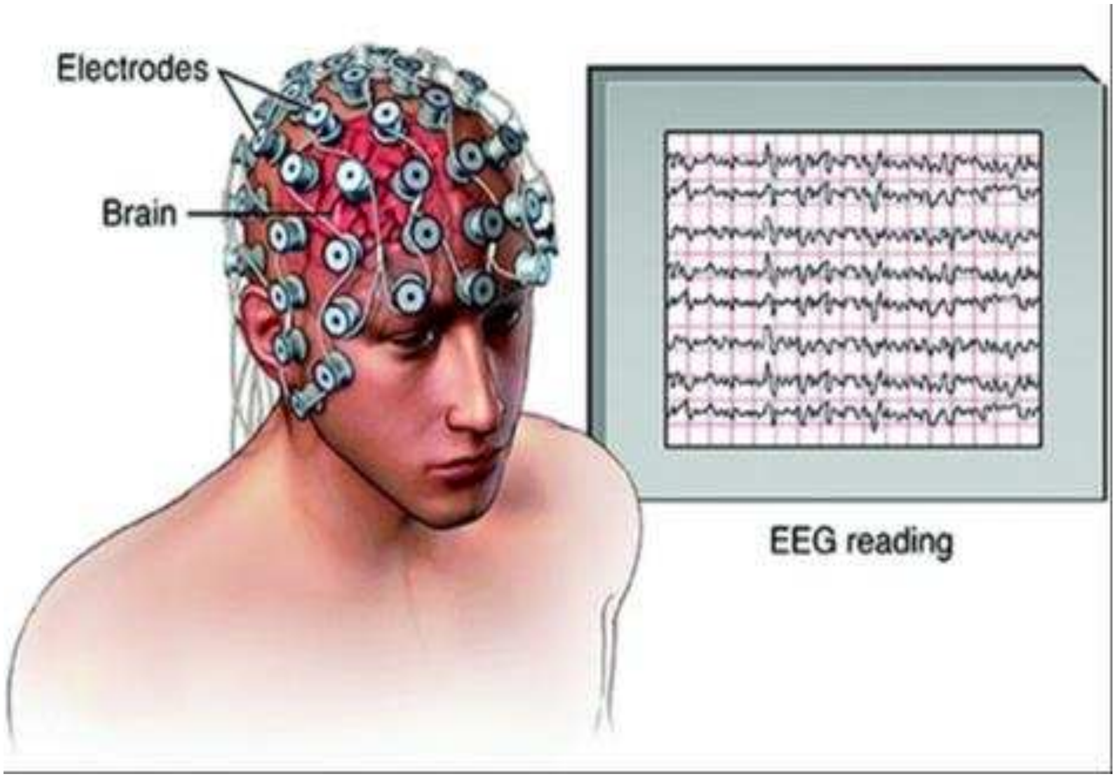


Fig.3.2 Electroencephalogram (EEG)

3.3 Uses

- EEG is an aid to diagnose epilepsy. Abnormal patterns such as spikes, sharp waves, and/or spike and wave complexes can be seen
- EEG studies can also be used in patients who are deeply unconscious, to distinguish between brain death and possible reversible conditions.
- It is used to investigate other conditions that may affect brain function such as strokes, brain injuries, liver and kidney disease and dementia.
- The EEG plays an important role in localizing the damaged tissues.
- An EEG test can also be used to monitor activity during brain surgery.

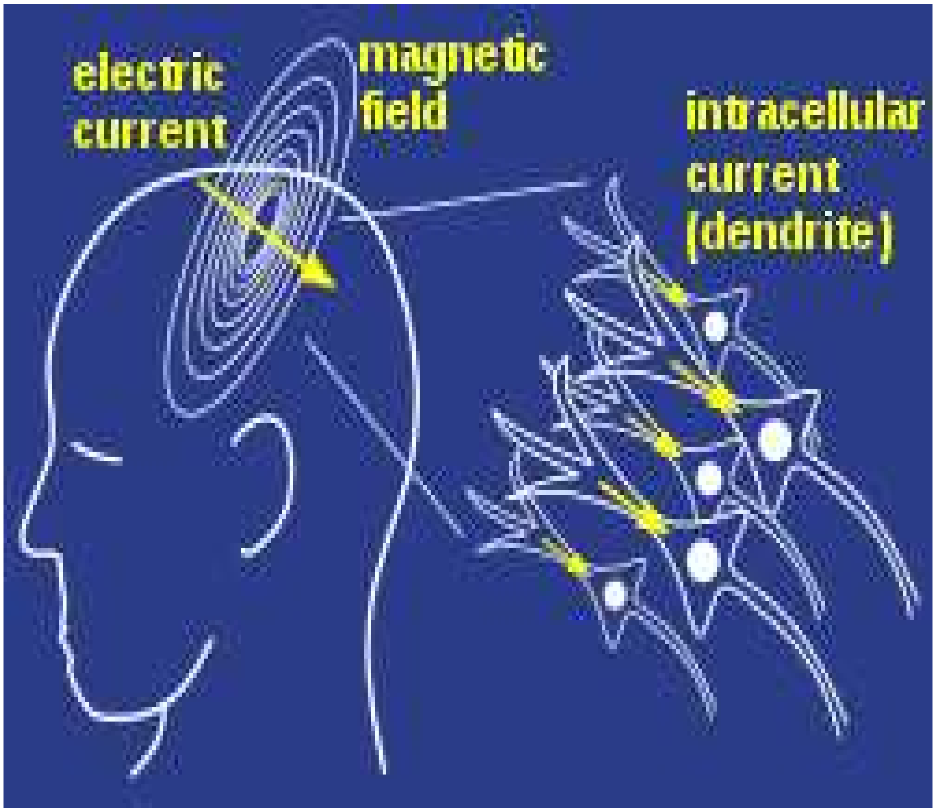


Fig.3.3 EEG processing

4 HEMODIALYSIS

Hemodialysis is a procedure where a dialysis machine and a special filter called an artificial kidney, or a dialyzer, are used to clean our blood. To get the blood into the dialyzer, the doctor needs to make an access, or entrance, into the blood vessels. This is done with minor surgery, usually to our arm. The dialyzer, or filter, has two parts, one for the blood and one for a washing fluid called dialysate. A thin membrane separates these two parts. Blood cells, protein and other important things remain in our blood because they are too big to pass through the membrane. Smaller waste products in the blood, such as urea, creatinine, potassium and extra fluid pass through the membrane and are washed away. In dialysis center, hemodialysis is usually done 3 times per week for about 4 hours at a time. The dialysis care team will monitor the treatment with monthly lab test to ensure the right amount of dialysis. For this, our Kt/V should be at least 1.2 or our URR should be at least 65%.

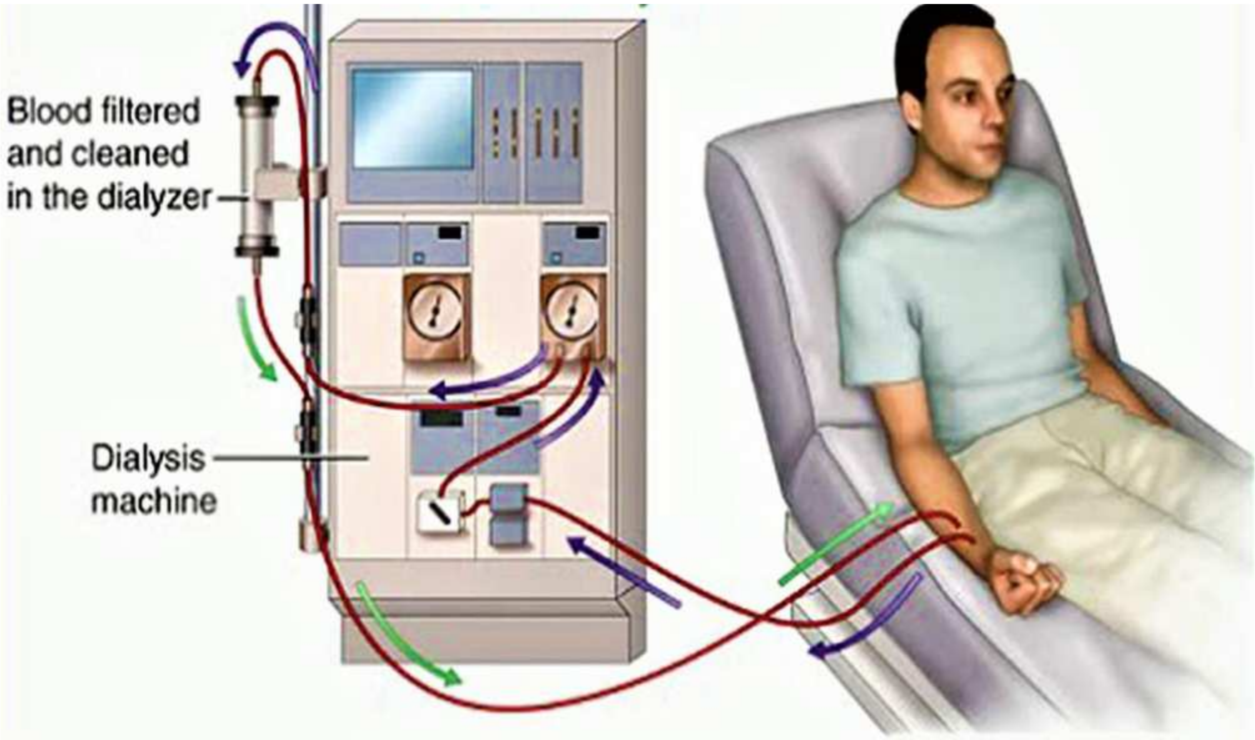


Fig.4 Hemodialysis

4.1 Benefits of Hemodialysis

- Treatment to filter wastes and water from the blood, as the kidneys did when they were healthy.
- It helps to control blood pressure.
- Balance important minerals such as, potassium, sodium, and calcium in the blood.
- Most common way to treat kidney failure.
- Nurses perform treatments for the patient.
- No equipment or supplies have to be at home.

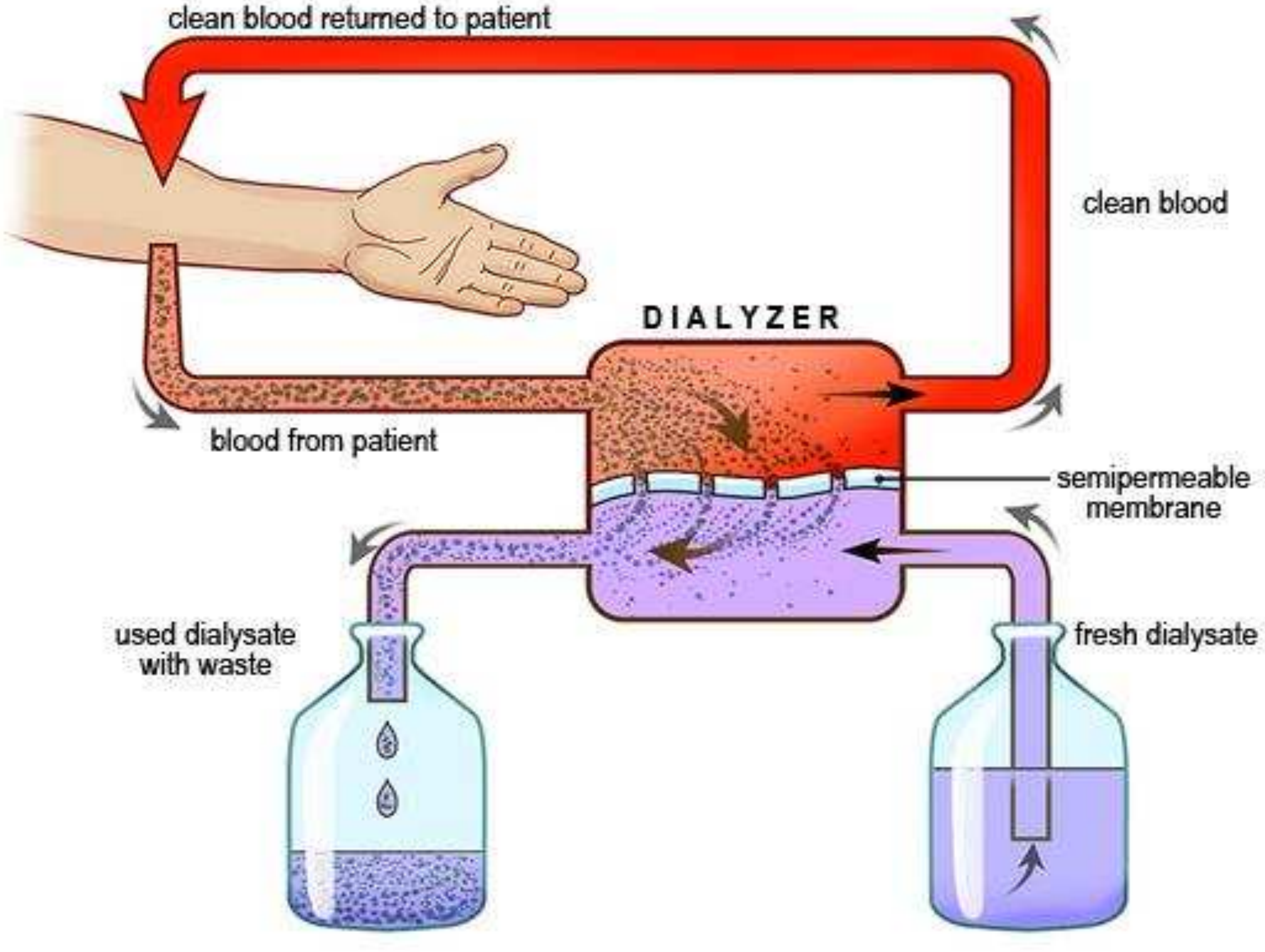


Fig.4.1 Hemodialysis process

4.2 Ventilator

A Ventilator is a machine that provides mechanical ventilation by moving breathable air into and out of the lungs, to deliver breaths to a patient who is physically unable to breathe, or breathing insufficiently. Ventilators are computerized microprocessor- controlled machines, but patient can also be ventilated with a simple, hand operated bag valve mask. Ventilators are chiefly used in intensive- care medicine, home care and emergency medicine and in anesthesiology. Ventilators are sometimes called “respirators”, a term commonly used in 1950s. However, contemporary hospital and medical terminology uses the word “respirator” to refer to a protective face-mask.

Fig.4.2 ICU ventilator

In its simplest form, a modern positive pressure ventilator consist of a compressible air reservoir or turbine, air and oxygen supplies, a set of valves and tubes, and a disposable or reusable “patient circuit”. The air reservoir is pneumatically compressed several times a minute to deliver room-air, or in most cases, an air/oxygen mixture to the patient. If a turbine is used, the turbine pushes air through the ventilator, with a flow valve adjusting pressure to meet patient-specific parameters. When over pressure is released, the patient will exhale passively due to the lungs’ elasticity, the exhaled air being released usually through a one- way valve within the patient circuit called the patient manifold. Ventilators may also be equipped with monitoring and alarm systems for patient-related parameters and ventilation function, backup batteries, oxygen tanks and remote control. The pneumatic system is nowadays often replaced by a computer- controlled turbopump.

The patient circuit usually consist of a set of three durable, yet lightweight plastic tubes, separated by function. Determined by the type of ventilation needed, the patient-end of the circuit may be either noninvasive or invasive. They may also have safety valves, which open to atmosphere in the absence of power to act as an anti-suffocation valve for spontaneous breathing of the patient. Some systems are also equipped with compressed-gas tanks, air compressors or backup batteries to provide ventilation in case of power failure or defective gas supplies, and methods to operate or call for help if their mechanisms or software fail. An open-source ventilator is a disaster- situation ventilator made using a freely- licensed design, and ideally, freely-available components and parts. Designs, components and parts may be anywhere from completely reverse- engineered to completely new creations, components may be adaptations of various inexpensive existing products, and special hard-to-find and/or expensive parts may be 3D printed instead of sourced.

4.3 Benefits of mechanical ventilator

- Machine that helps a patient breathe when he or she cannot breathe on his or her own for any reason.
- Helps a patient when they are having surgery or cannot breathe on their own due to a critical illness.
- The patient is connected to the ventilator with a hollow tube that goes in their mouth and down into their main airway or trachea. They remain on the ventilator until they improve enough to breathe on their own.
- Used to decrease the work of breathing until patients improve enough to no longer need it.
- Machine makes sure that the body receives adequate oxygen and that carbon dioxide is removed. This is necessary when certain illness prevent normal breathing.
- The patient does not have to work as hard to breathe-their respiratory muscles rest.
- The patient's as allowed time to recover in hopes that breathing becomes normal again.
- Helps the patient get adequate oxygen and clears carbon dioxide.
- Preserves a stable airway and preventing injury from aspiration.

Fig.4.3 Mechanical Ventilator

4.4 Ultrasound

Ultrasound is an imaging technology that uses high-frequency sound waves to characterize tissue. It is a useful and flexible modality in medical imaging, and often provides an additional or unique characterization of tissues, compared with other modalities such as conventional radiography or CT. An ultrasound scan is a medical test that uses high frequency sound waves to capture live images from the inside of our body. It is also known as sonography. The technology is similar to that used by sonar and radar, which help the military detect planes and ships. An ultrasound allows the doctor to see problems with the organs, vessels, and tissues without needing to make an incision. Unlike other imaging techniques, ultrasound uses no radiation. For this reason it is the preferred method for viewing a developing fetus during pregnancy.

Fig.4.4 Ultrasound

Ultrasound relies on properties of acoustic physics to localize and characterize different tissue types. The frequency of the sound waves used in medical ultrasound is in the range of millions of cycles per second. In contrast, the upper range of audible frequencies for human is around 20 thousand cycles per second(20 kHz).

An ultrasound can provide a view of the:

- Bladder
- Brain (in infants)
- Eyes
- Gallbladder
- Kidneys
- Liver
- Ovaries
- Pancreas
- Spleen
- Thyroid
- Testicles
- Uterus
- Blood vessels

4.5 Advantages of Ultrasound

- Ultrasound uses non- ionizing sound waves and has not been associated with carcinogens. This is particularly important for the evaluation of fetal and gonadal tissue.
- In most centers, ultrasound is more readily available than advanced cross-sectional modalities such as CT or MRI.
- Ultrasound examination is less expensive to conduct than CT or MRI.
- There are few contraindications to the use of ultrasound, compared with MRI or contrast-enhanced CT.
- The real time nature of ultrasound imaging is useful for the evaluation of physiology as well as anatomy.
- Doppler evaluation of organs and vessels adds a dimension of physiologic data, not available on other modalities.
- Ultrasound images may not be as adversely affected by metallic objects, as opposed to CT or MRI.
- An ultrasound exam can easily be extended to cover another organ system or evaluate the contralateral extremity.

Fig.4.5 Ultrasound system

Disadvantages of Ultrasound

- Training is required to accurately and efficiently conduct an ultrasound exam and there is non-uniformity in the quality of examinations.
- Ultrasound is not capable of evaluating the internal structure of tissue types with high acoustical impedance. It is also limited in evaluating structures encased in bone.
- The high frequencies of ultrasound result in a potential risk of thermal heating or mechanical injury to tissue at a microscopic level. This is most concern in fetal imaging.
- Ultrasound has its own set of unique artifacts, which can potentially degrade image quality or lead to misinterpretation.
- Some ultrasound exams may be limited by abnormally large body habitus.
- Bone blocks ultra sound waves. As such imaging of the spine is increasingly difficult with increasing age.

5 INFANT INCUBATORS

Infant incubator is a Biomedical device which provides warmth, humidity and oxygen all in a controlled environment as required by the new born. The infant incubator is normally in the form of a trolley with a small mattress on the top covered by a rigid clear plastic cover. Incubator chamber provides a clean environment, and helps to protect the baby from noise, dust, infection, and excess handling. A temperature sensor is taped to the baby's skin, and the incubator heater adjusts to maintain the baby at a constant temperature or, the temperature is controlled by a thermostat in the heated air system. Underneath the baby is an air-blown electric heating system and humidification system which circulates heated humid air at a desired temperature and humidity through the incubator chamber. Additional oxygen may also be introduced into the chamber. The incubator keeps the baby warm with heated moist air in a clean environment.

Fig. 5 Infant Incubators

5.1 Advantages of incubator

- It provides the closest environment to that of the mother’s uterus.
- Temperature at a uniform airflow and the humidity can be controlled to the desired level.
- It protects the baby from all the disturbances and infection in the NICU.

5.2 Disadvantages of incubator

- The disadvantage is that since the baby lies in a closed hood it is difficult to access the baby for medical procedure or care.
- It is expensive to buy an incubator.
- The incubator requires power source to work. In most rural and remote areas, reliable source of power is a major challenge.
- It requires a lot of skills in order to manage and maintain an incubator.
- It forms a barrier between the infant and the family.

6 CONCLUSION

Biomedical instrumentation is the application of engineering principles and techniques to the medical field. Biomedical instrumentation science is emerging as an exciting branch of study. It is very clear and easy to understand the concepts, principles, techniques, process of various bio-medical instruments and their vast applications to humans. This field visit to AVM hospital was very useful for me to understand the basic principles of physics used in these instruments. These instrument plays a vital part in medical field and it is very useful to patients to analyse, identify and to get cure easily from the diseases. Their way of teaching, demonstration of instruments, approaching to patients was very good. This study on biomedical instrumentation was very useful to gain more knowledge in medical field and also the basics principles of physics behind the instruments.

STUDY ON FABRICATION OF STEEL

A field work report submitted to
DEPARTMENT OF PHYSICS
ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI
Affiliated to
MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI
In partial fulfilment of the requirements for the award of
MASTER OF SCIENCE IN PHYSICS
Submitted by
S.P.PRIYA DHARSHNI
Reg. No : 20SPPH10
Under the guidance of
Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS
ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI
(Re-accredited with 'A+' Grade by NAAC)
2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled **"STUDY ON FABRICATION OF STEEL "** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 -2021** by **S.P.PRIYA DHARSHNI** (Register No: 20SPPH10)

Signature of the Staff – in - Charge

Signature of the Co-ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

12/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled **"STUDY ON FABRICATION OF STEEL"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field work report has been submitted for any Degree, Diploma or other similar titles.

Priya Thar

Station : Thoothukudi

Signature of the Student

Date : 10·04·2021

(S.P.PRIYA DHARSHNI)

ACKNOWLEGEMENT

On the very outset of this report, I would like to extend my sincere and heartfelt obligation towards all the personages who have helped me in this endeavor.

I wish to record our profound gratitude to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for her motivation.

I sincerely thank our Director of SSC, Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D.,for her encouragement and support.

I wish to thank Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., HOD & Associate Professor for her inspirational work to complete this work.

I owe a great deal to Mrs. P. PADMAVATHI M.Sc., M.Phil., SET., SSC Coordinator for supporting me throughout this field work.

I am indebted Ms. A. VALENTINA M.Sc., M.Phil., for her guidance and support for the successful completion of this field work report.

Its my pleasure to thank Mr. A. SIVA , the Proprietor, VEL ENGINEERING, Thoothukudi, for all the facilities provided to me in the pursuit of this field work.

I am deeply grateful to all the staff members of Department of Physics (SSC) for supporting us in all aspects.

CONTENT **Page. no.**

1 INTRODUCTION

The History of Metal Fabrication

Humans have been mining and machining metal for the past 10 millennia, as evidenced by a copper pendant archaeologists found in northern Iraq that dates back to about 9,000 BCE. Fabrication shops as we know them today began to exist around the Industrial Revolution, when sheet metal was in much higher demand than before. The invention of the hydraulic press, which allowed manufacturers to apply unprecedented pressures to pieces of metal, transformed the metal fabrication industry.

The History of Metal Fabrication

Humans have been mining and machining metal for the past 10 millennia, as evidenced by a copper pendant archaeologists found in northern Iraq that dates back to about 9,000 BCE.

Fig. 1 History

Metal fabrication on a broad scale was necessary to form systems of railroads, telegraph lines, weapons, tools, printing presses and other implements that have been so instrumental in our history. All of these advances relied on machine shops performing joints, cuts, bends and forming operations, just as is done today. The advent of compressed air has made riveting, another important part of fabrication, much easier and more efficient.

With the onset of the 20th century, metal fabrication has assumed an even larger role in our lives. We now perform machining on grand scales, ranging from small, family-run operations to large manufacturing plants employing thousands of people.

Metal Fabrication Process:

Metal fabrication starts with an idea, typically born out of necessity, that involves a piece of metal suited for some particular task. For example, a tech company may need a machined aluminum case for a new gadget. Their engineers design the part and send it out to several machine shops as part of a request for a quote. The machine shops analyze the schematic, calculate the cost of production and reply with both cost and lead time.

At this point, the company chooses the machine shop they wish to work with. The shop then puts the order in their queue and sets about ordering materials for the machining job. These may consist of sheet metal, metal bars, metal rods and more. As soon as the parts arrive and the job is in the queue, the team sets to work building the part itself.

The time it takes to fabricate depends on the complexity of the part and the demand on the machine shop. The fabrication shop may also provide assistance in both design and production, though this is more common for custom parts that require unique processes to complete. Skilled machinists can produce practically any shape or design once they figure out the best way to solve the problem.

Problem-solving includes conceptualizing the best way to create the part, which may mean figuring out what material characteristics are necessary to accomplish the design. Computer-aided design has made parts much easier to fine-tune, and it allows engineers to figure out crucial information instantaneously, including information on spots that may be structurally weak.

Steel Fabrication

Steel fabrication involves taking raw materials and shaping them to their desired form. The raw materials are melted down and mixed into steel before being constructed into the desired shape. The process requires a skilled technician who has the experience in taking raw components and transforming them into marketable items, and there is often very little room for error. Industrial facilities use steel fabrication to create everything from vehicular parts to household appliances. The basic methods of fabricating include cutting or burning, forming, machining, or welding. Here is a brief overview of how each of these tactics work:

- **Machining:** This process involves using a specialized piece of equipment to shave away parts of the metal to make it into the shape that is needed. Some of the tools that are involved include lathes, mills and drills.
- **Cutting:** We utilize water jet cutting, an abrasive process that uses high pressure water to cut virtually any material with a high level of precision and no distortion. Check out the benefits of water jet cutting here.
- **Welding:** This is a common form of steel fabrication. Welding is used to bend or combine pieces to make them one piece. As a CT welding contractor, we specialize in MIG & TIG welding of Steel, Stainless Steel and Aluminum and use Pulsed welding machines to help control the heat put into a part, minimize distortion, and improve the quality of the parts we produce.

Machinists who are tasked with steel fabrication would first have to gauge the original shape of the raw material which might exist in the form of a flat plate, reshaped channels, pipes or many other starting forms. Once the steel has been processed, the next step to be taken by the fabricator entails determining its shape. There are two factors which govern this outcome, namely the software package and the equipment available in the machine shop. In this regard, most of the metal fabrication companies prefer using cutting-edge technology to keep track of the operation and maintain the proficiency of the process.

2 BASIC RAW MATERIALS INVOLVED WITH METAL FABRICATION

There's quite a few raw materials that are necessary for metal fabrication. Knowing which items to keep on hand can help speed up the fabrication process, ensuring that workers always have access to a full supply of what they need to get the job done. Here are a few basic materials that are necessary for many metal fabrication projects:

- **Plate Metal:** fabricators use this to shape the pieces that are working with so that they can have a better range of what they can do.
- **Fittings:** these are often necessary for creating and completing pieces
- **Castings:** these are often used to add visual interest to the fabrication. Keeping them on hand may help speed the creation process.
- **Formed and Expanded Metal:** Expanded metal is grate-like so it is well suited for things like outdoor furniture that need to be able to let moisture flow off.
- **Sectional metal:** "L" beams are an example of a type of commonly used sectional metal. Z shapes (they resemble the letter Z) are also used as well as bar metal and rod metal
- **Flat metal:** Flat metal like sheet metal and plate metal are all great for fabrication and can be added to pieces to create visual interest and texture. These are well suited for making shapes as well.
- **Welding Wire:** Since fabrication requires that metal pieces be welded together, it's critical to keep various types and thicknesses of welding wire on hand so that pieces can be joined to one another.

Quality work and timely delivery are the principles that Al focused on as a one man operation and they are the same principles that drive our company today.

3 BASIC PROCESSES

Steel fabrication services have come a long way over the years, thanks in large part to the evolution of high-tech computer software. For example, Computer Numerical Control (CNC) systems now monitor and control the movement of machines such as routers, welders and laser cutters, while 3D modelling has made it easy to visualize even the most complex components. The fabrication process itself involves a wide array of manipulation techniques, with the following being some of the most common

- **Shot blasting:** Steel sections are blasted with shot in order to prepare them for fabrication. The main purpose of shot blasting is to provide a clean finish that will be easy to weld as well as a rough surface that will accept paint.
- **Cutting :** Steel sections are easier to work with when they are cut to length prior to fabrication and this can be done in a number of ways, such as by using circular saws, flame cutting or plasma cutting techniques.
- **Bending :** Many modern structures incorporate beautifully curved steel elements that require the fabricator to utilize various rolling and bending techniques. For example, steel can be passed through a set of bending rolls numerous times until the right level of curve has been established, while press braking can be used for more straightforward bends involving lengths of steel up to 12 meters long.
- **Welding :** Steel fabrication involves a whole lot of welding, for instance it is used to attach fixtures and fittings as well as to prepare connections for installation on site. Welding uses high heat to melt the parent material

along with whatever is being attached to it, so that as the weld pool solidifies the two materials are fused together.

- **Coating :** Coatings are applied to steel for both practical and aesthetic purposes and are most commonly applied towards the end of the fabrication process. High-tech coatings can protect the steel against corrosion as well as fire and they are also used to provide a custom look when requested by the architect.

4 STEEL FABRICATION SERVICES

Any industry that deals with metal requires steel fabrication services. Apart from playing a vital role in both the residential and commercial construction industries, fabricators also work closely with shipbuilding, mining and auto manufacturing as well. The following are just some of the many items that are commonly fabricated.

- Universal beams
- Universal columns
- Bar joists
- Platforms
- Ladders
- Pipe racks
- Trusses
- Grating
- Skids
- Steel stairs

5 MARKET OUTLOOK

The Steel fabrication market can be segmented based on type of industry. Austenitic stainless steel, super-austenitic stainless steel, ferritic stainless steel, martensitic stainless steel, and duplex stainless steel are the different types of stainless steel. The different types of stainless steel fabrication market are classified based upon their crystalline structure. Austenitic stainless steel products are widely used as compared to other stainless steel. It comprises austenitic crystalline structure, which exhibits a face-centered cubic crystalline structure. Super-austenitic stainless steel contains high amount of molybdenum, nitrogen additions, and nickel. It reduces the sensitization effect caused by high temperatures.

- **Indian Steel Industry:**

Steel fabrication industry in India has come a long way over the last few years from a remote traditional welding of some structures to the manufacture of complete designed and innovative sheet metal for diverse direct applications. Technological up-gradation in this sector has not only helped industry reduce delivery time but also the leak proof and accurate designing of the structure.

In fact, fabrication industry which was considered until recently as the perennial business with new generations automatically passed on to from the previous one, has seen many new players entering into this segment with automated machines for various applications.

Interestingly, many highly qualified engineers and trained technicians have become entrepreneurs with own set of manufacturing unit which over the years have generated huge interest of next generations. Fabrication shops and machine shops have overlapping capabilities, but fabrication shops generally concentrate on metal preparation and assembly as described above. By comparison, machine shops also cut metal, but they are more concerned with the machining of parts on machine tools.

The Indian steel industry is very modern with state-of-the-art steel mills. It has always strived for continuous modernization and up-gradation of older plants and higher energy efficiency level.

6 ADVANTAGES

There's not much need to sell anyone on metal fabrication these days. Metal has demonstrated its aesthetic quality, longevity and structural strength for millennia now, and with new alloys continuing to emerge, it is only continuing to improve. Here are some of the benefits of metal fabrication:

- **Superior strength:** Metal is a cut above the rest in terms of its strength. Particularly important is its high tensile strength, or resistance to being pulled apart, that makes it useful for wires, cables, screws and other hardware. It also demonstrates great compressive strength and nearly unparalleled hardness. All of these qualities come coupled with the fact that metal is easy to manipulate, bend, drill and shape.
- **Stronger than plastic**: Plastic is metal's main competitor. However, while plastic is suitable for certain applications, there is a compelling reason metal often wins out: It is vastly stronger. Metal is also more durable and more resistant to wear than plastic. If there is a risk of high temperatures, metal also wins in that it can handle a range of temperatures that would cause most plastics to melt. Metal can also undergo a wider range of manufacturing processes than plastic.
- **Aesthetic quality:** There is hardly a product in the world that doesn't benefit at least partially from aesthetic quality. Whether it is a consumer product or a piece of industrial equipment, metal bespeaks strength and

smooth operation. We largely associate our perception of its beauty with its advantages — that's why the latest technological revolution has mostly centered on sleek, elegant metal forms such as laptops and smartphones.

- **Heat resistance**: Beyond its comparison with plastic, metal is capable of withstanding dramatic increases in temperature. Assuming the manufacturer has accounted for the expansion that results with increased temperature, this heat is unlikely to damage the metal part.
- **Versatility in fabrication**: Metal can withstand lots of different manufacturing processes. These include deep drawing, forging, casting, welding, soldering, chipping, peening and more, making a wide array of metal shapes and geometries feasible. The sky is the limit with what parts will be required in the future, so metal will likely remain the material of choice.
- **Cost-efficiency**: Particularly in high-volume production, metal is extremely cost-efficient. Machine shops can replicate procedures and create large runs of product for relatively little cost per unit.

DISADVANTAGES

- **High Maintenance cost:**

Structures and machines made of structural steel require timely maintenance. Repairs and small fixtures can incur high costs.

Steel loses its strength in high temperature.

It is a scientific fact that steel tends to lose its strength at high temperatures. It is for this reason that fabricators engage in fireproof treatment for structural steel. In addition to that buildings have to be installed with sprinkler systems. These measures are expensive and add to the overall cost of the construction project.

Fatigue and Buckling : Steel structures tend to get fatigued over a period of time. After being exposed to different kinds of pressures, there are variations in the tensile strength of the frames. This can lead to buckling of the steel structure. Metal fabricators usually prefer steel over any other metal. Northern Weldarc is one such company, they are a team of professional fabricators and they specialize in structural steel fabrication. They are the perfect choice for all your fabrication requirements.

Corrosion: Steel is susceptible to corrosion as it reacts with atmospheric oxygen to form rust. This deteriorates the quality of the structure. Various expensive treatments are done over structural steel to prevent it from corrosion, some of them are dry abrasive blasting, water blasting, and coal tar paintings.

7 METAL FABRICATION APPLICATIONS

To give some idea of the breadth of industries where metal fabrication is an indispensable tool, let’s take a look at the applications of fabrication in everyday life:

- **Automobile bodies:** Automobiles may contain plenty of materials, but their skeleton and skin are completely reliant on metal. A car’s chassis is metal, typically steel or aluminum, as are most of its exterior panels, suspension riggin, and frame. Without metal, a car would not have the structural integrity to handle bumps on the road or heavy cargo.
- **Automobile engines:** Automobile engines consist of tightly machined parts that interlock to form a functioning whole. Metal fabrication techniques make everything from the long, snaking pipes of the exhaust system to the crankshaft and pistons. Other components include the crankcase, oil pump, spark plugs, fuel injection system, chain, throttle and

gudgeon pin. Bolts and rivets hold most of these components together, which also rely on metal fabrication.

- **Tools and hardware:** Our homes, automobiles, appliances and everyday conveniences would not exist as we know them without metal fabrication. That is thanks to the fact that the majority of our tools and hardware get produced by machine. Hammers, air compressors, nail guns, drill bits, grinders and saws are all the result of metal fabrication. Of equal importance are the pieces of hardware they are responsible for installing, such as nails, screws, bolts and tension rods.
- **Smartphone and laptop shells:** The computers and phones we have come to know and love are the results of metal fabrication. Particularly with the popularization of simple, sophisticated products that have served to tame the growing complexity of user interfaces, a phone or laptop's case can, in many ways, define it as a product. For instance, what would the iconic iPhone be without its smooth backing of anodized aluminum and stainless steel?
- **Kitchen hardware:** Look around your kitchen, and you will soon realize all the tiny, fabricated parts that make it functional. There are metal handles on the cabinets and drawers. Hinges and drawer slides make the cabinets open and close easily. Faucets and entire sinks are made from low-maintenance stainless steel. Toaster ovens, tea kettles, stove grills, vent fans, refrigerators and trash cans — metal fabrication makes all these things possible.
- **Gadgets and electronics:** Electronics rely on metal fabrication for more than just their shells. Fabrication is responsible for creating wires of different sizes and materials, as well as piping and internal architectures that allow for the placement of circuit boards and components. Cooling fans and parts like potentiometers are also often made with metal fabrication.

- **Aerospace:** One growing sector of industry is aerospace, whose components and craft must follow tight tolerances and uncompromised integrity. These parts must withstand sustained use, extreme temperatures, pressure fluctuations and chemical exposure — the perfect job for metal. Metal fabrication jobs for aerospace range from large, industrial plants to smaller operations specializing in a specific part or component.
- **Medical:** The medical industry and the metal fabrication industry are inextricably connected. From hospital beds to surgical tools, and from ventilation systems to lifesaving defibrillating devices, metal fabrication has helped build the medical industry. Metal is also advantageous to this industry because it provides an easily sterilized material that does not trap bacteria, moisture or germs.

8 DIFFERENT TYPES OF FABRICATION MACHINERY

The most commonly used types of fabrication machines:

- Waterjets
- Rolling machine
- Press brakes
- Laser systems
- Plasma systems
- Shears
- Hydraulic Press Brakes
- Ironworkers
- Horizontal Band Saws

Water jets

Fig. 8 Waterjets

Water jets are, by far, the most useful and cost-efficient method of cutting a variety of materials. These industrial machine tools use a combination of water and an abrasive substance to cut virtually anything, including*:*

- Stainless steel,
- Carbon steel,
- Aluminum,
- Titanium,
- Plastics,
- Copper,
- Brass,
- Rubber,

- Glass,
- Ceramics, and
- Stones like granite and quartz.

These machines are so versatile because almost no heat is generated to the work piece — unless, of course, you're cutting steel that is at least two inches thick, which can cause temperatures to reach 120 degrees F.

Water jets work by using high-pressure pumps, which reach speeds of anywhere from 30hp to 100+ hp, to force water out through the nozzle (commonly referred to as the "head") to cut your material.

Almost all jets have an "abrasive hopper system." This feature incorporates a metered flow of granular abrasive, usually garnet, to aid in cutting the aforementioned materials.

Whether you are considering opening your own machine shop, or you're looking for that perfect machine to give you an edge to help your existing business grow, a waterjet is the best and most versatile machine to invest in..

7 feet Lathe machine

Fig. 8.1 Lathe

A **lathe** is a machining tool that is used primarily for shaping metal or wood. It works by rotating the workpiece around a stationary cutting tool. The main use is to remove unwanted parts of the material, leaving behind a nicely shaped workpiece.

Heavy duty turning lathes are machines made of high-quality materials compared to conventional machine tools and incorporate the most advanced technology. Various designs of heavy duty CNC lathes involve their center height, bed width, maximum swing, spindle type, travel time, etc. Center lathe or engine lathe machine: This is a type of lathe that is currently widely used and can perform operations such as turning, end face, grooving, knurling, and threading. The feed mechanism of the engine lathe can operate the cutting tool in both the longitudinal and lateral directions Lathe machine is one of the most important machine tools which is used in the metalworking industry. It operates on the principle of a rotating work piece and a fixed cutting tool. The cutting tool is feed into the work piece which rotates about its own axis causing the workpiece to form the desired shape.

Lathes can be roughly divided into three types, engine lathes, turret lathes, and special lathes. The basic engine lathe is used for most lathes, with the smaller bench or portable machines, or larger vertical tables standing on the floor.

Shapping machine:

A shaper is a type of machine tool that uses linear relative motion between the workpiece and a single-point cutting tool to machine a linear toolpath. Its cut is analogous to that of a lathe, except that it is (archetypally) linear instead of helical.

A metalworking shaper is somewhat analogous to a metalworking planer, with the cutter riding a ram that moves relative to a stationary workpiece, rather than the workpiece moving beneath the cutter. The ram is typically actuated by a mechanical crank inside the column, though hydraulically actuated shapers are increasingly used. Adding axes of motion to a shaper can yield helical toolpaths, as also done in helical planing.

Fig. 8.2 Shapper

A single-point cutting tool is rigidly held in the tool holder, which is mounted on the ram. The work piece is rigidly held in a vice or clamped directly on the table. The table may be supported at the outer end. The ram reciprocates and the cutting tool, held in the tool holder, moves forwards and backwards over the work piece. In a standard shaper, cutting of material takes place during the forward stroke of the ram and the return stroke remains idle. The return is governed by a quick return mechanism. The depth of the cut increments by moving the workpiece, and the workpiece is fed by a pawl and ratchet mechanism.

The workpiece mounts on a rigid, box-shaped table in front of the machine. The height of the table can be adjusted to suit this workpiece, and the table can traverse sideways underneath the reciprocating tool, which is mounted on the ram. Table motion may be controlled manually, but is usually advanced by an automatic feed mechanism acting on the feedscrew. The ram slides back and forth above the work. At the front end of the ram is a vertical tool slide that may be adjusted to either side of the vertical plane along the stroke axis. This tool-slide holds the clapper box and tool post, from which the tool can be positioned to cut a straight, flat surface on the top of the workpiece. The tool-slide permits feeding the tool downwards to deepen a cut. This flexibility, coupled with the use of specialized cutters and tool holders, enable the operator to cut internal and external gear teeth.The ram is adjustable for stroke and, due to the geometry of the linkage, it moves faster on the return (non-cutting) stroke than on the forward, cutting stroke. This return stroke is governed by a quick return mechanism.

Rolling machine :

A plate roll machine is a piece of equipment that is used to roll various types of sheet metal into round, semi round, round with varying radii or conical shapes (some machines specialize in rolling materials back to flat too!). The rolling machine boasts a working mechanism that allows it to bend flat sheet metal into a large arc or cylinder or even a square, an ellipse shape and a multi-section arc.

Fig. 8.3 Rolling machine

Utilizing a series of precise and strong hardened rolls powered by either hydraulic or mechanical methods, the rolls are brought into a pitching position with the material desired to be shaped. Once the material is firmly held between two of the rolls, a third and sometimes fourth roll is brought into position pushing the material causing the initial bend, or what is referred to as the pre-bend. The rolls then begin to rotate pulling material through the pinched rolls and past the pushing rolls forcing an arc into the material.

Usage of plate rollers:

Sheet rolling machines are used in the production of nearly all types of cylindrical products. Their application extends to a vast array of items including pressure vessels (Heavily used in the Oil and Gas Industries), home appliances, ships, wind power, military arsenal, aerospace and automobile refit. Since not all rolled metals are created equal, every project may require a specialized type of plate roll machine.

Press brakes :

Old Reliable" should be stenciled on the side of every press brake in the world. Press brakes are, without a doubt, the sturdiest, strongest, and most dependable bulls in the pasture. It is common when searching for used press brakes to find many of the top brands like Amada and Cincinnati with vintages from the 60s and 70s still kicking and in great condition.

This is because press brakes have only one function: bending metals.Press brakes have a simple operation: Secure the work piece on the bed and the ram will descend upon it, using its tonnage to accurately bend the metal to the specified degree. The different types of metals commonly fabricated by these machines include steel, aluminum, brass, and sheet metal.Press brakes are rated by their pressing capacity (tonnage) and the bed length, which dictates the overall length of your work piece that can fit in the bending zone. Tonnage capabilities range anywhere from 25 tons all the way up to 1,000 tons. The smallest bed lengths start at four feet, whereas the longest beds can reach a length of almost 30 feet.

There are four types of press brakes:

- Mechanical
- Hydraulic
- Pneumatic
- Servo-electric.

The two most common brakes used in nearly all contemporary machine shops are mechanical and hydraulic. Mechanical brakes dominated the industry until the 1950s when advances in technology introduced computer controls. This made the hydraulic brakes much more popular and user-friendly.

Fig. 8.4 Press brakes

If you have lower tonnage requirements, mechanical brakes should be at the top of your list of machines to invest in because they are simple to maintain and will not break the bank. If your shop is bending very thick metal, you will need higher tonnage capabilities. In this case, go with a hydraulic press brake. It's the most powerful and efficient type of machine for larger jobs using thicker metals.

Laser systems :

Laser cutting systems are quite advanced. The most common applications that lasers can be used for includes:

- Cutting,
- Welding,
- Marking, and
- Surface treatment

Industries with high demand for these operations are usually ones that require high precision for cutting complex parts. These include parts for automotive, shipbuilding, aerospace, steel, electronics, and medical industries.

Laser systems work by using thermal energy to remove material from the work piece by melting, vaporizing, burning, or blowing it away. This leaves a high-quality surface finish that is critical to the success of the finished product as a whole. During operation, Computer Numerical Control (CNC) technology directs the laser head to move about the work piece, cutting the desired shapes with an accuracy of up to 10 micrometers on newer machines. This cutting process maintains *very* tight tolerances — often within .001 of an inch.

Fig. 8.5 Laser systems

If you are on the machining side of any of the previously mentioned industries, you know there is zero room for error. These machines make that level of precision possible.

Plasma systems :

While it might seem fictional, plasma is actually a common and widespread method of cutting certain materials. But, unlike some of the aforementioned cutting methods, the "certain materials" that can be cut using plasma must be electrically conductive — such as steel, aluminum, brass, and copper.

Plasma cutting systems use an accelerated jet of extremely hot, electrically ionized gas (plasma) to form an electric channel from the cutting head through the work piece, and then back to the cutting head. These fabrication machines can be found in a number of different operations because they are fast, precise with their cuts, and are relatively inexpensive to operate.

Fig. 8.6 Plasma systems

Companies that benefit the most from this particular cutting process tend to vary from large industrial manufacturers that need to make the same cut hundreds of times to small hobbyist shops that create metal art from recycled pieces.

Shears :

Shears are one of the cheapest, simplest, and most common machines on our list. These machines do exactly what you think they do: cut metal. Typically used for cutting sheet metal and aluminum, shears can also be found in places other than machine shops that cut paper, plastic, and wood.

Fig. 8.7(a) Shears

With regard to metal thickness, shearing capabilities can range anywhere from the smallest gauges (thinnest material) all the way up to work pieces that are an inch thick. Whenever machine shops place an order for more material — whether it be mild steel, aluminum, brass, etc. — it will usually arrive in sheets. You can bet that wherever that shipment came from, those sheets were formed by a shearing machine. Shears are the backbone of the metal forming world.

There are many more types of fabrication machines out there that are crucial to certain industries and have capabilities that the machines on this list cannot perform. However, you can bet that wherever one of those unnamed machines is being used, there also is a waterjet, press brake, laser, plasma or shear in the same shop sitting nearby.

Fig. 8.7(b) Shears

Hydraulic press brakes :

Hydraulic press brakes offer accuracy and versatility for bending simple or complex metal parts. Press brakes have multiple axes and come in a wide range of lengths and tonnages.

The fully welded all steel construction is designed for maximum rigidity and minimum deformation during the bending process. A heavy duty torque tube connects a pair of hydraulic cylinders so that they are synchronized and stay parallel to the bending table at all times.

Fig. 8.8 Press brakes

Ironworkers :

An ironworker can be the “Swiss Army Knife” — with stations for punching, notching, shearing and more, this versatile piece of equipment should be indispensable in your metal fabrication operation. It saves labor, time, energy and cost.

The heavy-duty Ironworker has 5 work stations that are fully integrated:

Punch Work Table: Includes back gauge and adjustable stops. Adjustable See-Through Punch Stripper: For fast and easy setup. Die Holder: Adjustable in machined T-slots for quick punch and die alignment. Support Table: Includes guides for accurate positioning and indicator lines at 30 and 45 degrees.

9 CONCLUSION

Based on this report, steel can be fabricated into any shape or size using different methods. In structural and fabrication operations, steel provides various services which is used in our day to day life. The field consisted of various fabrication machinery which had many physics principles. They explained to me about the basic raw materials used or the fabrication process and the advantages and disadvantages that follow them. Our economy relies on metal fabrication processes. Without it, we wouldn’t be able to run our electrical systems or create the parts that keep our houses, kitchens, businesses, computers, and vehicles operational. However, it is difficult for many of us to understand what precision metal fabrication entails, as well as all of the areas of our lives it affects. This field visit has explained to me the essentials of metal fabrication: its definition, history, process, benefits, types, and applications. By the end, you will have a more in-depth understanding of how crucial this process is to civilization and how many different parts of our lives it touches.

STUDY ON MANUFACUTURING OF GYM EQUIPMENTS

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

B. SANGEETHA

Reg. No : 20SPPH11

Under the guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled **"STUDY ON MANUFACTURING OF GYM EQUIPMENTS"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 -2021** by **B. SANGEETHA** (Register No: 20SPPH11)

Signature of the Staff – in - Charge

Signature of the Co-Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/9/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled **"STUDY ON MANUFACTURING OF GYM EQUIPMENTS"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field work report has been submitted for any Degree, Diploma or other similar titles.

Sangeetha. B

Station : Thoothukudi

Date : 10. 04. 2021

Signature of the Student

(B. SANGEETHA)

ACKNOWLEGEMENT

On the very outset of this report, I would like to extend my sincere and heartfelt obligation towards all the personages who have helped me in this endeavour.

I wish to record our profound gratitude to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for her motivation.

I sincerely thank our Director of SSC, Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her encouragement and support.

I wish to thank Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., HOD & Associate Professor for her inspirational work to complete this work.

I owe a great deal to Mrs. P. PADMAVATHI M.Sc., M.Phil., SET., SSC Co-ordinator for supporting me throughout this field work.

I am indebted Ms. A. VALENTINA M.Sc., M.Phil., for her guidance and support for the successful completion of this field work report.

Its my pleasure to thank Mr. J. ARASANAYAGAM, The Proprietor, Uma Health Equipments, Chennai for all the facilities provided to me in the pursuit of this field work.

I am deeply grateful to all the staff members of Department of Physics (SSC) for supporting us in all aspects.

I acknowledge my deep sense of gratitude to my loving parents for being a constant source of motivation.

CONTENT **Page.no.**

1 INTRODUCTION

Based on the partial fulfilment of the requirements for the award of Master of Science in Physics, I have carried out my fieldwork at Uma Health Equipment, Chennai. Uma Health Equipment is a popular manufacturer and distributors of top-quality fitness equipment's for home and profitable markets. They are established in 2001 and have been present a comprehensive range of products in the industry that include multi posting gyms, free weight machines, weight plates, dumb bells and all fitness equipments.

The Company gives its goods all around India. The quality craftsmanship, customer service and worth are their motto, which supports them to develop a premier reputation in the fitness equipment industry. In certain, Uma health Equipment is known for its quality products and its commercial product guarantee in this industry.

Whether our attention is in strength training, multi-station home gyms, high quality single station or any other gym equipment's, they are the definitive choice for availing quality grade fitness machines and equipment's. Their products are planned in such a way which helps you to lead a better life. The custom - made equipment is available with them at cheap rates.

Fig. 1.1 Interaction with the proprietor

2 EQUIPMENT DESIGNING

The equipment to be made is planned and designed by using software like AUTOCAD and CREO.

2.1 AUTOCAD

AutoCAD is a computer-aided design software developed by the company Autodesk (hence the name AutoCAD). It allows us to draw and edit digital 2D and 3D designs more quickly and easily than we could by hand. The files can also be easily saved and stored in the cloud, so they be accessed anywhere at any time.

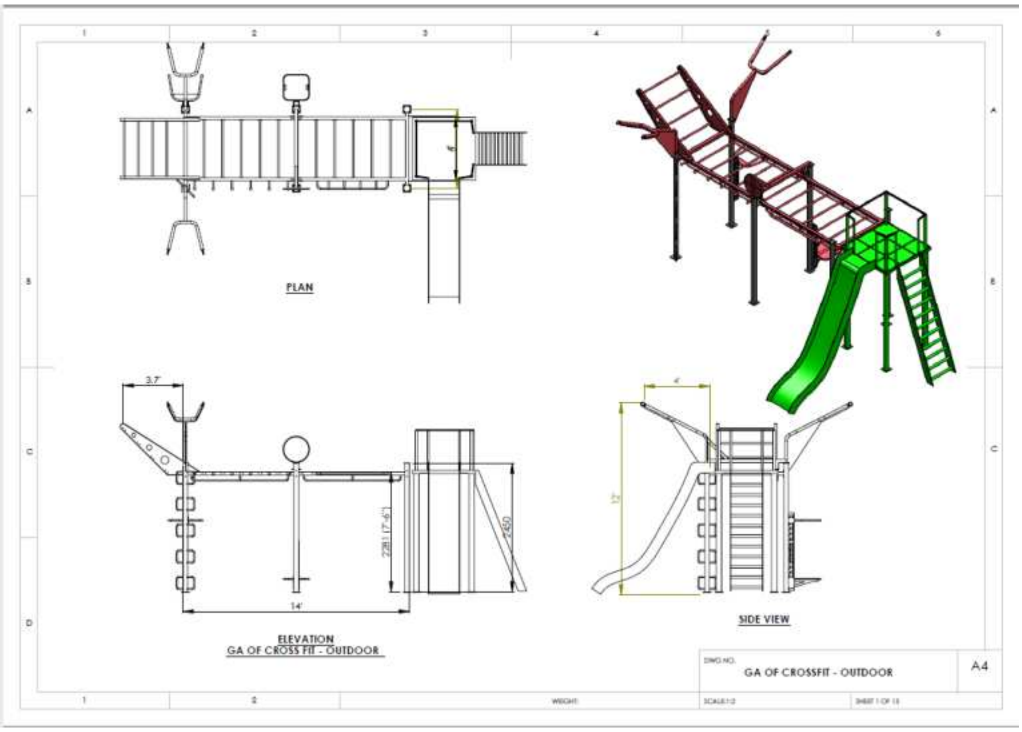


Fig. 2.1 AutoCAD image of an outdoor equipment

The above image is an example of product designed using AutoCAD. The product designed in the above sketch is cross-fit outdoor.

2.2 CREO

Creo is a family or suite of Computer-aided design apps supporting product design for discrete manufacturers and is developed by PTC. The suite consists of apps, each delivering a distinct set of capabilities for a user role within product development.

With Creo Parametric, and its extensions, we can create, analyse, view, and share designs downstream using 2D CAD, 3D CAD, and parametric and direct modelling capabilities.

Creo runs on Microsoft Windows and provides apps for 3D CAD, 3D direct modelling, 2D orthographic views, Finite Element Analysis and simulation, schematic design, technical illustrations, and viewing and visualization.

Fig. 2.2 Connecting rod designed using Creo

3 RAW MATERIAL

Raw materials are materials or substances used in the primary production or manufacturing of goods. Raw materials are commodities that are bought and sold on commodities exchanges worldwide.

Fitness equipment is primarily made of aluminium, carbon steel, or some other metal alloy. Such metals are preferred because they are both light and durable.

3.1 ALUMINIUM

Aluminium is about one-third the weight of steel, meaning parts can be made thicker and stronger while still reducing weight in equipment's.

Fig. 3.1 Aluminium rods

3.2 CARBON STEEL

Carbon steel is a special type of steel that, as the name suggests, has a higher concentration of carbon than other types of steel. Most types of steel have a relatively low carbon content of about 0.05% to 0.3%. In comparison, carbon steel has a carbon content of up to 2.5%.

Fig. 3.2 Carbon steel pipes

3.3 CAST IRON

Grey cast iron is characterised by its graphitic microstructure, which causes fractures of the material to have a grey appearance. It is the most commonly used cast iron and the most widely used cast material based on weight. Most cast irons have a chemical composition of 2.5–4.0% carbon, 1–3% silicon, and the remainder iron. Grey cast iron has less tensile strength and shock resistance than steel, but its compressive strength is comparable to low- and medium-carbon steel. These mechanical properties are controlled by the size and shape of the graphite flakes present in the microstructure and can be characterised according to the guidelines given by the ASTM.

Fig. 3.3 Cast iron rods

4 MACHINERIES

A machine (or mechanical device) is a mechanical structure that uses power to apply forces and control movement to perform an intended action. Machines can be driven by animals and people, by natural forces such as wind and water, and by chemical, thermal, or electrical power, and include a system of mechanisms that shape the actuator input to achieve a specific application of output forces and movement. They can also include computers and sensors that monitor performance and plan movement, often called mechanical systems.

4.1 LATHE

A lathe is a machine tool that rotates a workpiece about an axis of rotation to perform various operations such as cutting, sanding, knurling, drilling, deformation, facing, and turning, with tools that are applied to the workpiece to create an object with symmetry about that axis.

Fig. 4.1 Lathe machine

4.2 CUTTING MACHINE

A cutting machine or cutter is any tool that is used to remove some material from the work piece by means of shear deformation. Cutting may be accomplished by single-point or multipoint tools. Single-point tools are used in turning, shaping, planning and similar operations, and remove material by means of one cutting edge. Milling and drilling tools are often multipoint tools. It is a body having teeth or cutting edges on it. Grinding tools are also multipoint tools. Each grain of abrasive functions as a microscopic single-point cutting edge (although of high negative rake angle), and shears a tiny chip.

Cutting tool materials must be harder than the material which is to be cut, and the tool must be able to withstand the heat and force generated in the metal-cutting process. Also, the tool must have a specific geometry, with clearance angles designed so that the cutting edge can contact the workpiece without the rest of the tool dragging on the workpiece surface. The angle of the cutting face is also important, as is the flute width, number of flutes or teeth, and margin size. In order to have a long working life, all of the above must be optimized, plus the speeds and feeds at which the tool is run.

Fig. 4.2 Cutting machine

4.3 DRILLING MACHINE

A drill or drilling machine is a tool primarily used for making round holes or driving fasteners. It is fitted with a bit, either a drill or driver, depending on application, secured by a chuck. Some powered drills also include a hammer function. Drills vary widely in speed, power, and size.

They are characteristically corded electrically driven devices, with hand-operated types dramatically decreasing in popularity and cordless battery-powered one's proliferating.

Fig. 4.3 Drilling machine

4.4 BENDING MACHINE

A bending machine is a forming machine tool. Its purpose is to assemble a bend on a workpiece. A bend is manufactured by using a bending tool during a linear or rotating move.

Fig. 4.4 Bending Machine

4.5 POWDER COATING

Powder coating is a type of coating that is applied as a free-flowing, dry powder. Unlike conventional liquid paint which is delivered via an evaporating solvent, powder coating is typically applied electrostatically and then cured under heat or with ultraviolet light. The powder may be a thermoplastic or a thermoset polymer. It is usually used to create a hard finish that is tougher than conventional paint.

Fig. 4.5 Powder coating

4.6 SPRAY PAINTING

Spray painting is a painting technique in which a device sprays coating material paint, ink, varnish, etc. through the air onto a surface. The most common types employ compressed gas usually air to atomize and direct the paint particles. Spray guns evolved from airbrushes, and the two are usually distinguished by their size and the size of the spray pattern they produce. Airbrushes are hand-held and used instead of a brush for detailed work such as photo retouching, painting nails, or fine art. Air gun spraying uses generally larger equipment. It is typically used for covering large surfaces with an even coating of liquid. Spray guns can be either automated or hand-held and have

Fig. 4.6 Spray Painting

interchangeable heads to allow for different spray patterns. Single colour aerosol paint cans are portable and easy to store.

4.7 FITTING

Working on components with hand tools and instruments, mostly on work benches is generally referred to as fitting work. The hand operations in fitting shop include marking, filing, sawing, scraping, drilling, tapping, grinding, etc., using hand tools or power operated portable tools.

5 OUTDOOR EQUIPMENTS

5.1 Monkey bar

Fig. 5.1 Monkey bar

A three-dimensional framework of horizontal and vertical bars from which children can hang and swing.

Swinging forward and backward with their legs tucked up help children improve and develop the right posture. They will also improve body strength at the same time. In the meantime, they also train to attain full control over their balance and hand-eye coordination.

The length of the metal rods for each monkey bar rung should be just over 1 1/2 feet long to cover the space between your support beams. Your monkey bar rungs should be about 1 1/2 feet long, spaced 1 foot apart.

Insert an end of a 1-inch Aluminium pipe into each of the holes. They are snug, so place a small piece of scrap wood over the other end of the pipe and gently hammer it down into the hole.

5.2 Leg press

The leg press is a compound weight training exercise in which the individual pushes a weight or resistance away from them using their legs.

The term leg press machine refers to the apparatus used to perform this exercise. The leg press can be used to evaluate an athlete's overall lower body strength (from knee joint to hip). It can help to build squat strength.

Leg Press provide great mass building exercise. Perfect leg press machine has much fashionable function that helps you to achieve the aim at the earliest possible.

Features both back pads utilizes a quick flip and lock mechanism, relaxed access under bearing plate load system. Three lock out positions for user security.

Fig. 5.2 Leg press

5.3 Seated chest press machine

Fig. 5.3 Seated chest press machine

The seated chest press machine is an upright version of the standard lying bench press machine. The arms, placed under a weight-bearing load, are pushed away from the chest and returned to starting position. The chest press helps build the pectoral muscles as well as the biceps, deltoids, and latissimus dorsi muscles.

The Vertical Chest Press Machine provides a fixed line of movement and focuses on the muscles of the chest. The machine features two stiff bars that raise to chest height and allow you to press outward in a motion similar to rowing while providing adjustable resistance.

5.4 Sit up bench

Fig. 5.4 Sit up bench

A sit up bench is an exercise equipment that has an inclined or declined position which can be either stationary or adjusted for the comfort you want, and the position that would better suit your exercise style.

The Bench provides perfect training for the core and lower back muscles by doing exercises such as leg lifts and sit ups. However, this bench is actually multi-use and also allows push-ups, stretching.

A sit up bench is designed for intense abdominal exercises during which you can aspire to have rippling abs as a result. It can also be used for chest presses, and other different kinds of exercises. Sit up benches include a padded backrest and support pads that provide maximum comfort and stability during exercises.

5.5 Dip station

Fig. 5.5 Dip station

A dip station is a fixed frame piece of exercise equipment that helps you to perform multiple exercises targeting multiple muscle groups and joint movements. They can be used to work muscle groups such as chest, triceps, back or abs and when combined with a dip belt, these can provide a killer workout.

On average, most dip bars are 18 to 24 inches wide. Some machines have adjustable grip widths. Larger individuals rotate the handles outward for a wider grip and smaller individuals rotate them inward for a closer grip.

5.6 The horse rider station

Fig. 5.6 Horse rider station

Horse Rider Station is the widely used outdoor fitness equipment designed especially for Pneumonic function, enable full movement of limbs, and building up the strength of legs and chest muscles.

6 INDOOR EQUIPMENTS

6.1 Single station gym

Fig. 6.1 Single station gym

Single station gym equipment refers to machines that are designed and built specifically for one exercise or body part. The single station machines will be often arranged according to the muscle group they are targeting and/or by their resistance method.

6.2 Bench Press

Fig. 6.2 Bench Press

The bench press is an upper-body weight training exercise in which the trainee presses a weight upwards while lying on a weight training bench. The exercise uses the pectoralis major, the anterior deltoids, and the triceps, among other stabilizing muscles. A barbell is generally used to hold the weight, but a pair of dumbbells can also be used.

6.3 Multi Bench

Fig. 6.3 Multi Bench

A multi exercise bench is a great equipment for those who are looking forward to increase their upper body strength. This equipment has 3 adjustable back angles; flat, incline and decline. By performing a workout in different angles, users can strengthen their back muscles and improve flexibility.

6.4 Push-up bar

Fig. 6.4 Push-up bar

Push-ups is one of the most common ways of getting strong and toned biceps. However, to reach an advanced level of fitness and do push-ups in a more regulated manner, you need to use push-up bars.

6.5 Double twister

Fig. 6.5 Double twister

Twister are designed to tone your physique and improve balance. They do this by working your entire core, or midsection.

The core comprises muscles that support and stabilize your body. These include the abdominals, lower back muscles, glutes, hips, and pelvis.

People also use twist boards as a form of exercise to help burn calories.

Twist boards strengthen your core, so they may help you avoid back injury. A strong core is also important for physical strength and balance.

Twist boards may help you achieve some muscle tone and whittle away fat around your midsection. For some women, this can translate into a flatter stomach, tighter hips, and a smaller waist.

6.6 Wall mounting chin up bar

Fig. 6.6 Wall mounting chin up bar

Chin-ups can help improve grip strength, posture and appearance, while also helping to strengthen muscles that stabilize the spine. This, in turn, can help reduce one’s risk of back pain and injury. Even if a client is only able to do one or two chin-ups at a time, this exercise offers tremendous benefits, especially for the back, shoulders, forearms and biceps.

In addition to helping develop strength in the involved muscles, the ability to lift one’s own body weight can provide clients with an enormous sense of empowerment.

6.7 Single twister

Twister are designed to tone your physique and improve balance. They do this by working your entire core, or midsection.

The core comprises muscles that support and stabilize your body. These include the abdominals, lower back muscles, glutes, hips, and pelvis

Twist boards strengthen your core, so they may help you avoid back injury. A strong core is also important for physical strength and balance.

Fig. 6.7 Single twister

Twist boards may help you achieve some muscle tone and whittle away fat around your midsection. For some women, this can translate into a flatter stomach, tighter hips, and a smaller waist.

People also use twist boards as a form of exercise to help burn calories.

6.8 Abdominal Bench

Fig. 6.8 Abdominal Bench

The Abdominal bench resembles a small, decline weight bench. Designed specifically to work on your abs, this bench features pads at the top end of the bench to hold your feet in place. These benches are designed to be flexible, many of them are made to be adjustable.

The design is such that the steeper the design, the more difficult it will be to carry out the crunch. With the ab bench, you can work extensively on your entire midsection and your rectus abdominis, the main ab muscles and the oblique. Also, this bench can be used to exercise the side abs.

6.9 Multi bench press

Fig. 6.9 Multi bench press

A multi bench press is actually a fairly simple exercise, simple yet hard. It involves lying down in a supine position, or in other words, flat on your back, usually on a bench, hence the name bench press. This is actually one of the three exercises which power lifters engages in.

It involves lying on your back and pressing a certain amount of weight vertically upwards from your chest until your arms are extended. Usually, a barbell is used to hold the weight, but dumbbells can also be used. The barbell is often preferred because it can hold a lot of weight and is also more stable than using individual dumbbells.

7 CURRENT PROJECTS

7.1 Outdoor equipment

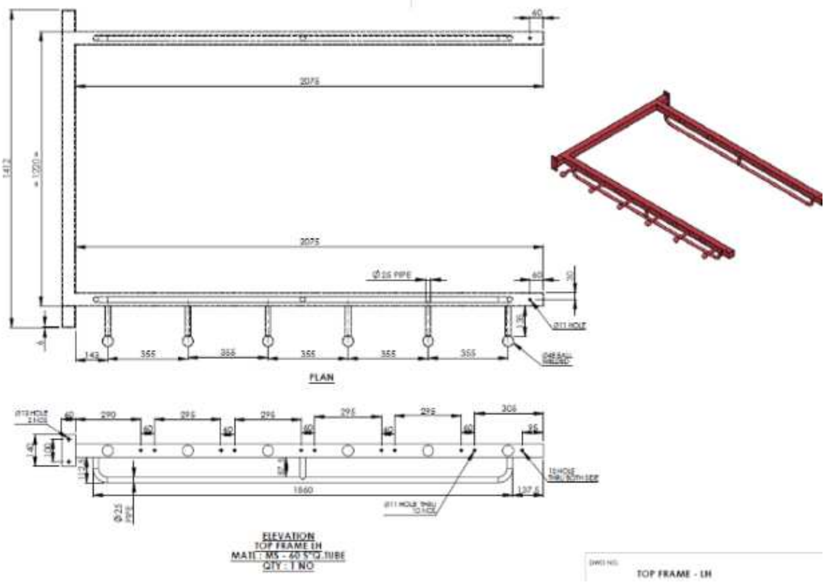


Fig. 7.1.1 GA of crossfit outdoor

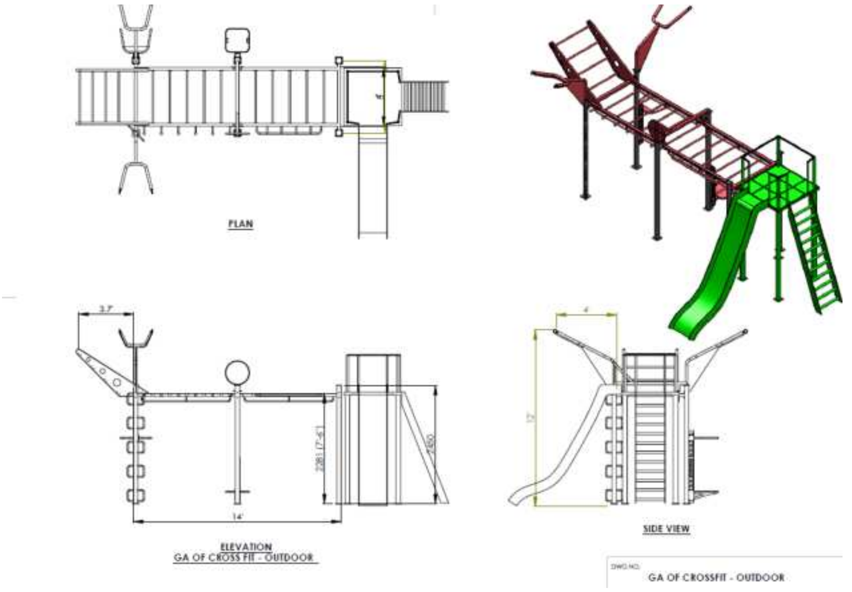


Fig. 7.1.2 Top frame - LH

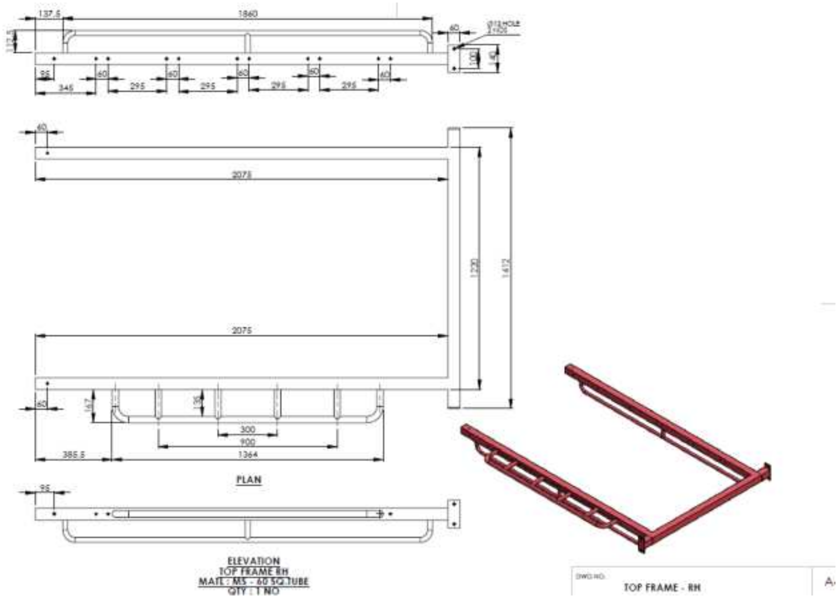


Fig. 7.1.3 Top frame – RH

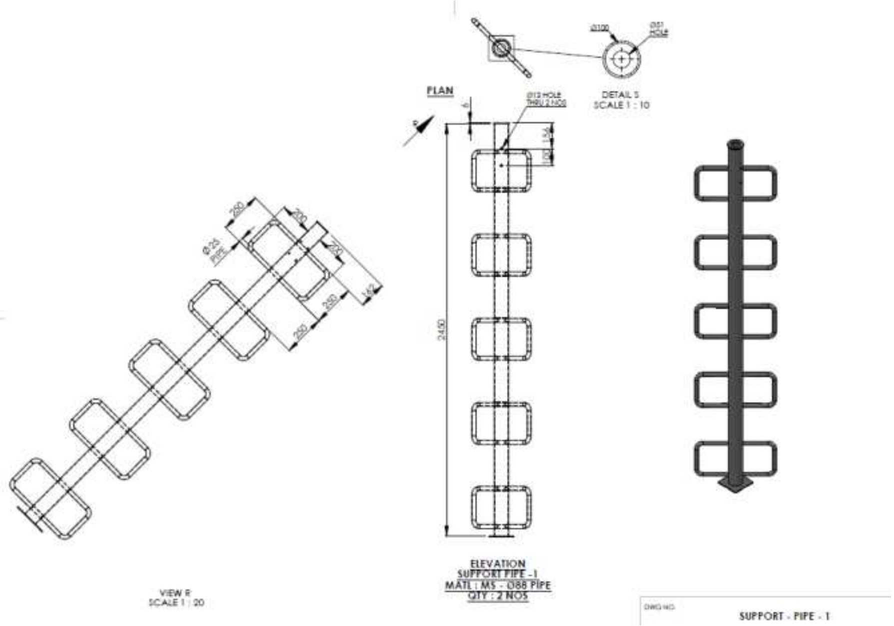


Fig. 7.1.4 Support pipe

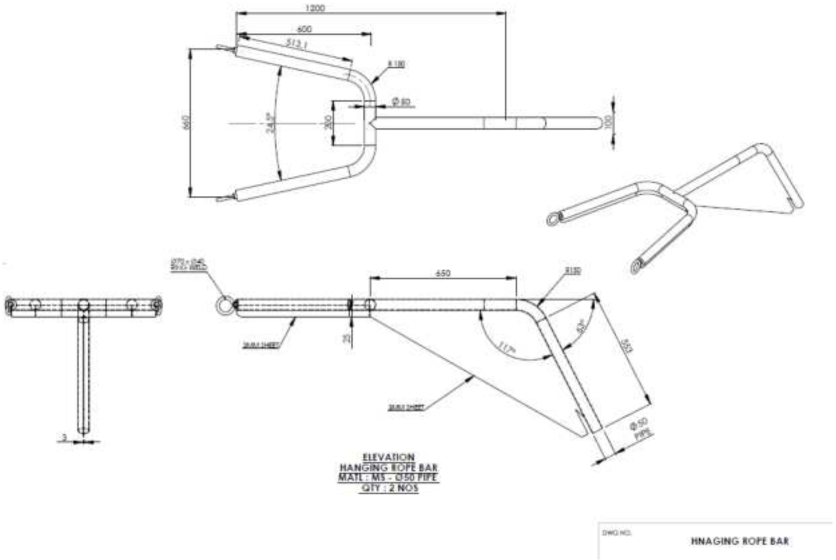


Fig. 7.1.5 Hanging rope bar

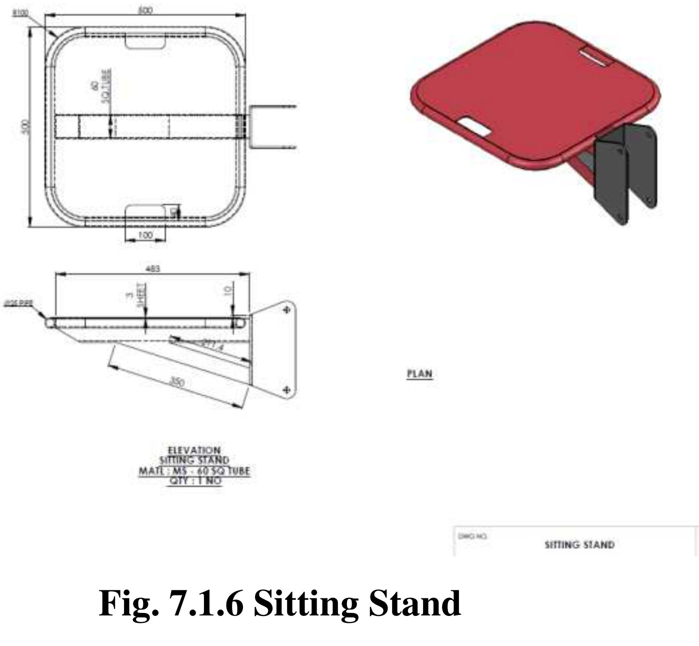


Fig. 7.1.6 Sitting Stand

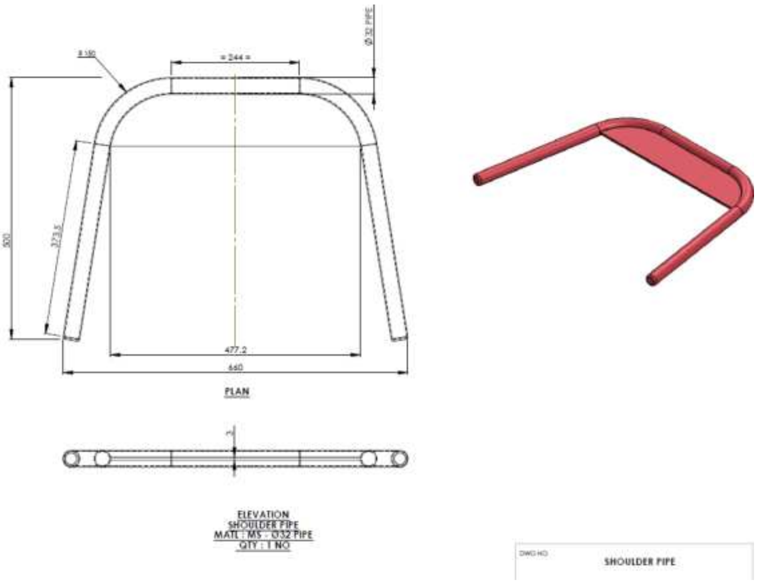


Fig. 7.1.7 Shoulder pipe

7.2 Indoor equipment

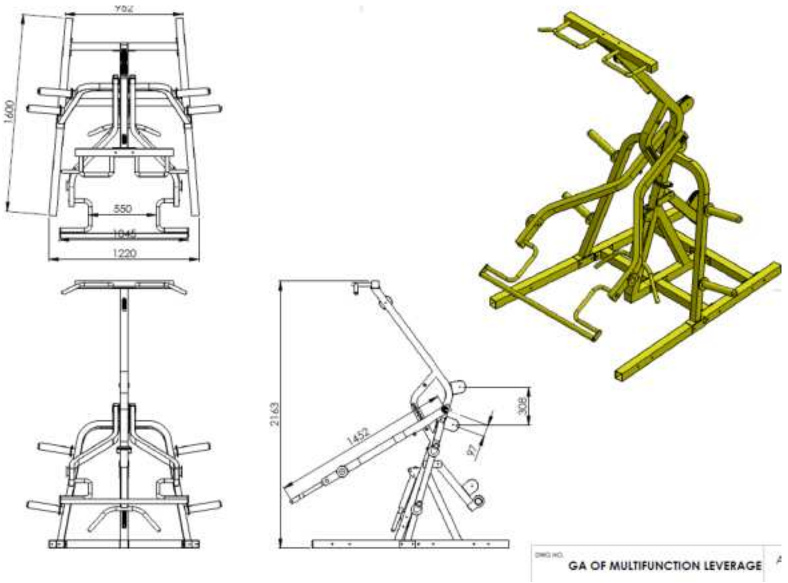


Fig. 7.2.1 GA OF Multifunction leaverage

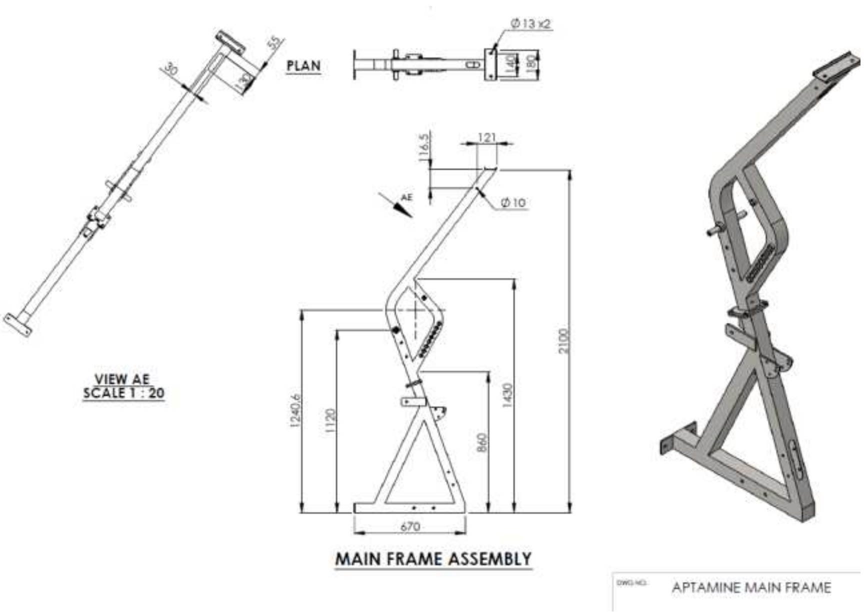


Fig. 7.2.2 Aptamine main frame

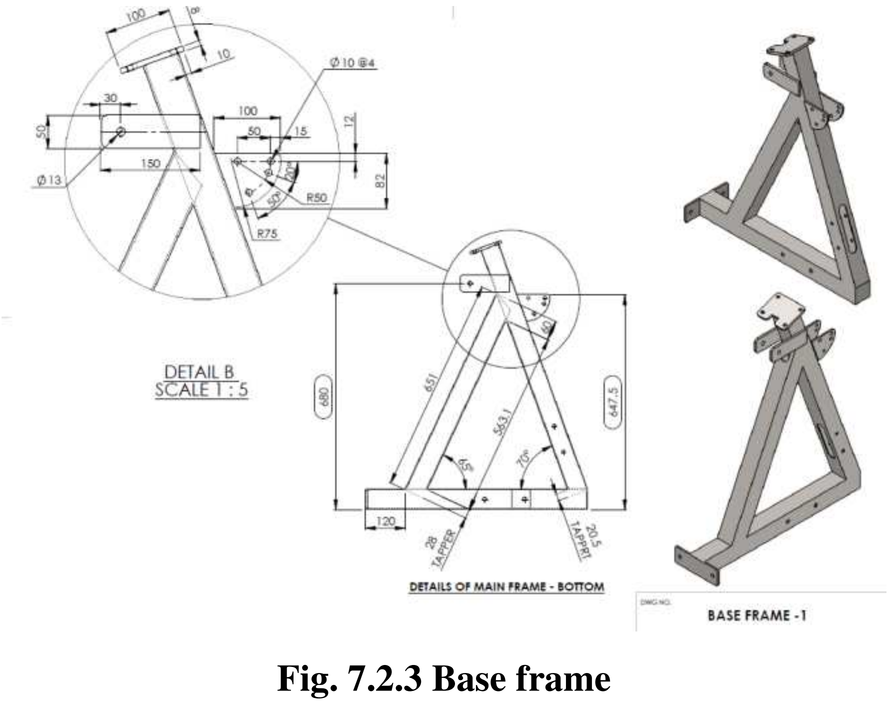


Fig. 7.2.3 Base frame

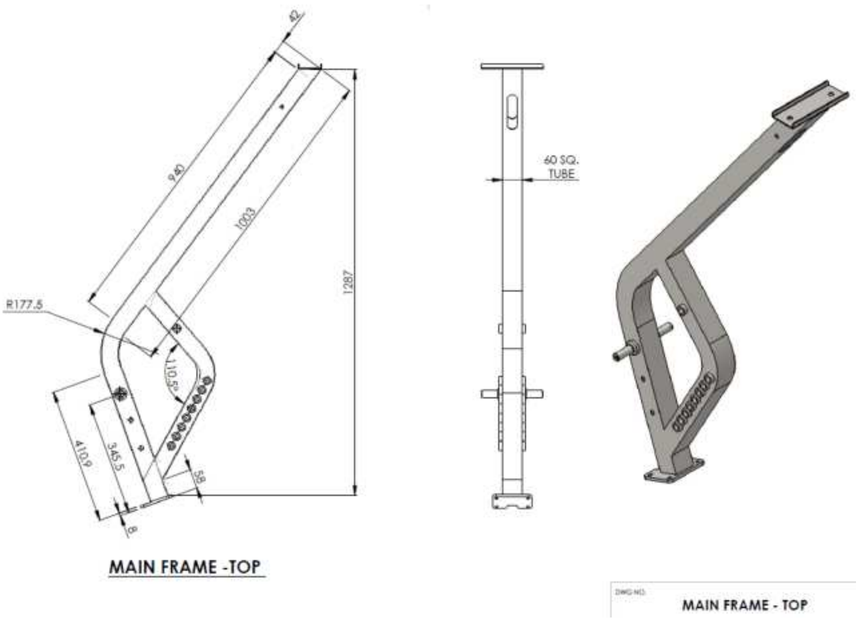


Fig. 7.2.4 Main frame top

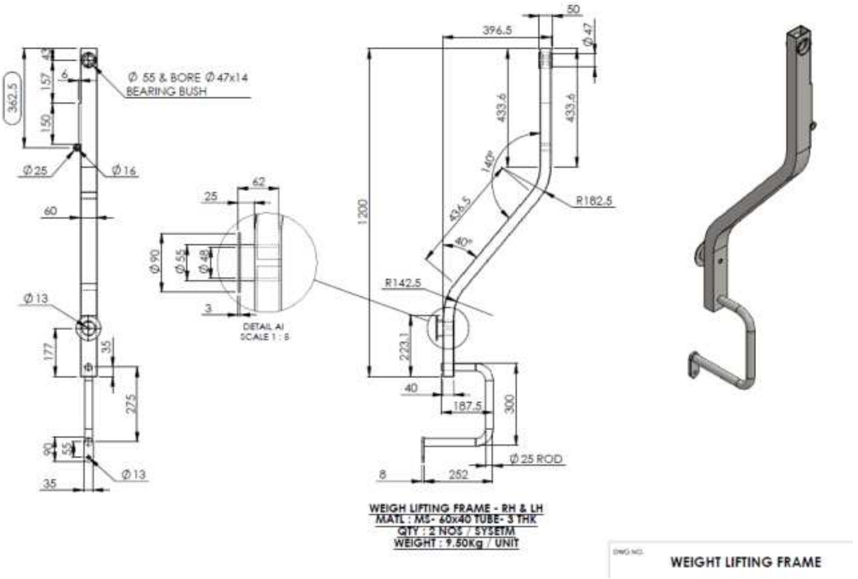


Fig. 7.2.5 Weight lifting frame

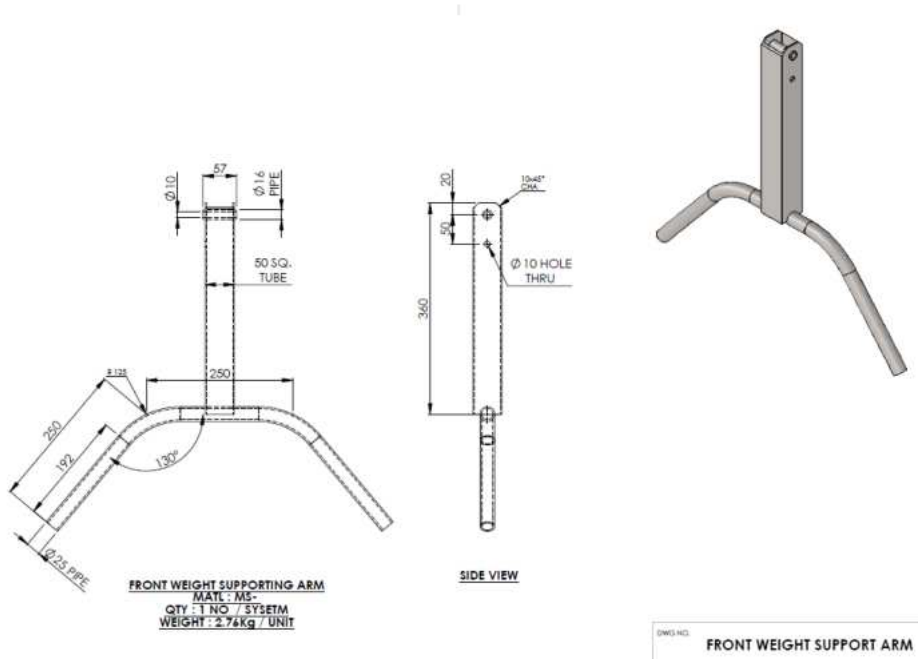


Fig. 7.2.6 Front weight support arm

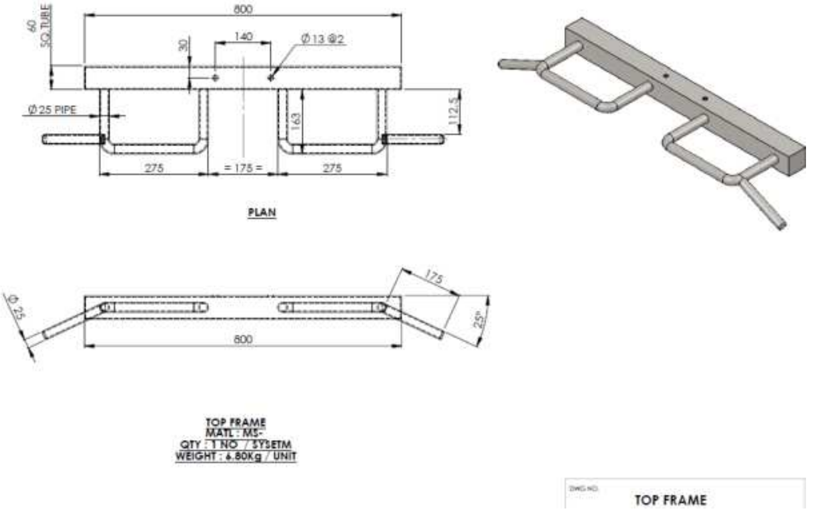


Fig. 7.2.7 Top frame

8 CONCLUSION

Based on this report I would like to conclude that my field work is about the study of manufacturing of gym equipment, exercise benches and indoor and outdoor fitness equipment. The company I chose is a popular manufacturer and distributors of top-quality fitness equipments for home and profitable markets in Chennai. The core work of the company is to collect raw materials from the market, design the desired equipment with the help of computer software, manufacture the equipment with help of machineries, powder coat the manufactured parts and assembling of the parts to get the desired equipment. The current project of the company was cross fit outdoor equipment and null indoor equipment. This field work helped me to gain knowledge in the field of fitness equipment and their manufacturing processes and the other techniques.

STUDIES ON X-RAY MACHINE

A field work report submitted to

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

K. SANGEETHA

Reg. No: 20SPPH12

Under the guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to verify that this field work report entitled **"STUDIES ON X-RAY MACHINE"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 -2021** by **K. SANGEETHA** (Register No: 20SPPH12)

Signature of the Staff-in-Charge

Signature of the Co-Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, **"STUDIES ON X-RAY MACHINE"** is submitted to **ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNEVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree, Diploma or other similar titles.

K.Sangeetha

Signature of the student

Station: Thoothukudi

(K.SANGEETHA)

Date: 10.04.2021

ACKNOWLEDGEMENT

First of all, I thank the Lord Almighty for his blessing and grace to complete this Report work.

I am deeply indebted to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, Rev.Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her support in my work.

I would like to express my special gratitude to Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., Head of Department for her inspirational words to complete this report work.

I would convey my heartfelt thanks to Mrs. P. PADMAVADHI M.Sc., M.Phil., SET., SSC Co-Ordinator, Department of Physics for her efficient and encouragement in successful completion of this report.

I wish to record my sincere thanks to Ms. A. VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her enthusiastic guidance and support for completion of this field work report.

It is my pleasure to extend my thanks to Mr. M. MUTHU SELVAM E.E.E., General Manager, Aarthi scans and labs, Thoothukudi, for help and support to complete my Field work.

CONTENT **Page.no.**

1 INTRODUCTION

X-rays are a form of electromagnetic radiation, similar to visible light. Unlike light, however, X-rays have higher energy and can pass through most objects, including the body. Medical X-rays are used to generate images of tissues and structures inside the body. If X-rays travelling through the body also pass through an X-ray detector on the other side of the patient, an image will be formed that represents the “shadows formed by the objects inside the body. One type of X-ray detector is photographic film, but there are many other types of detectors that are used to produce digital images. The X-ray images that result from this process are called radiographs. X-rays from nature come from extraterrestial sources, such as distant suns and stars, however these X-rays simply contribute to background radiation that is all around us. The ground and soil are also sources of natural background radiation. Depending on where a person lives will determine how much exposure they will receive from natural background radiation sources, however this type of exposure is typically not dangerous. Medical X-rays come from a machine that is designed to emit radiation on command. The history of how X-rays were discovered is interesting. In the late 1800’s there were many scientists of that era hat were experimenting with electricity which at that time was a new phenomenon. One particular experiment involved the behavior of electricity in a vacuum. Radiography uses a very small dose of ionizing radiation to produce pictures of the body’s internal structures.

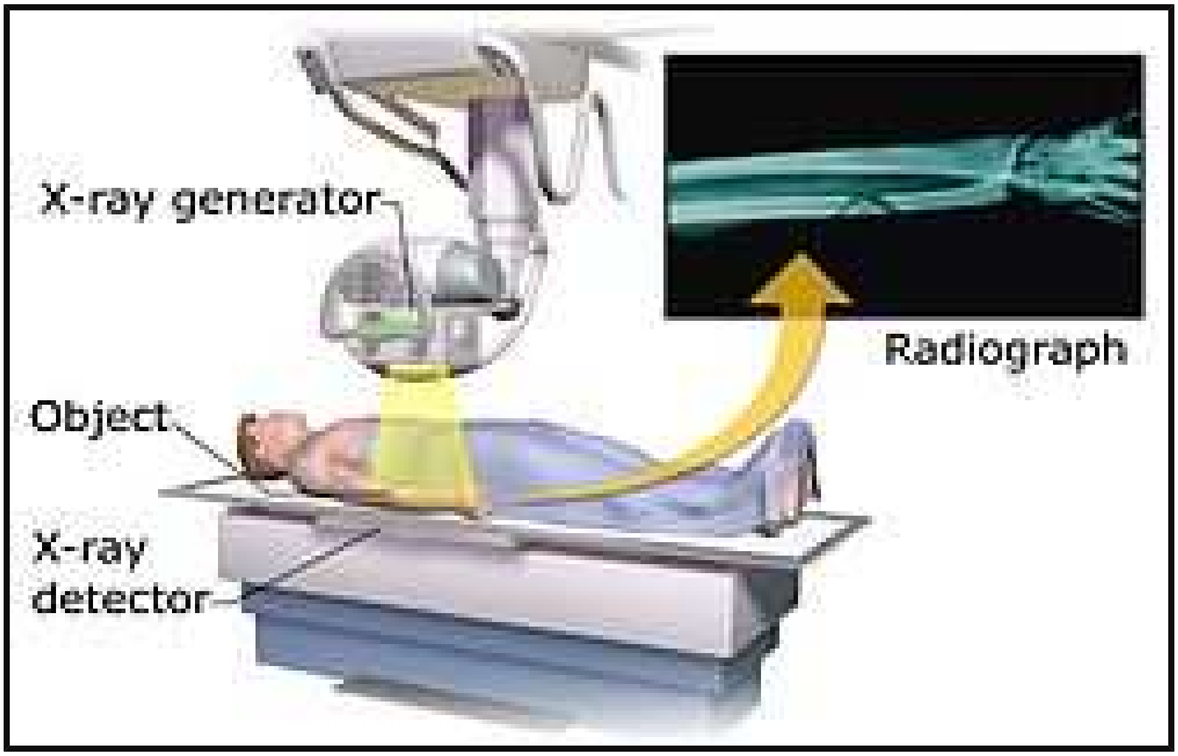


Fig. 1 projectional radiography

2 DISCOVERY OF X-RAYS

The experiments that scientists were conducting involved a bulb like device called a Crooks tube which is illustrated here. You will notice that the tube has two electrodes; an anode which is electrically positive and a cathode which is negative. The idea here was to pass electricity from the cathode to the anode. Because electricity is comprised of electrons flowing in a conductor, what they did in this case they made the electrons stream across the space between the cathode to the anode. If there is air in the tube, this means that any electrons that are streaming across the space between the cathode and anode will most likely collide with the atoms whatever gas is in the tube. These collisions will reduce the efficiency of transmitting the electricity (current) and this is why they tried to remove as much of the air as they could in the Crookes tube. One thing that they did not know at the time, whenever the electrons streamed across the distance between the cathode and anode, the electrons would accelerate to a very high velocity. The electrons that were streaming across the space between the cathode and anode were called “cathode rays”. This velocity was controlled by the voltage applied to the Crookes tube. The higher the voltage, the greater the velocity of the electron stream. Little did the scientists know that when the electrons arrived at the anode as well as the surrounding glass tube, collisions between the high-speed electrons and the atomic structure of the anode metal and glass would take place. It is these interactions that that are responsible for the production of X-rays as well as a “glowing effect” in the glass tube that was often observed when the tube was energized.

Fig 2 William Roentgen

William Conrad Roentgen who is credited for the discovery of X-rays was a professor and physicist at the University of Wurzburg in Germany. In the Fall of November,1895 he was conducting an experiment where he was discharging high voltage in a Crookes tube which was partially evacuated. The tube he was using happened to have a black cardboard cover and he happened to notice that whenever he energized the Crookes tube, there was a faint glowing of a small screen laying close by. It was this observation of the glowing effect that led to additional investigation of the phenomena. There were many famous people that were conducting the electrical experiments at the time. Besides Roentgen, there were other scientists that were involved in the early experiments. Later even individuals like Thomas Edison were credited with producing the first fluoroscopic device which uses X-rays and can provide “moving X-ray images”. An X-ray or Radiography is a penetrating form of high-energy electromagnetic radiation. Most X-rays have a wavelength ranging from 10 picometers to 10 nanometers, corresponding to frequencies in the range 30 petahertz to 30 exahertz (30×10^{15} Hz to 30×10^{18} Hz) and energies in the range 124 eV to 124 keV. X-ray wavelengths are shorter than those of UV rays and typically longer than those of gamma rays. In many languages, X-radiation is referred to as Rontgen radiation, the discovery of X-rays stimulated a veritable sensation. Rontgen’s biographer Otto Glasser estimated that, in 1896 alone, as many as 49 essays and 1044 articles about the new rays were published. This was probably a conservative estimate, if one considers that nearly every paper around the world extensively reported about the new discovery, with a magazine such as Science dedicating as many as 23 articles to it in that year alone. Sensationalist reactions to the new discovery included publications linking the new kind of rays to occult and paranormal theories, such as telepathy.

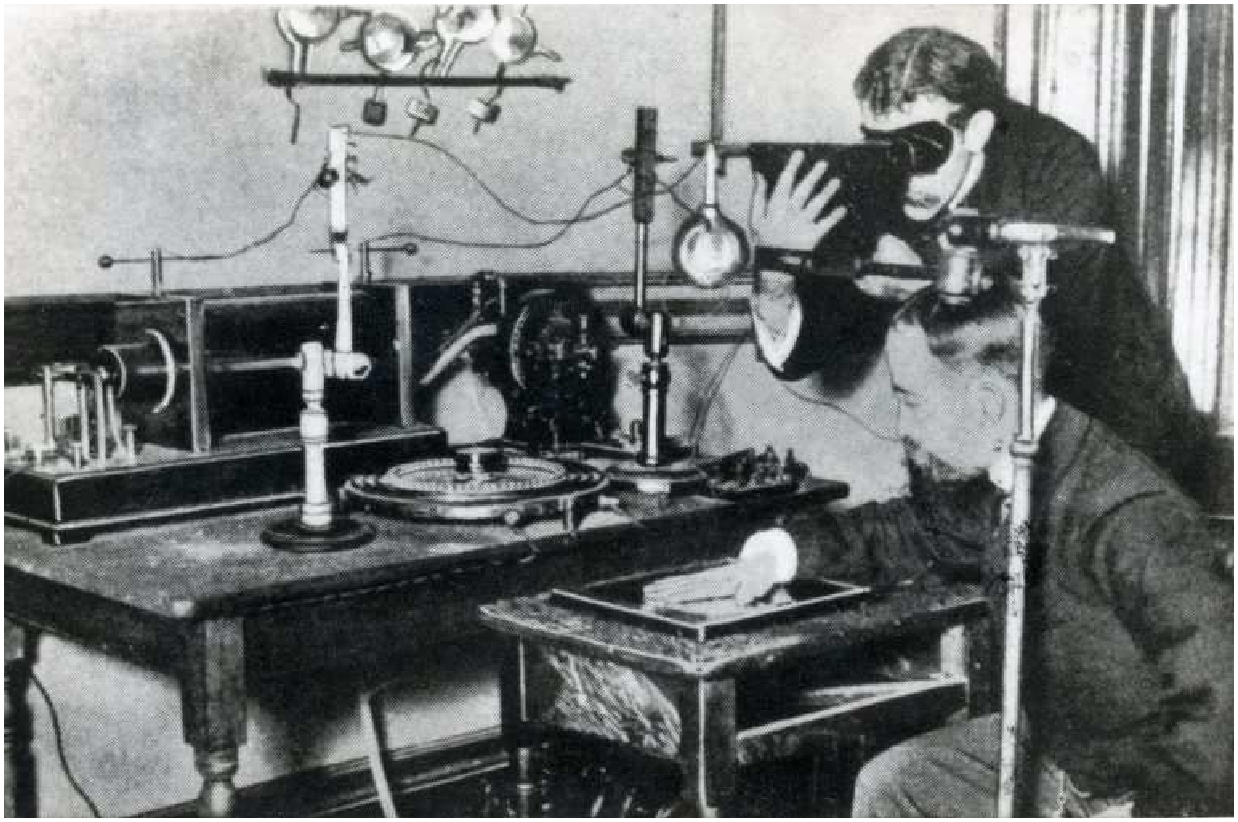


Fig 2.1 Fist X-ray machine discovered by Rontgen

3 PROPERTIES OF X-RAYS

3.1. Physical properties:

- X-rays belong to a family of electromagnetic radiations having a wavelength between 10 Å and 0.01 Å.
- They travel with the same speed as that of visible light.
- They are invisible to the eye and cannot be seen, heard or smelt.
- They cannot be reflected, refracted and deflected by a magnet or electric field as they do not possess any charge.

- X-rays are pure energy no mass and they transfer energy from place to place in the form of quanta(photons)

3.2. Chemical properties:

- X-rays induce color changes of several substances.
- X-rays bring about chemical changes in solutions which are otherwise completely stable.
- X-rays cause destruction of fermenting power of enzymes.

3.3. Biological properties:

- When X- rays are incident on an atom, one of the reactions it produces is ‘excitation’.
- These state of ‘excitation’ in biological materials enable it to take part in a chemical process into which in the normal state it would not enter.
- This is an important cause of biological damage produced by radiation.

4 PRODUCTION OF X-RAYS

X-rays can be produced with the help of high vacuum tube with a heater, cathode and anode. Vacuum tube is operating at very high voltage. A special electron tube (vacuum tube) is shown. which is used for production of X-rays. Such a tube has a hot filament cathode an anode made a very heavy metal. Electron flow from the cathode to anode as in any diode tube. However, a large DC voltage is used between cathode and anode of X-rays tube.

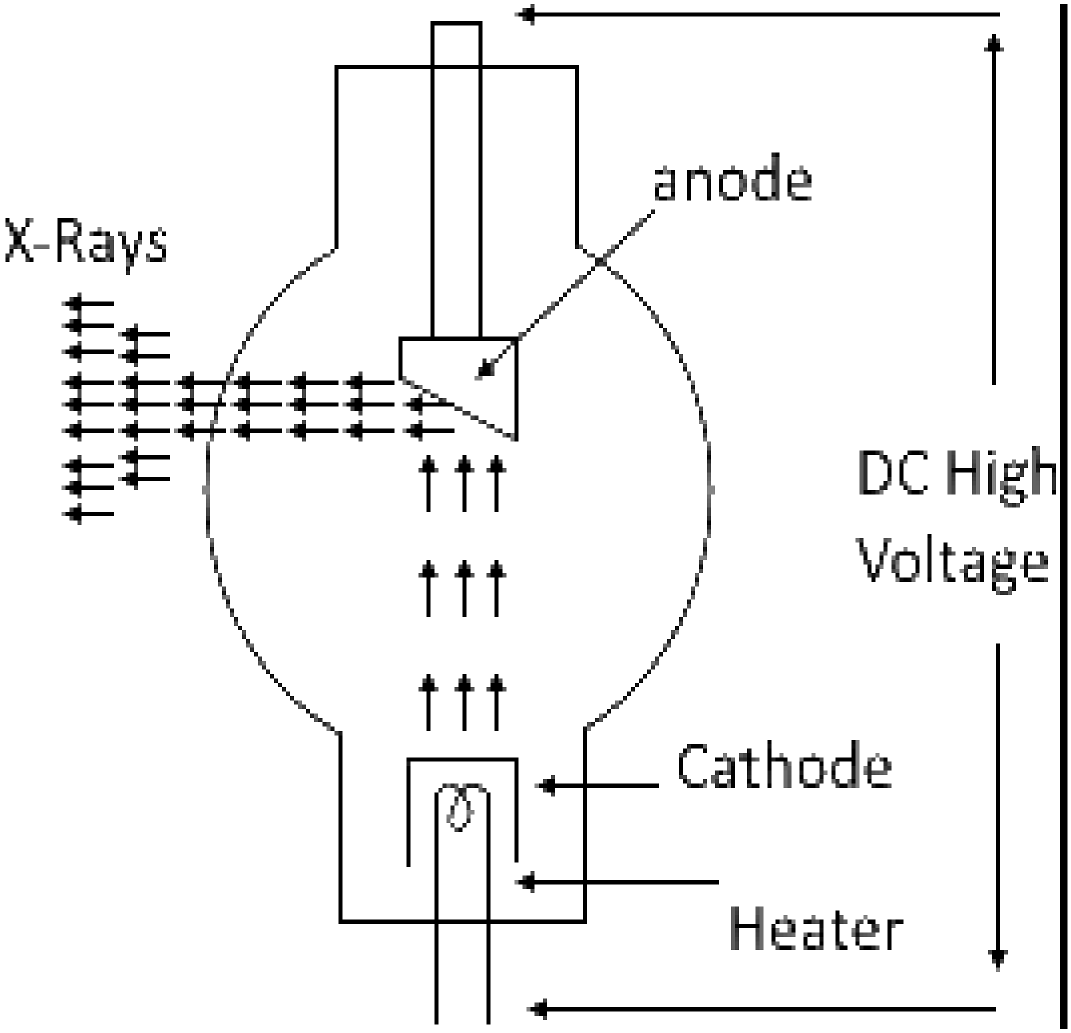


Fig 4 X-ray tube

When heater is on and very high anode to cathode voltage is applied the electron emits from cathode and travel toward the anode with very high Velocity, as clear from diagram, this beam of electron strikes the metal anode such speed that new rays are made from the slanting surface of the anode these X-rays seem to bounce sideways ad out thought the well of the tube. As the DC voltage (anode-to-cathode of the X-rays tube) is increased, the wavelength of X-rays decreases. Same tubes now operate at more than a million volts.

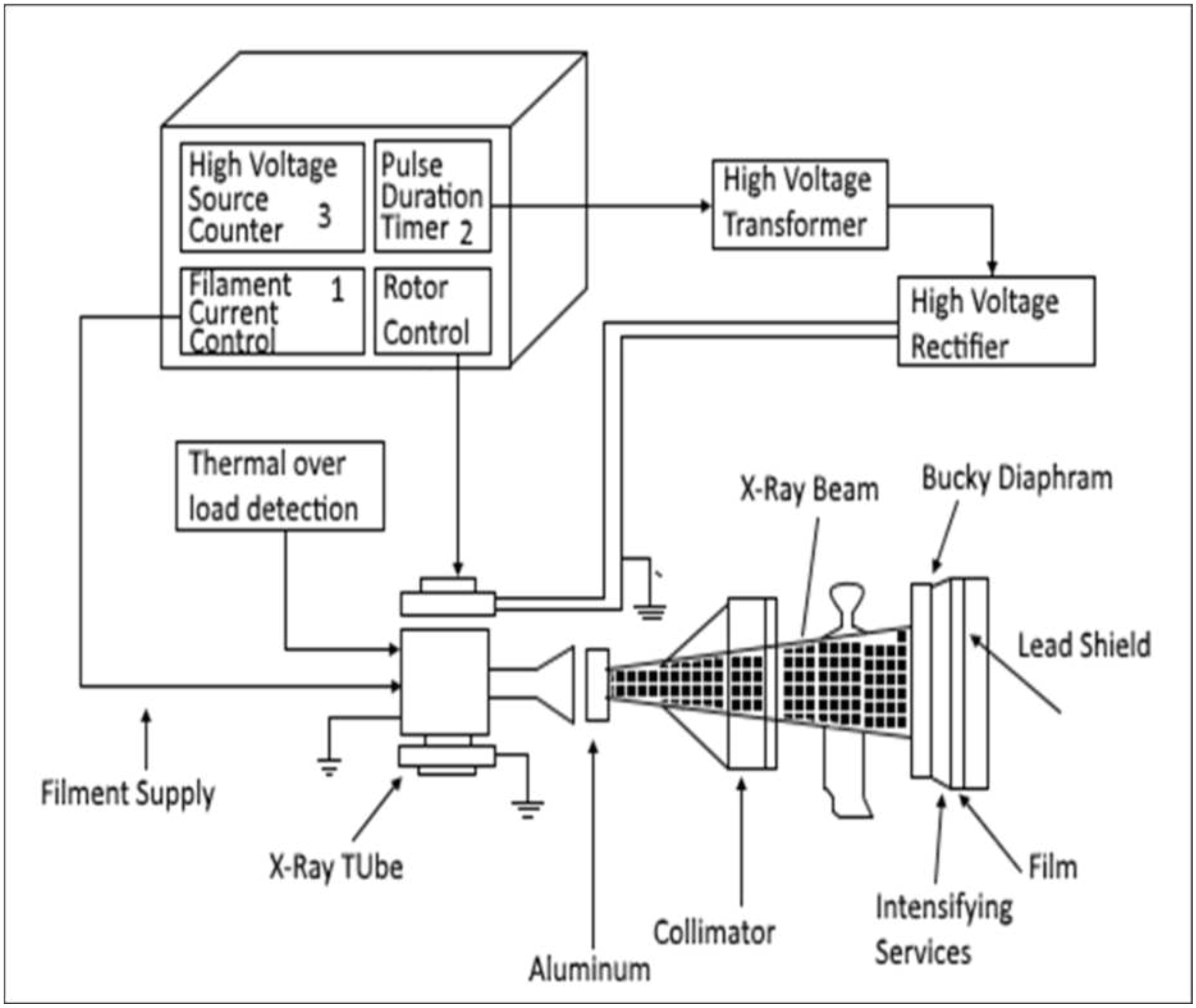


Fig 4.1 Block diagram of X-ray machine

5 WORKING OF X-RAY MACHINE

To create a radiograph, a patient is positioned so that the part of the body being imaged is located between an X-ray source and an X-ray detector. When the machine is turned on, X-rays travel through the body and are absorbed in different amounts by different tissues, depending on the radiological density of the tissues they pass through. Radiological density is determined by both the density and the atomic number (the number of protons in an atom's nucleus) of the materials being imaged. For example, structures such as bone contain calcium, which has a higher atomic number than most tissues. Because of this property, bones readily absorb X-rays and, thus, produce high contrast on the X-ray detector. As a result, bony structures appear whiter than other tissues against the black background of a radiograph. Conversely, X-rays travel more easily through less radiologically dense tissues such as fat and muscle, as well as through air-filled cavities such as the lungs. These structures are displayed in shades of gray on a radiograph.

- **High voltage source and High voltage transformer:**

High voltage source is responsible for providing high voltage to the H.V transformer for a decided time. The H.V transformer produces 20 KV to 200 KV at the O/P. These voltages are used to determine the contrast of the image. High voltages have higher contrast.

- **High voltage rectifier:**

This rectifier rectifies the high voltage produced by the H.V.T and supplies them to the anode of the X-ray tube.

- **Thermal overload detector**

The heat of the X-ray tube (should not be increase by a specified range). If the heat is exceeded from a specified value, and then the thermal over load detector is used to turn off system.

- **Rotor control:**

Most of the X-ray tube anodes are rotated by an induction motor, in order to limit beam power at any spot and helps to cool the anode.

- **Pulse duration timer:**

The duration of the time must be very small so that

1.The patient does not receive the excessive dose,

2.The film does not become over exposed.

3.The X-ray tube does not over neat. The pulse duration timer determines this pulse duration

- **Aluminum Filter:**

  The X-ray beam used in the medical field which contains a broad band of frequencies. The unwanted frequencies in the X-ray based create side effects for example extra dose for patient causing tumor also reduce the contrast in the image. These are called soft X-ray. To eliminate these effects Aluminum filter is used.

- **Collimator:**

Another mean to reduce the dose of patient is to confine the X-ray beam only on the region of interest on the body of patient. An external collimator placed between patient and filter does this.

- **Diaphragm:**

X-rays inside the patient create X-ray scattering, which tends to burned the image to absorb the scattered X-rays and eliminate the burning of an image a lead grid is used which is called diaphragm.

- **Film and lead shield:**

The X-rays passed from the desired region of the patient body are made to strike on the film where they produce an image of the body soft and hard parts. A lead shield is use to collect the X-rays after striking on film.

The H.V. source produces high voltage supply, which are rectified by rectifier and applied to anode of the X-ray tube. Filament supply is also provided. As a result,

X-ray tube producing an X-ray beam which is passed through the body and produces image of body and the film, which is examined in laboratory.

6. TYPES OF X-RAY RADIOGRAPHY

The X-ray radiography classified into following types.

- Abdominal X-ray
- Barium X-ray
- Bone X-ray
- Chest X-ray
- Dental X-ray
- Extremity X-ray
- Hand X-ray
- Joint X-ray
- Lumbosacral spine X-ray

- Neck X-ray
- Pelvis X-ray
- Sinus X-ray
- Skull X-ray
- Thoracic X-ray
- Upper GI and small bowl series
- X-ray of the skeleton

6.1 Hand PA X-ray:

Indications:

The PA hand view is requested for diagnosing a variety of clinical indications such as rheumatoid arthritis, osteoarthritis, suspected fracture or dislocation and localizing foreign bodies.

This view complements the ball-catcher view as it is particularly useful for diagnosing early signs of rheumatoid arthritis and osteoarthritis in the metacarpals, carpal bones and distal radio ulnar joint.

Patient position:

- Patient is seated alongside the table
- The affected arm if possible is flexed at 90° so the arm and hand can rest on the table
- The affected hand is placed, palm down on the image receptor
- Shoulder, elbow, and wrist should all be in the transverse plane, perpendicular to the central beam

- The hand and elbow should be at shoulder height which makes radius and ulna parallel (lowering the arm makes radius cross the ulna and thus relative shortening of radius).

Technical factors:

- Posteroanterior projection
- Centering point: Third metacarpal head

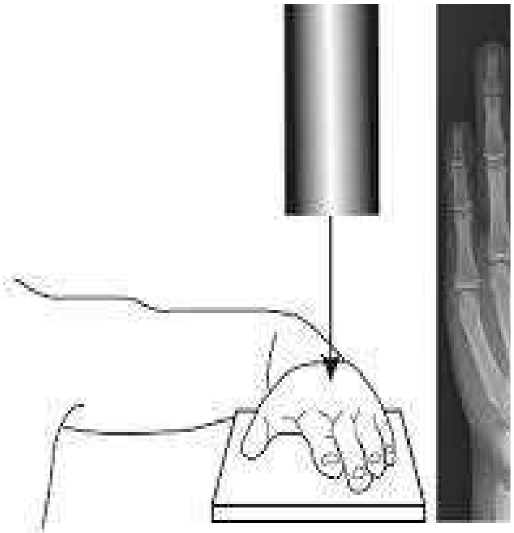


Fig 6.1 Hand PA X-ray positioning

- Collimation
    - Laterally to the skin margins
    - Proximal to include distal radioulnar joint
    - Distal to the tips of the distal phalanges
- Orientation: portrait
- Detector size:18 cm x 24 cm

- Exposure: 50-60 kVp and 1-5 mAs
- SID: 100 cm
- Grid: No

Fig 6.1.1 Hand AP X-ray positioning

Image technical evaluation:

Fifth finger is positioned PA, with no rotation as evidenced by the symmetric appearance of the concavities of the phalanges. Interphalangeal and metacarpophalangeal joint spaces of digits 2 to 5 appear open.

The concavity of the metacarpal shafts is equal.

Practical points:

The hand is not a technically challenging radiograph, always ensure the fingers are equal distance apart and the detector is high enough to avoid overlap at the wrist.

Always include the wrist joint on your PA radiograph, patients may have referred pain from pathology other than the hand.

Fig 6.1.1 Hand PA X-ray image

6.2 Chest X-ray:

A Chest radiograph is called a Chest X-ray is projection radiograph of the chest, used to diagnose conditions affecting the chest, its contents and nearby structures. The chest X-ray is performed to evaluate the lungs, heart and chest wall. A chest X-ray is typically the first imaging test used to help diagnose symptoms such as:

- Breathing difficulties
- A bad or persistent cough
- Chest pain or injury
- Fever

Physicians use the examination to help diagnose or monitor treatment for conditions such as:

- Pneumonia
- Heart failure and other heart problems
- Emphysema
- Lung cancer
- Positioning of medical devices
- Fluid or air collection around the lungs
- Other medical conditions

Types of Chest X-ray projection:

Commonly the types of Chest X-ray projections are following as,

- PA Projection
- AP Projection
- Lateral Projection

PA Projection:

The posteroanterior (PA) view is the standard frontal chest projection. The X-ray beam transverses the patient from posterior to anterior. It is performed standing and in full inspiration with the patient hugging the detector to pull the scapulae laterally. It is the best general radiographic technique to examine the lungs, bony thoracic cavity, mediastinum and great vessels. It gives technically excellent visualisation of the mediastinum and lungs, with accurate assessment of heart size. Disadvantage of this is patient able to stand erect.

AP Projection:

The anteroposterior (AP) erect view is an alternative frontal projection to the PA projection with the beam traversing the patient from anterior to posterior. It can be performed with the patient sitting up on the bed and even performed outside the radiology department using a mobile X-ray unit. It is more convenient for intubated and sick patients who will not able to stand for a PA projection. Disadvantage of this is mediastinal structures may appear magnified as the heart is further away from the detector, often poorly inspired, more likely to be rotated and to create skin folds, scapulae often cover some the lungs.

Lateral Projection:

Lateral view of the chest is performed erect left lateral and labelled with the side closest to the cassette. A paravertebral gutter technique involves rotating the right-side 5-10° anterior (RAO) to align the posterior ribs along the divergent beam. It allows for localisation of suspected chest pathology when assessed in conjunction with a PA view. Examines the retrosternal and retrocardiac spaces. It allows assessment of the posterior costophrenic recesses.

Technical factors:

- Posteroanterior projection
- Suspended inspiration
- Centring point

The level of the 7th thoracic vertebra, approximately the inferior angle of the scapulae.

- Collimation
  - Superiorly 5 cm above the shoulder joint to allow proper visualisation of the upper airways
  - Inferior to the inferior border of the 12th rib
  - Lateral to the level of the acromioclavicular joints
- Orientation: Portrait or Landscape

- Detector size: 35 cm x 43 cm
- Exposure: 100-110 kVp and 4-8 mAs
- SID: 180 cm
- Grid: Yes

Image technical evaluation:

The entire lung fields should be visible from the apices down to the lateral costophrenic angles.

- The chin should not be superimposing any structures
- Arms are not superimposed over lateral chest wall (this can mimic pleural thickening)
- Minimal to no superimposition of the scapulae borders on the lung fields
- Sternoclavicular joints are equidistant from the spinous process
- The clavicle is in the same horizontal plane
- A maximum of ten posterior ribs are visualised above the diaphragm
- The 5th-7th anterior ribs should intersect the diaphragm at midclavicular line
- The ribs and thoracic cage are seen only faintly over the heart
- Clear vascular markings of the lungs should be visible

Practical points:

The phase of respiration has a profound effect on the appearance of several structures on the chest radiograph. A poor-inspiratory PA radiograph can mimic pathology. Structures that can appear different on expiration include:

- Heart size
- Mediastinal contours and width
- Lung inflation
- Diaphragm contours

Rotation of a chest radiograph can simulate common pathological processes and make it hard to produce an appropriate diagnosis.

The PA view is used to investigate a plethora of conditions and it is the radiographer's responsibility to ensure high-quality diagnostic images are achieved consistently.

The sternoclavicular joints are a sound indicator for positional rotation, if one sternoclavicular joint is notably wider than the other, that respected side needs to be rotated toward the image receptor to correct rotation.

Patients with a longstanding history of emphysema or COPD will have abnormally long lungs compared to the general population, remember this when collimating superior to inferior.

Side marker placement is imperative; patients can have congenital conditions that mimic a mirrored image.

Remember to explain to your patient what you are about to do; that is ask them to take a breath in and hold it. Many times, this gives the patient time to prepare and results in a better breath hold and therefore a higher quality radiograph.

Fig 6.2 Chest X-ray PA Projection

Preparation:

A chest X-ray requires no special preparation. You will be asked to remove some of your clothes and to wear a gown during the exam. You may also be asked to remove jewellery, removable dental appliances, eye-glasses and any metal objects or clothing that might interfere with the X-ray images. Women should always inform their physician and X-ray technologist if there is any possibility that they are pregnant. Many imaging tests are not performed during pregnancy so as not to expose the fetus to radiation. If an X-ray is necessary, precautions will be taken to minimize radiation exposure to the baby.

Fig 6.2.1 Chest X-ray AP Projection

Arrangement of equipment:

The equipment typically used for chest X-rays consists of a wall-mounted, box-like apparatus containing the X-ray film, or a special plate that records the image digitally. An X-ray producing tube is positioned about six feet away.

The equipment may also be arranged with the X-ray tube suspended over a table on which the patient lies. A drawer under the table holds the X-ray film or digital recording plate. A portable X-ray machine is a compact apparatus that can be taken to the patient in a hospital bed or the emergency room. The X-ray tube is connected to a flexible arm that is extended over the patient while an X-ray film holder or image recording plate is placed beneath the patient.

Fig 6.2.2 Chest X-ray image

6.3 Sinus X-ray:

A Sinus X-ray is an imaging test that uses X-rays to look at your sinuses. The sinuses are air-filled pockets (cavities) near your nasal passage.X-rays use a small amount of radiation to create images of your bones and internal organs. X-rays are most often used to find bone or joint problems, or to check the heart and lungs. A sinus X-ray is one type of X-ray. A sinus X-ray is simple and quick, and does not involve any instruments that are put into your body (non-invasive). It can give your healthcare provider useful information. But a sinus X-ray can only tell your provider that a problem exists. It does not show a specific cause of the problem. The Sinus X-ray is not painful. But you may have some discomfort or pain from moving into different positions if you have had recent surgery or an injury. The technologist will use all possible comfort measures and do the scan as quickly as possible to minimize any discomfort or pain.

Patient position:

- Rest the lateral aspect of the patient's head (with the side of interest) against the image detector.
- Adjust the head into a true lateral position, with the midsagittal plane parallel to the image detector.
- For patient's comfort, adjust the patient's body into an oblique position

.

Fig 6.3 Sinus X-ray positioning

Technical factors:

- Lateral projection

- Centring point
- Zygoma (cheek prominence), midway between outer canthus and the external auditory meatus (EAM)
- Collimation
    - Superior to include frontal sinus
    - Inferior to include chin (especially important to include soft tissue to assess for foreign body or air in a trauma setting)
    - Anterior to include skin margins
    - Posterior to the EAM
- Orientation: landscape
- Detector size: 24 cm x 30 cm
- Exposure: 80 kVp and 20-25 mAs
- SID: 100 cm
- Grid: No

Image technical evaluation: Temporomandibular joints are superimposed

Practical points:

- Remove earrings, glasses, piercings, and dentures to avoid artifact obscuring important pathology
- Encourage patients to raise their chin to prevent superimposing the mandibular angle over the anterior cervical spine
- To ensure true lateral, the floor of the anterior cranial fossa should be superimposed

Fig 6.3.1 Sinus X-ray image

8 ADVANTAGES AND DISADVANTAGES OF X-RAY RADIOGRAPHY

ADVANTAGES:

- It is cheaper and simple technique.
- It has lower radiation compare to CT scan.
- X-rays are not absorbed very much by air; hence specimen need not be in an evacuated chamber.
- It helps to diagnose tumours easily without the need of surgery.
- X-ray equipment is relatively in expensive and widely available in emergency rooms, physician offices, ambulatory care centres, nursing

homes and other locations, making it convenient for both patients and physicians.

- It helps to locate an alien objects inside or around bones.
- X-rays are widely used by radiologists to identify cracks, for infections to identify the level of injury, and to identify abnormal bones.
- Because X-ray imaging is fast and easy, it is particularly useful in emergency diagnosis and treatment.

DISADVANTAGES:

- It does not provide 3D information.
- Bones can block significant diagnostic data as it absorbs the radiation.
- They do not interact very strongly with lighter elements.
- Due to its radiation, it mutates cells which causes ionisation. This often leads to cancer.
- It does not produce the best image but medium quality image.
- X-rays have also been linked to cataracts in the eyes and skin burns, but only at extremely high levels of radiation.

8 CONCLUSION

Based on this report, X-rays are used in different types of applications in many industries. But X-rays are most useful for human beings in medical field. We can easily find out which part of human body or organs are diseased using these X-rays. And it gives less disadvantage to compare this advantage. But we should not take X-rays continuously and it affects our body. And it is less cost compare to other methods and the same technique with some difference is called fluoroscopy. Fluoroscopy is based on the same techniques, with the photographic plate replaced by a fluorescent screen. X- rays are also used with computers in CAT (Computerized Axial Tomography) scans to produce cross-sectional images of the inside of the body. Now the X-ray method is too advanced and it is known as Digital radiography. Digital radiography is a form of radiography that uses X-ray–sensitive plates to directly capture data during the patient examination, immediately transferring it to a computer system without the use of an intermediate cassette. Also, less radiation can be used to produce an image of similar contrast to conventional radiography.

STUDIES ON CATARACT SURGERY

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,

TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

V. SANGEETHA

Reg. No: 20SPPH13

Under the guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled, " **STUDIES ON CATARACT SURGERY"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020-2021** by **V. SANGEETHA** (Register No:20SPPH13)

A. Lalitha

Signature of the Staff-in-charge

Padmavathi

Signature of the Co-Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

Padmavathi 18/9/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, "**STUDIES ON CATARACT SURGERY**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field report has been submitted for any Degree, Diploma or other similar titles.

V. Sangeetha

Signature of the Student

(V. SANGEETHA)

Station: Thoothukudi

Date: 10-04-2021

ACKNOWLEDGEMENT

First of all, I thank the Lord Almighty for his blessing and grace to complete this report work.

I am deeply indebted to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA. M.Phil., Ph.D., for the encouragement she bestowed upon us.

I would express my sincere thanks to our Director of SSC, Rev. Dr. Sr. F.MARY JOYCE BABY M.A., M.Phil., Ph.D., for her support in my work.

I would like to express my special gratitude to Rev.Dr.Sr.JESSIE FERNANDO M.Sc., M.Phil., Ph.D., HOD, for her inspirational words to complete this report work.

I would convey my heartfelt thanks to Mrs. P. PADMAVADHI M.Sc., M.Phil., SET., SSC Co-ordinator, Department of Physics for her efficient and encouragement in successful completion of this report.

I wish to record my sincere thanks to Ms. A. VALENTINA M.Sc., M.Phil., Assistant Professor, Department of Physics for her enthusiastic guidance and support for completion of this field work report.

It is my pleasure to extend my thanks to Mrs. P. SANKARI Dopt., Councelling dept, Vasan Eye Care, Thoothukudi, for her help and support to complete my field work.

I am deeply grateful to all staff members of Department of Physics (SSC) for supporting us in all aspects.

CONTENT **Page. no.**

1 INTRODUCTION

Vasan Health Care Group is a health care group in India. Founded by, A.M.Arun, the group is based in Trichy and has more than 170 eye care hospitals in India and 27 dental hospitals across 4 states in South India. Company also operates two multi-speciality hospitals in Trichy. Vasan Eye Care Hospitals are day care centres for treating eye aliments.

Fig.1 vasan eye care

1.1 History

Vasan Medical Centre, a chain of medical stores, established at Trichy and Thanjavur in1947 by Late AR. Murugaiah Ex.MP of karur constituency. His son Dr.A.M.ARUN , the founder of Vasan Eye Care, took the business in 1991 after the sudden demise of his father, established a diagnostic centre and laboratory and started the group’s first eye care hospital in 2002 in Trichy.

1.2 Cataract Surgery

The clouding of the natural crystalline lens and typically occurs because of the ageing, although other reasons may be prolonged use of steroids,exposure to ultra violet and associated health problems like diabetes and eye injuries.

Surgery is the only known effective treatment for cataract removal. All cataract surgeries are aimed at removal of the cloudy natural lens and replacing it with an Intra Ocular Lens(IOL).

At Vasan Eye Care Hospitals Phacomulsification is performed and a foldable IOL is inserted. There are multiple IOL choices available for the surgery which are decided upon examination by our Ophthalmologists.

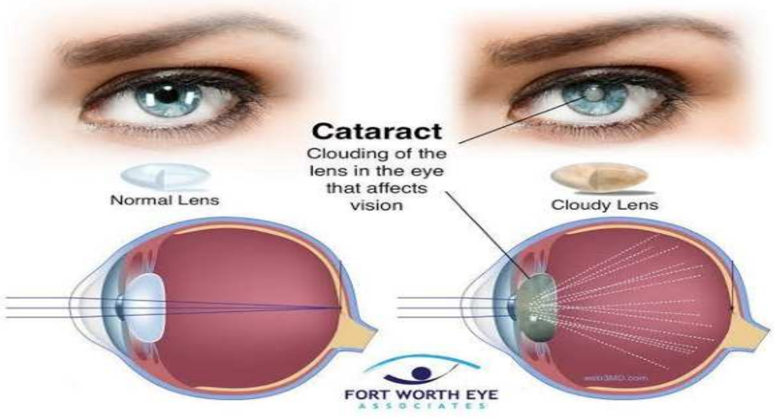


Fig.1.2 cataract

1.3 Cataract Surgery Outcomes

- Poor Outcome: -<20/200 best corrected.

  -<5% at two months.

- Borderline Outcome: -<20/60 – 20/200.
- Good Outcome: -20/60 + best corrected.

  ->90% at two months.

1.4 Improving Outcomes

- **5 s.**
- Selection.
- Sterlity.
- Soft eye.
- Safe surgery.
- Spectacles

1.5 Cataract symptoms

- Cloudy vision.
- Glare.
- Seeing double (when you see two images instead of one).
- Having trouble seeing well at night.
- Seeing bright colours as faded

1.6 Cataract investigation

- Vision.
- Refraction.
- Duct.
- Dilatation.
- Funds examination (Doctor opinion).
- A-Scan using Keratometer (to calculate power).

1.7 Keratometer

A keratometer, also known as an ophthalmometer, is a diagnostic instrument for measuring the curvature of the anterior surface of the cornea, particularly for accessing the extend and axis of astigmatism. It was invented by the German physiologist HERMANN VON HELMHOLTZ in 1851, although an earlier model was developed in 1796 by JESSE RAMSDEN and EVERARD HOME.

Fig.1.7 Keratometer

A keratometer uses the relationship between object size(O), image size(I), the distance between the reflective surface and the object (d), and the radius of the reflective surface(R). If three of these variables are known, the fourth can be calculated using the formula

$$\mathbf{R = 2d\,(I/O)}$$

Javal – schiotz principles:

The Javal- schiotz keratometer is a two position instrument which uses a fixed image and doubling size and adjustable object size to determine the radius of curvature of the reflective surface.

The Bausch- lomb principles:

The Bausch-lomb keratometer is a position keratometer that gives reading in dioptric form. It differs from the Javal- Schiotz in that object size is fixed, image size is the manipulable variable.

2 CLASSIFICATION OF CATARACT SURGERY

2.1 Morphological Classification

- **Subcapsular cataract:** Anterior subcapsular cataract
  Posterior subcapsular cataract
- **Nuclear cataract:** Involves the nucleus of the lens. Yellow to browncoloration.
- **Cortical Surgery:** Wedge shaped or radial spoke – like opacities.
- **Polar cataract:** Central posterior part of the lens.

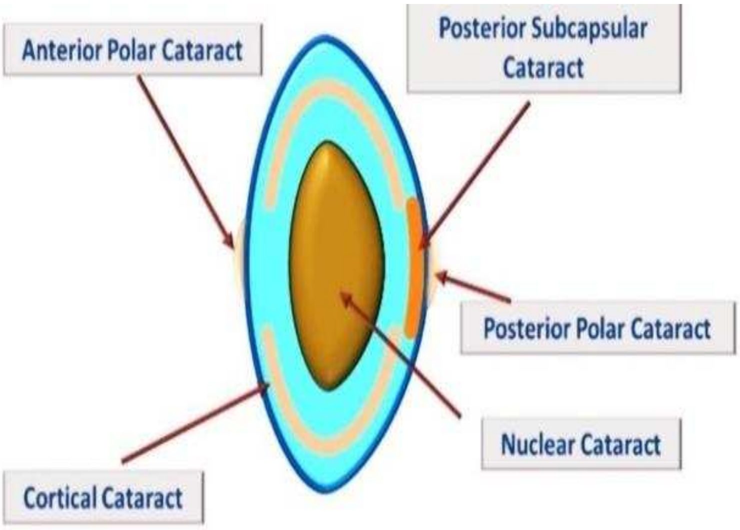


Fig.2.1 Morphological classification of cataract surgery

2.2 Based on the degree of maturity

- **Mature:** Cataract is one in which the lens is completely opaque.
- **Immature:** Cataract is one in which the lens is partially opaque.
- **Hypermature:** Cataract is shrunken and wrinkled anterior capsule due to leakage of water out of the lens.

- **Morgagnian:** Cataract is a hypermature cataract in which liquefaction of the cortex has allowed the nucleus to sink inferiorly.

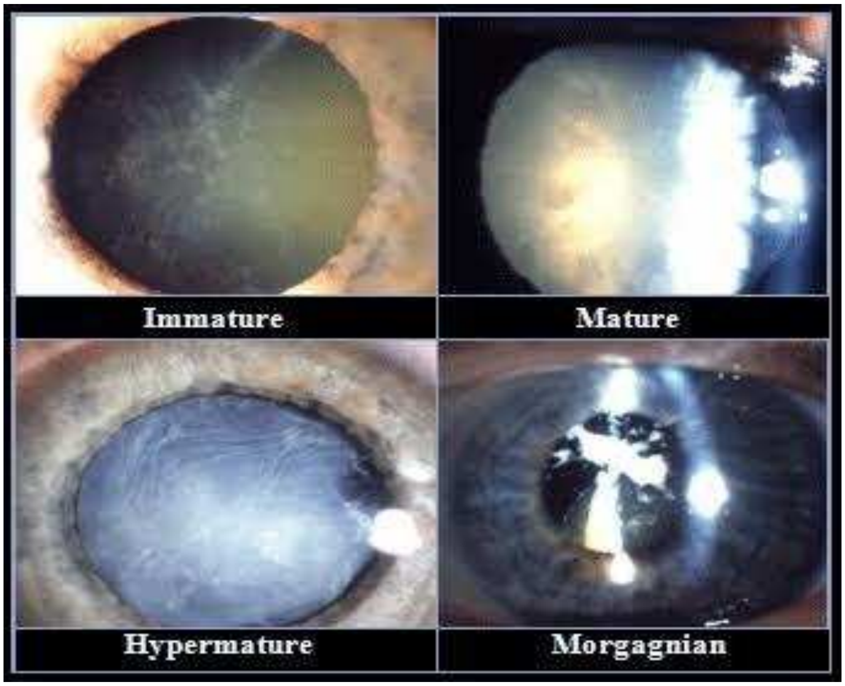


Fig.2.2 Classification depends on maturity

2.3 Pre – operational evaluation

- General Medical Examination of the patient.
- Ocular Examination:

Retinal Functioal Test

  - Light perception
  - Test for marcus gunn pupillary response.
  - Projection of rays – Test for function of peripheral retina.
  - Laser interferometry.

  - Objective tests for evaluating retina, ultrasonic evaluation, ERG, EOG, VER and indirect ophthalmoscopy.
- Search for local source of infection- to rule out conjunctival infection .
- Anterior segment evaluation.
- IOP measurement – raised IOP needs priority management.

2.4 Pre- operational medications and preparation

- Topical antibiotics.
- They must have a headbath.
- They have to take their regular medicines.
- Drugs to Lower IOP – Acetazolamide 500mg stat 2hrs before surgery and glycerol 60 ml mixwd with watwe 1hr before surgery.
- Drugs to be dilated using eyedrops.

3 TYPES OF CATARACT SURGERY

- Phacomulsification.
- Extracapsular cataract surgery.
- Intracapsular cataract surgery.

3.1 Phacomulsification

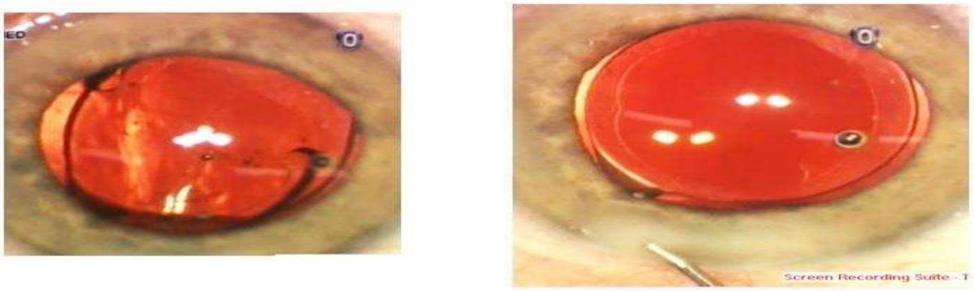


Fig.3.1 Phacomulsification

In this modern method, cataract surgery can usually be performed in less than 30 minutes and usually requires only minimal sedation. Numbing eyedrops or an injection around the eye is used and in general, no stitches are used to close wound and no eye patch is required after surgery.

Surgical steps of phacomulsification

- Corneoscleral incision – very small 3mm.
- Continuous curvilinear capsulorhexis of 4-6 mm.
- Hydrodissection.
- Nucleus is emulsified and aspirated.
- Remaining cortical lens matter is aspirated.
- IOL implantation.

- Removal of viscoelastic material.
- Wound closure.

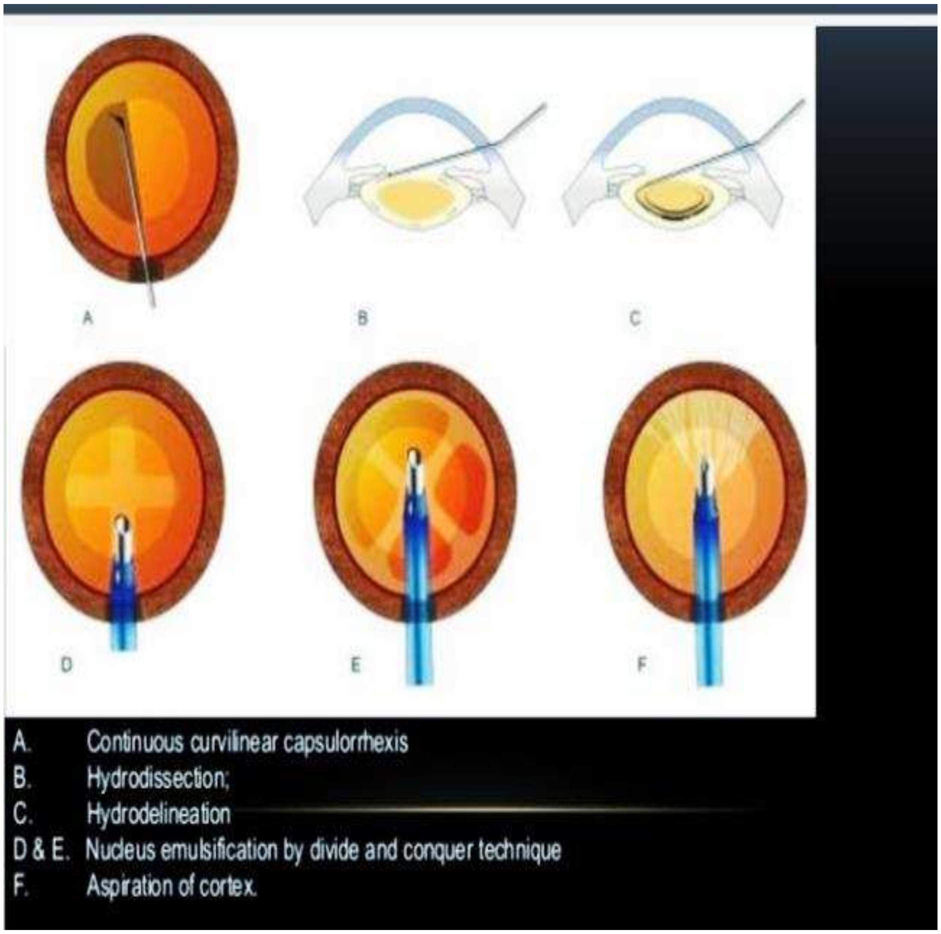


Fig.3.1.1 surgical image of Phacomulsification

3.2 Extracapsular cataract surgery (ECCS)

This surgery is used for mainly for advanced cataracts where the lens is too dense to dissolve into fragments. This technique requires a large incision so that the cataract can be removed in one piece without being fragmented inside the eye. Extracapsular cataract extraction usually requires an injection of numbing medication around the eye and an eye patch after surgery.

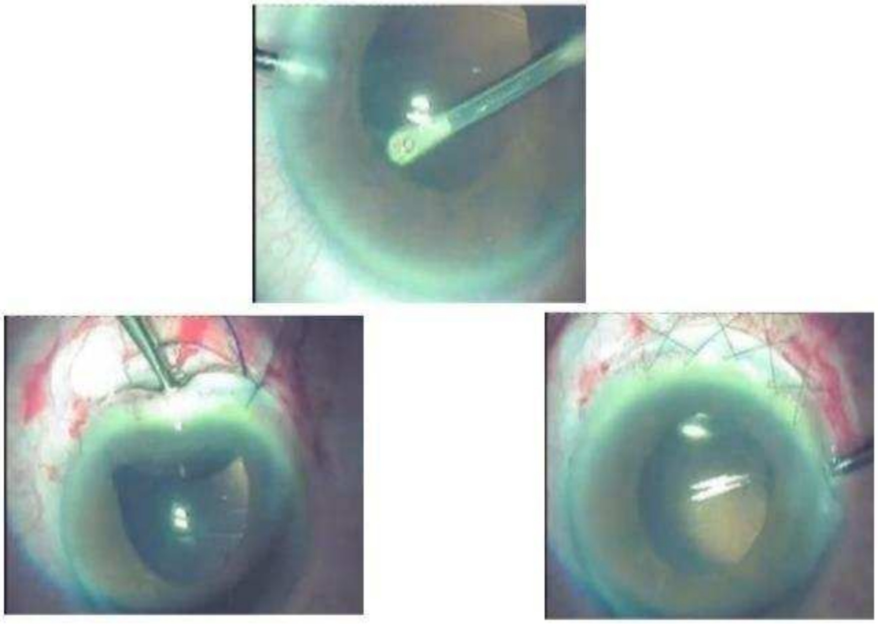
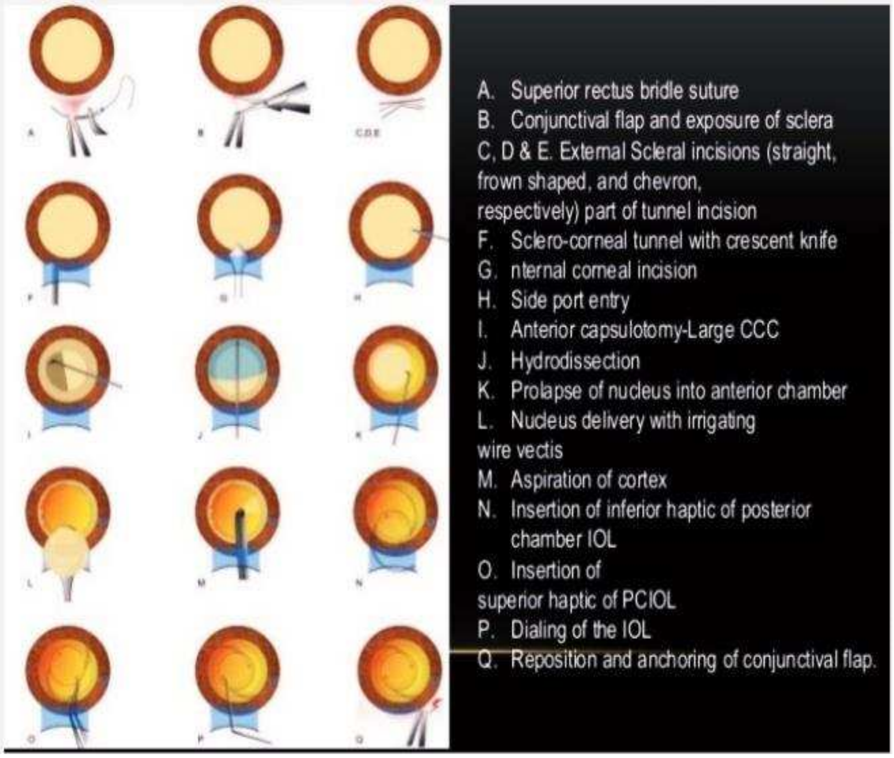


Fig.3.2 Extracapsular cataract surgery

Surgical steps of ECCS

- Superior rectus suture.
- Conjunctival flap (fornix based).
- Partial thickness groove/ gutter.
- Corneoscleral section.
- Injection of viscoelastic substance in anterior chamber
- Anterior capsulotomy:
    - Can opener’s technique
    - Linear capsolotomy
    - Continuous circular capaulorrhexis(CCC)
- Removal of anterior capsule.

- Completion of corneoscleral section.
- Hydrodissection.
- Removal of Nucleus.
- Aspiration of the cortex.
- Implantation of IOL.
- Closure of the incision – 3-5 interrupted sutures.
- Removal of Viscoelastic substance.
- Conjunctival injection.
- Subconjunctival injection.
- Patching of the eye.



A. Superior rectus bridle suture
B. Conjunctival flap and exposure of sclera
C, D & E. External Scleral incisions (straight, frown shaped, and chevron, respectively) part of tunnel incision
F. Sclero-corneal tunnel with crescent knife
G. nternal corneal incision
H. Side port entry
I. Anterior capsulotomy-Large CCC
J. Hydrodissection
K. Prolapse of nucleus into anterior chamber
L. Nucleus delivery with irrigating wire vectis
M. Aspiration of cortex
N. Insertion of inferior haptic of posterior chamber IOL
O. Insertion of superior haptic of PCIOL
P. Dialing of the IOL
Q. Reposition and anchoring of conjunctival flap.

Fig.3.2.1 Surgical steps of ECCS

3.3 Intracapsular Cataract Surgery (ICCS)

This surgical technique requires an even larger wound than the extracapsular surgery. The surgeon removes the entire lens and the surrounding capsule together. This method is rarely used today but can still be useful in cases of siginificant trauma.

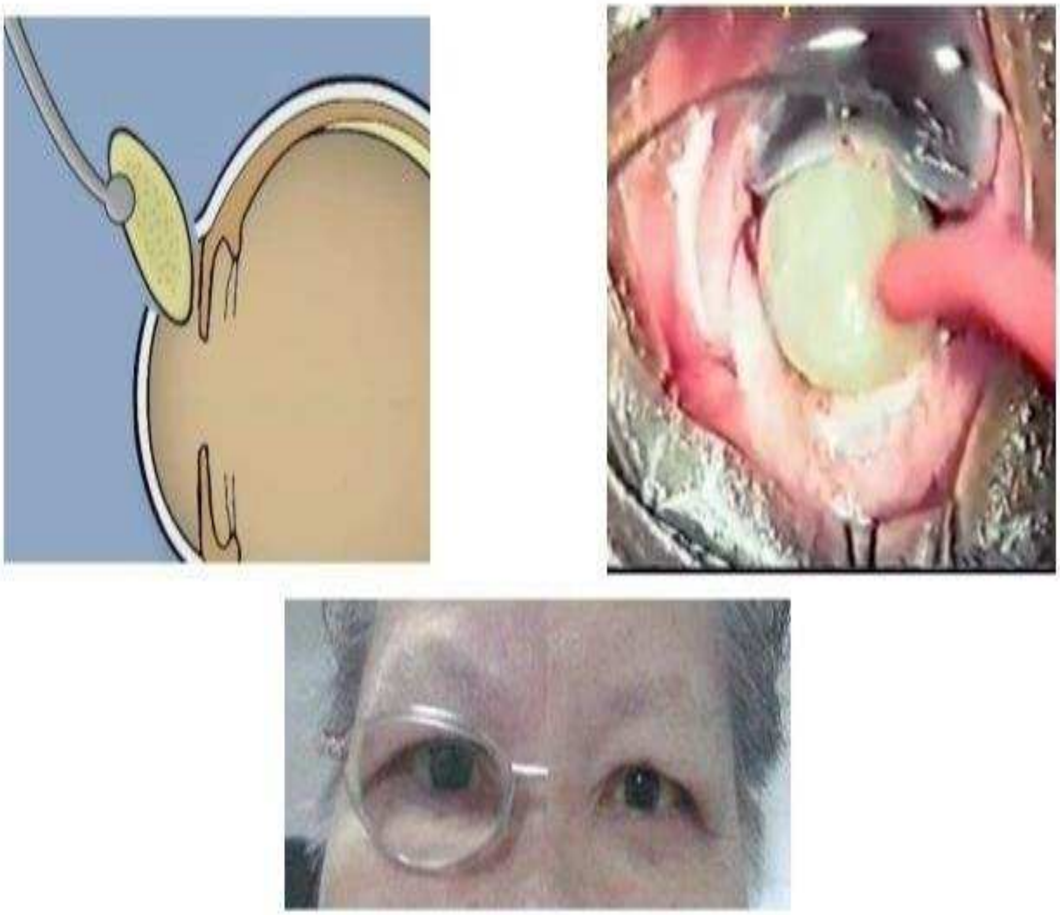
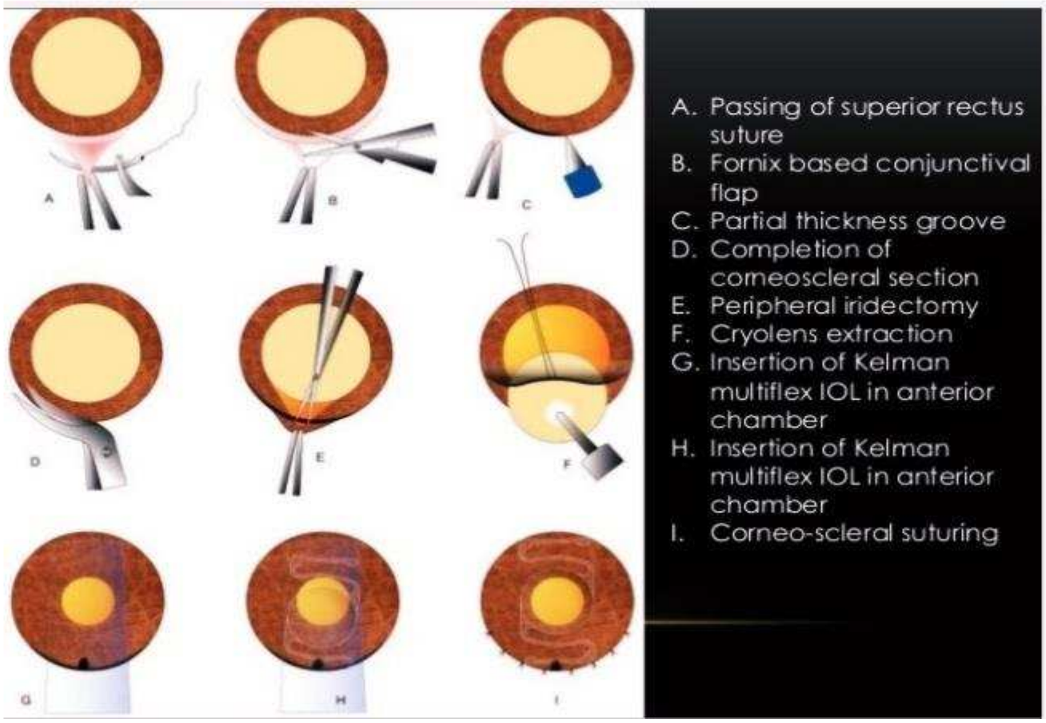


Fig.3.3 Intracapsular cataract surgery

Surgical steps of ICCS

- Superior rectus suture.
- Conjunctival flap (Fornix based).

- Partial thickness groove/ gutter.
- Corneoscleral section.
- Irdectomy.
- Method of lens delivery.
- Formation of anterior chamber.
- Implantation of anterior chamber IOL.
- Closure of incision- 5-7 interrupted sutures.
- Conjunctival flap reposited.
- Subconjunctival injection – dexamethasone 0.25ml and gentamicin 0.5 ml given.
- Patching of the eye



A. Passing of superior rectus suture
B. Fornix based conjunctival flap
C. Partial thickness groove
D. Completion of corneoscleral section
E. Peripheral iridectomy
F. Cryolens extraction
G. Insertion of Kelman multiflex IOL in anterior chamber
H. Insertion of Kelman multiflex IOL in anterior chamber
I. Corneo-scleral suturing

Fig.3.3.1 Surgical Steps of ICCS

4 TYPES OF INTRAOCULAR LENS

- Unifocal lens.
- Multifocal lens

4.1 Unifocal lens

These lenses are the most commonly implanted lenses today. They have equal power in all regions of the lens and can provide high quality distance vision. Monofocal lens are in sharpest focus at only one distance. These does not make the surgery more dangerous. Patients who had monofocal intraocular lenses implanted usually require reading glasses.

Fig.4.1 Unifocal lens

4.2 Multifocal lens

Multifocal lenses are one of the latest advancements in lens technology. These lens have a variety of regions with different power that allows some individuals to see at a variety of distances, including distance, intermediate and near. Multifocal lenses cannot correct astigmatism and some patients require spectacles or contact lenses for clearest vision.

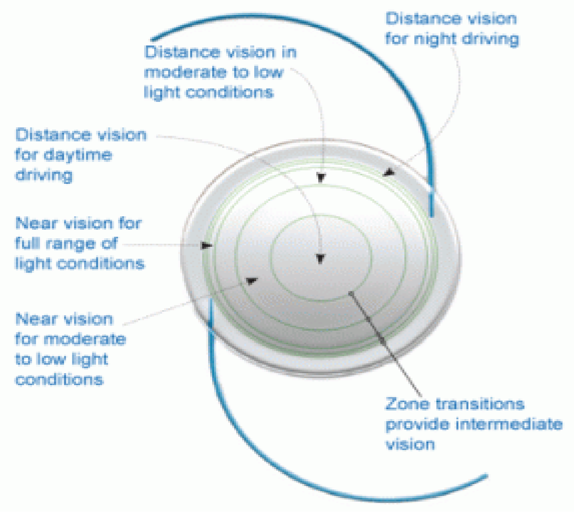


Fig.4.2 Multifocal lens

4.3 Intraocular Lens Implantation

Presently, intraocular lens implantation is the method of choice for correcting aphacia. The major classes of IOLs based on the method of fixation in the eye are as follows:

- **Anterior Chamber IOL:**
  - Lie entirely in front of the iris and are supported in the angle of anterior chamber.
  - ACIOL can be inserted after ICCS or ECCS.
  - Not very popular due to comparatively higher incidence of bullous keratopathy.
  - **IRIS supported lenses:**

  - These lens are fixed on the iris with the help of sutures or loops.
  - High incidence of postoperative complications.
  - Example of the supported lens is singh and worst's iris claw lens.
- **Posterior chamber lenses:**
- PCIOLs rest entirely behind the iris. They may be supported by the ciliary sulcus or the capsular bag.
- Depnding on the material of manufacturing , three types of PCIOLs are available:
    - Rigid IOLs - made entirely from PMMA.
    - Foldable IOLs - Made of silicone, acrylic, hydrogel and collamer.
    - Rollable IOLs are ultra thin IOLs - made of hydrogel.

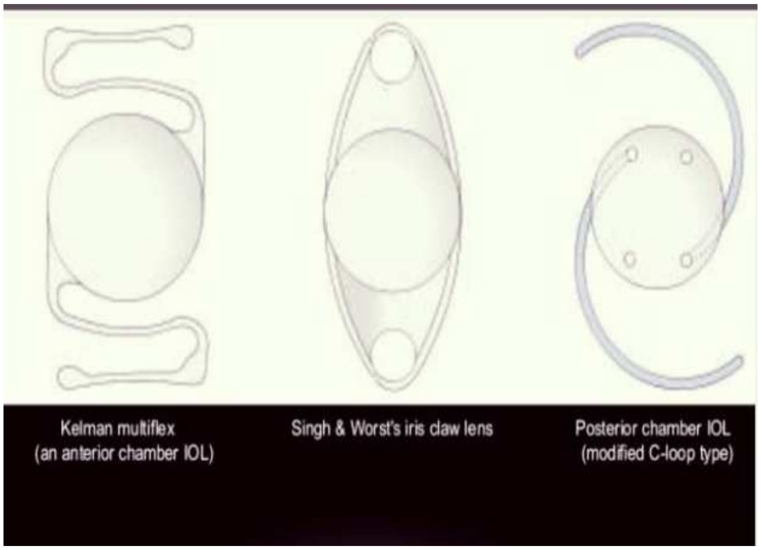


Fig.4.3 Three ways of implantation

4.4 Phaco laser

Fig.4.4 Phaco laser

In this phaco-technique,

- The first step is the creation of the capsularhexis and the lens fragmentation using the LenSx Laser.
- The second step is hydrodissection and the floating of the lens, as one piece, into the anterior chamber.
- The third step consists of cracking the laser prechopped lens into small fragments using an opposing action180deg with an ophthalmic viscosurgical device protecting the corneal endothelium.
- The fourth step is an aspiration of the lens fragments with the assistance of a second instrument.

- We have found that this new phaco free technique can be used for a cataract of up to grade 3+ in density.

4.5 Types of Phaco Cataract Surgery

- Regular Phaco Cataract Surgery
- Micro Phaco Cataract Surgery

Regular Phaco Cataract Surgery:

It is a surgical technique wherein the cataract is emulsified using ultrasonic energy. The incision size is about 3.0mm.

Micro Phaco Cataract Surgery:

- This is the technique where the cataractous lens is dissolved and through a 2.2mm micro incision and a special super soft Intraocular lens is introduced through the same incision.
- The incision in the Microphaco technique is much smaller than the incision in a regular Phaco technique.
- Micro phaco is designed to speed the recovery of vision, improve visual outcomes and reduce the restriction on your activities after the surgery.
- Features of Micro- phaco:
    - Micro Incision
    - No Stitch
    - Walk in – Walk out Surgery
    - Faster Recovery
    - Reduced need for glasses.

4.6 Benefits Of Phaco Surgery

- No Hospitalization.
- Smaller Incision.
- Stitchless Procedure.
- Faster recovery.
- No restriction on normal activities.
- Less chance for complications.

5 POST-OPERATIONAL MEDICATIONS

- Take normal diet.
- Avoid eating hard foods.
- To avoid taking the river bath and falls bath for 1month.
- Avoid injuries.
- Taking of regular medicines and regular eyedrops.
- Correct follow up.

5.1 Cost of Cataract Surgery

The cost of cataract surgery depends on many variables, such as the type of procedure you have and the intraocular lens implanted in your eye. The area where you live also can be a factor, depending on cost of living standards that help set the typical price of cataract surgery. On average cataract surgery in Tamil Nadu would cost you about Rs. 25,000 per eye if you paid for everything yourself.

5.2 Benefits of Cataract Surgery

- One of the greatest benefits of cataract surgeryis the increased quality of life.
- Activities such as reading, cooking, driving, using a computer and sewing become easier after the operation.
- Improved clarity of vision.
- Improved vision in dim light.
- Reduced glare in bright light or during right driving.

- Colors may seem richer.
- Improved vision may enable some patients to continue driving.

5.3 Risks Of Cataract Surgery

Possible Complications

- High pressure in the eye.
- Blood collection inside the eye.
- Infection inside the eye.
- Artificial lens damage.
- Drooping eyelids.
- Retinal detachment.
- Severe bleeding inside the eye.
- Swelling or clouding of the cornea.
- Blindness.

5.4 Congential and Developmental Cataract

- Congential cataract develops from some disturbance to normal development of lens.
- The disturbance occurs before the birth.
- The opacity may limit to embryonic or foetal nucleus.
- Developmental cataract occurs from infancy to adolescence.
- The opacity involves infantile or adult nucleus.
- 3 children out of 10,000 live births.
- Two third of the cases are bilateral.

5.5 Mechanism of loss of transparency

- Cortical Cataract
- Nuclear Cataract

Cortical Cataract:

- Denaturation and coagulation of lens proteins.
- Decrease level of aminoacids and protein synthesis.
- Increased hydration brought by decrease in potassium due to reversal of Na/K pump mechanism.

Nuclear Cataract:

- Degenerative changes occurring as nuclear sclerosis.
- Increase in water insoluble proteins.
- Compaction of nucleus resulting in a hard cataract.
- Disturbance of lamellar arrangement in fibres.

5.6 Laboratory Investigation

- Complete blood counts.
- Blood Sugar.
- Urine Analysis.
- Chest X-Ray.
- Conjunctival swab for C/S.

5.7 Evaluation – Outcome criteria

- Pain is relieved and infection is prevented.
- Cataract is removed and sight is restored with or without corrective glasses.
- Patient successfully adapts to vision change with planned rehabilitation.

6 CONCLUSION

Cataract surgery is one of the most commonly performed operations in India. It has a very high success rate. Developments have taken place to make it even safer, faster, more accurate and in some cases.It is able to free people from a glasses. The surgical procedure you choose to have will depend on your individual life circumstances. Cataract surgery is an effective secondary and tertiary public health strategy to prevent blindness. Cataract surgical rate is the number of cataract surgeries performed per million population per year. It always amazes me how quickly the field of ophthalmology and in cataract surgery has advanced. This includes the transistions from intercaps to extracaps to phaco and now femtosecond laser cataract surgery. IOL technology has also had a major impact on the success and appreciation of cataract surgery. We will pretreat the patients in the holding area follows the cataract operation and patients will no longer be required to use pre-operative or post-operative drops in future. Finally, alternative potential strategies involving genetics are being explored for the prevention of cataract that could lead to the end of cataract surgery.

STUDIES ON MACHINERIES AND ITS OPERATIONS

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfillment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

P. SANTHANA THIYAKA LAKSHMI

Reg. No: 20SPPH14

Under the guidance of

Ms. A. VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST. MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020 – 2021

CERTIFICATE

This is to verify that this field work report entitled **" STUDIES ON MACHINERIES AND ITS OPERATIONS"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS),THOOTHUKUDI** in partial fulfillment of the requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work during the academic year **2020- 2021** by **P. SANTHANA THIYAKA LAKSHMI**
(Register No: 20SPPH14)

Signature of Staff-in-Charge

Signature of the Co - Ordinator

Joyce
Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonomous
Thoothukudi - 628 001.

Lucia Rose
Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21
Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled "**STUDIES ON MACHINERIES AND ITS OPERATIONS**" is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field work has been submitted for any degree, Diploma or other similar titles.

P.S. Lakshmi

Station: Thoothukudi

Signature of the student

Date: 10/04/2021

(P. SANTHANA THIYAKA LAKSHMI)

ACKNOWLEDGEMENT

Foremost, I would like to express our gratitude to the Lord Almighty for the wisdom, he bestowed upon me, the peace of mind and strength in order to finish this field work report.

I am indebted to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA, M.Phil., Ph.D., for her untiring encouragement and motivation.

I would like to express my hearty thanks to our Director of SSC Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her untiring support.

I am thankful to Rev Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., Head of the Department for her motivational support, and encouragement in all our endeavors.

I am deeply grateful to Mrs. P.PADMAVATHI M.Sc., M.Phil., SET SSC Co-Ordinator, Department of Physics for her untiring academic guidance and encouragement in the successful completion of this field work report.

I would like to offer my sincere thanks to Ms. A. VALENTINA M.Sc., M.Phil., for her guidance and constant support for the successful completion of this field work report.

I wish to record my sincere thanks to Mr. TAMILSELVAN, Proprietor, Arun Engineering Works, Thoothukudi for sharing their knowledge and expertise with me.

I would like to thank and appreciate my parents, family and friends for their continual support towards the completion of my field work report.

CONTENT Page. no.

1 INTRODUCTION

Factories and the machines that they housed began to produce items faster and cheaper than could be made by hand. As the supply of various items rose, their cost to the consumer declined. Shoes clothing, household goods, tools and other items that enhance people's quality of life became more common and less expensive. Foreign markets also were created for these goods, and the balance of trade shifted in favor of the producer—which brought increased wealth to the companies that produced these goods and added tax revenue to government coffers. However, it also contributed to the wealth inequality between goods-producing and goods-consuming countries.

The rapid production of hand tools and other useful items led to the development of new types of tools and vehicles to carry goods and people from one place to another. The growth of road and rail transportation and the invention of the telegraph (and its associated infrastructure of telegraph) meant that word of advances in manufacturing, agricultural harvesting, energy production, and medical techniques could be communicated between interested parties quickly. Labor-saving machines such as the spinning jenny (a multiple-spindle machine for spinning wool or cotton) and other inventions, especially those driven by electricity (such as home appliances and refrigeration) and fossil fuels (such as automobiles and other fuel-powered vehicles), are also well-known products of the Industrial Revolution. In turn industrial revolution leads to the discovery of new machines. In this field report work we will be discussing about machineries which is collectively a sum of two or more machine and also this report deals with various machines, their types, applications and advantages.

2 CNC LASER CUTTING

A laser cutter is a prototyping and manufacturing tool used primarily by engineers, designers, and artists to cut and etch into flat material. Laser cutters use a thin, focused laser beam to pierce and cut through materials to cut out patterns and geometries specified by designers. Apart from cutting, laser cutters can also raster or etch designs onto work pieces by heating up the surface of the work piece, thus burning off the top layer of the material to change its appearance where the raster operation was performed.

Laser cutters are really handy tools when it comes to prototyping and manufacturing; they are used in machine shops on the industrial scale to cut large pieces of material, they are used by hardware companies to create cheap, quick prototypes, and they are tools used by makers and artists as a DIY fabrication tool to bring their digital designs into the physical world. In this guide I'll explain what laser cutters are, what they can do, and how you can use them, and I'll also provide some resources if you want to learn and do more with laser cutters.

2.1 CNC Laser Cutter

Fig. 2.1 CNC Laser Cutter

A laser cutter is a type of CNC (Computer Numerical Controlled) machine, meaning that it is controlled via a computer. A designer can design something in some sort of design software, and then send it to a laser cutter to have it cut out automatically, with just the push of a button. Once a design is sent to a laser cutter, the machine uses a laser beam to cut into or etch into the material on the cutting bed. Laser cutters are a great all around tool because they can be used to make so many different styles of design; laser cutters are used for anything from cardboard prototypes to rastered artwork. Common laser cutters are primarily used to cut materials like wood, some plastics, and paper and cardboard, although there are more powerful laser cutters that can cut through metals and much thicker materials.

Laser cutters can be very quick, and can churn out designed parts in just a few minutes. Like 3Dprinters laser cutters are rapid prototyping machines; they allow designers to quickly and cheaply iterate on their designs before they produce products on a larger scale.

2.2 Working of laser cutters

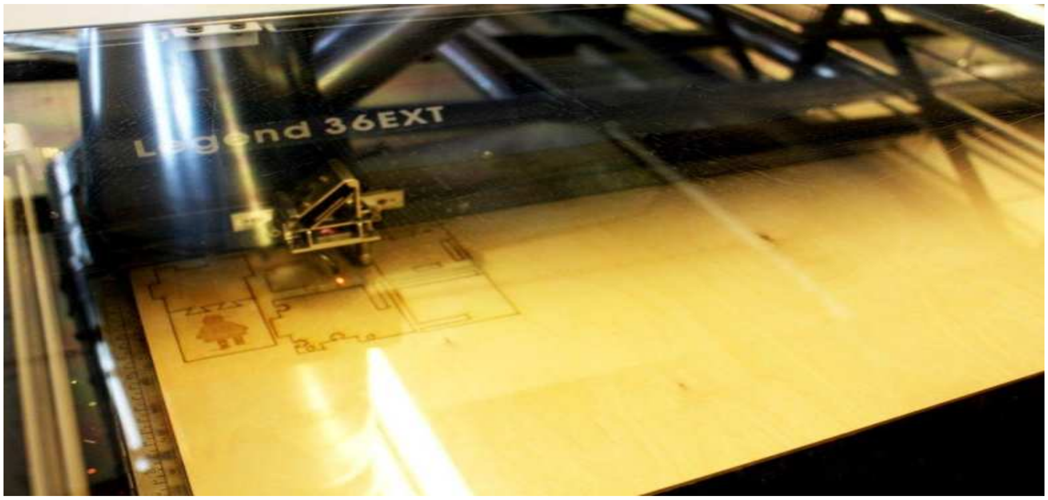


Fig. 2.2 Laser cutting process

There are a few different types of laser cutters, but they all essentially use the same process of using a laser to cut material. The laser originates from a laser resonator, which sends out a beam of intense light through reflects through a system of mirrors to the cutting head. Within the cutting head, the laser is focused through a lens and narrowed down to an extremely thin, concentrated beam. This beam is projected down at the material and can cut or raster the raw stock, which I'll cover in more detail later. The cutting head is usually mounted on what is called an XY gantry, which is a mechanical system driven usually by belt or chain that allows for the precise movement of cutting head within a given rectangular area, which is the size of the work bed. The gantry allows the laser head to move back and forth and forward and back over the work piece so that it can make precise cuts anywhere on the bed. In order for the laser to actually cut, the focal point of the lens, where the laser would be at its finest, needs to be on the surface of the material it is cutting through. All laser cutters require a focusing procedure before making their cuts to ensure that the laser cuts well.

The difference between different types of laser cutters comes from what types of lasers the machines have. The type of laser defines what type and thickness of material it can cut through, because different laser types have different power ranges. Usually, higher power lasers are used on the industrial scale to cut out large sections of sheet metal or plastics, while lower power lasers are used for a wide range of thinner, more potentially flammable materials like paper and card stock, wood, and some plastics. I'll cover the main types of laser cutters as well as the important settings laser on.

2.3 Types of Laser Cutters

Fig. 2.3 CNC Fiber laser

There are three main types of lasers used in laser cutters; CO_2 lasers, fiber lasers, and neodymium lasers. Although the laser cutters are all built very similarly, they are distinct in that each type of laser has a specific power range, thus each can be used to cut through different material types and thicknesses.

CO_2 Lasers: The laser is generated from electrically stimulated gas mixtures (mostly comprising of carbon dioxide). CO_2 lasers are the most common types of laser cutters because they are low power, relatively inexpensive, efficient, and can both cut through and raster a wide variety of materials.

Materials: wood, paper based products (cardboard, etc), leather, acrylic, glass, some plastics, and some foam (can raster on anodized metals)

Neodymium Lasers: The laser is formed from neodymium doped crystals. These lasers have a much smaller wavelength than CO_2 lasers, meaning they have a much higher intensity, and can thus cut through much thicker, stronger materials. However, because they are so high power, parts of the machine wear and tend to need replacing.

Materials: metals, plastics, and some ceramics

Fiber Lasers: These lasers are made from a "seed laser", and then amplified via special glass fibers. The lasers have an intensity and wavelength similar to that of the neodymium lasers, but because of the way they are built, they require less maintenance. These are mostly used for laser marking processes.

Materials*:* metals and plastics

2.4 Laser Cutting Design Software

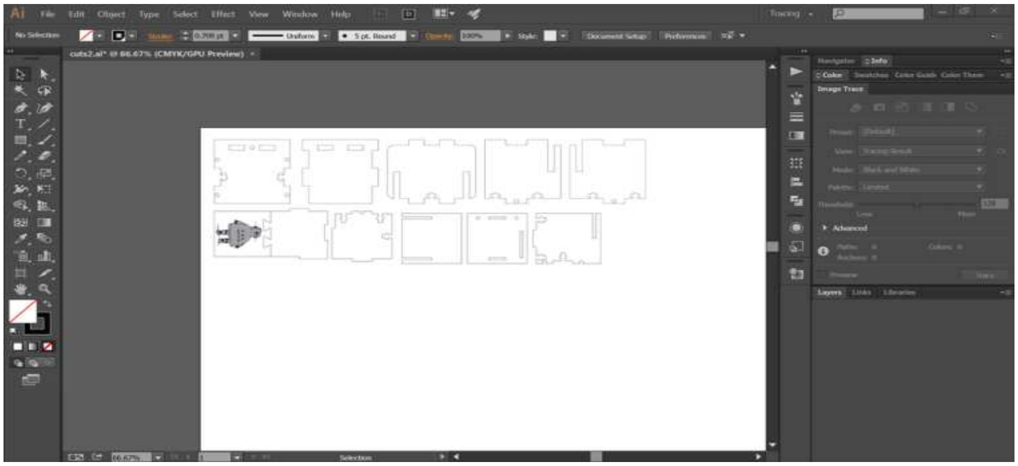


Fig. 2.4 Design modeling

A Laser cutter works very much like your everyday inkjet printer. Laser cutters come with specific drivers that allow them to take what is on the computer, convert it into a format that the laser cutter can read, and then allow the laser cutter to do its job. Many design software packages support laser cutter drivers; it is pretty common among 2D design programs, and some 3D design software can also support laser cutter drivers when dealing with 2D drawings or sketches. Here are couples you may already be familiar with or may want to try out:

2D Design

Corel DRAW: graphic design software with an extensive number of tools and applications

- **Adobe Illustrator**: Powerful graphic design software used to create high quality designs
- **AutoCAD** (for students): Great drawing software, primarily used by engineers and architects to create detailed drawings and product representations

- **Inkscape** (free):Free, open source graphic design software

3D Design:

- **Solid works**: Engineering 3D design software with multiple packages for aiding in design for specific applications
- **Autodesk inventor** (for students): Professional mechanical design software used to create and optimize designed systems
- **Autodesk Fusion** (for students): Cloud-based CAD platform used to help designers through the entire designing, engineering and manufacturing processes

2.5 Vector Cutting

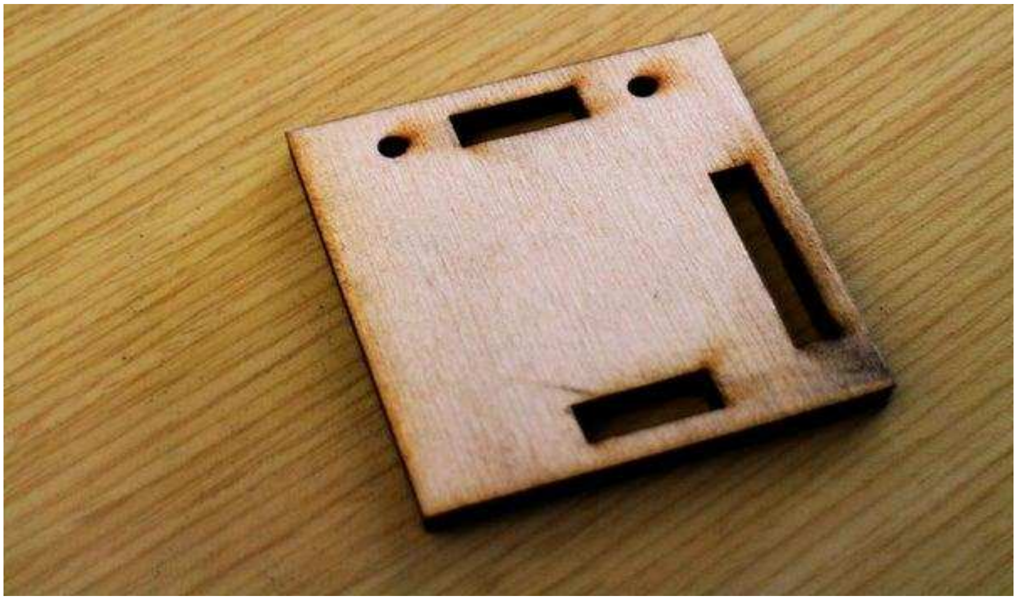


Fig 2.5 Vector Cutting template

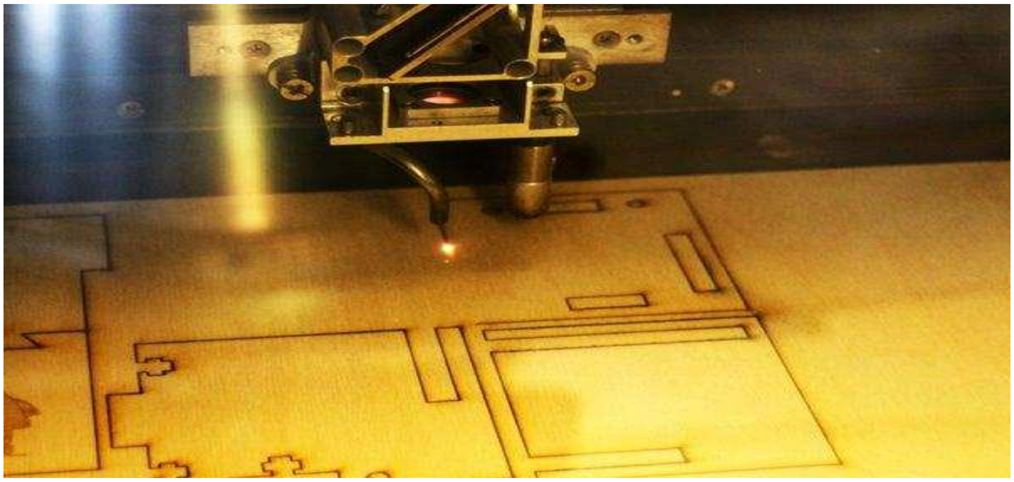


Fig. 2.5.1 Vector Cutting on process

During a cutting operation, the cutting head fires a continuous laser at the material to slice through it. In order to know where to cut, the laser cutter driver reads all of the vector paths in the designed piece. Once you send your file to a laser cutter, only lines that register as only hairline or vector graphics with the smallest possible line thickness will be cut by the laser. All other graphics, like any images or thicker lines, will be rastered, which I'll explain in a bit. The laser, when supplied with the right settings, will cut all the way through your material, so vector cutting is normally used for cutting out the outline of the part as well as any features or holes that you want to cut out of the material

2.6 Laser Rastering

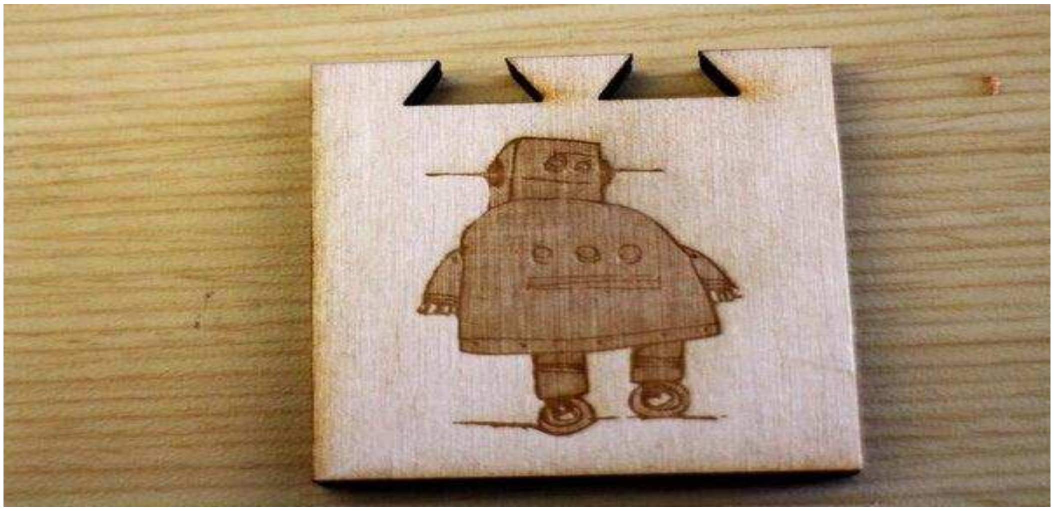


Fig. 2.6 Designed template

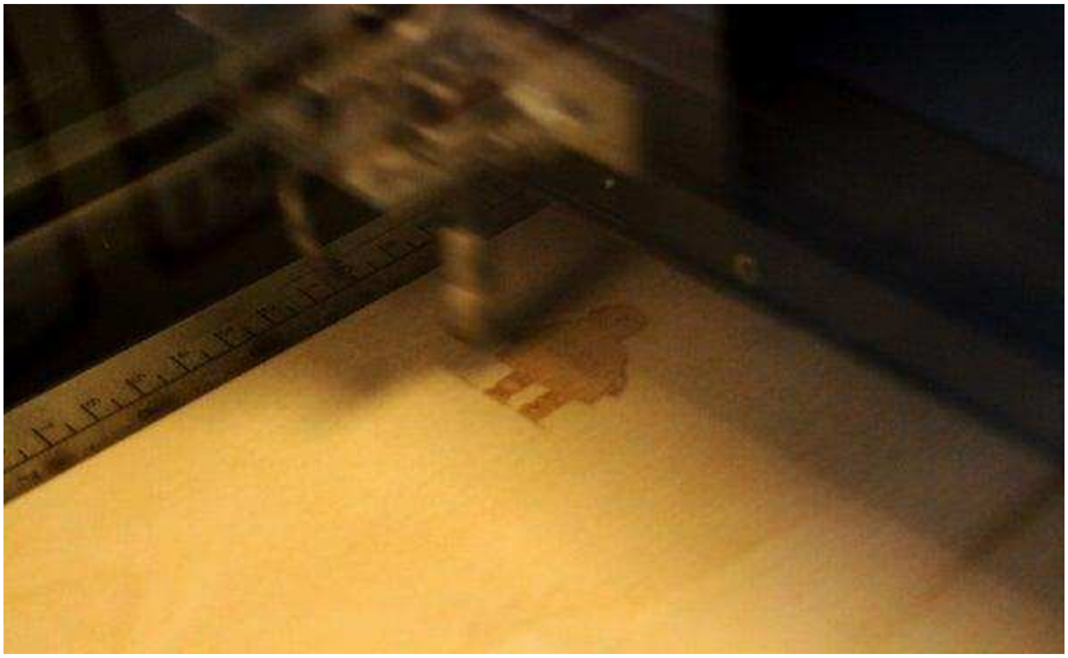


Fig. 2.6.1 Rastering the material

Rastering is a lot different than vector cutting; instead of cutting all the way through the work piece, the laser will burn off the top layer of the material you are cutting to create two color (and sometimes grayscale) images using the raster effect. In order to raster materials, the laser will usually be set to a lower power than it would when vector cutting material, and instead of shooting down a pulsing beam, it creates fine dots at a selected DPI (dots per inch) so that the laser doesn't really cut all the way through. The DPI directly correlates to the image resolution and affects how fine an image appears, exactly like image resolution on a computer. By adjusting the DPI you can control the laser's effect on the material. Rastering on some materials comes out really clearly, while you may not get exactly what you expected on other materials. Before you raster for the first time, make sure you experiment with the settings until you get the desired effect.

2.7 Laser Cutter Settings


Printing Preferences

Resolution: 600 DPI

Job Type:
○ Raster
○ Vector
● Combined

Raster Setting
Speed: 50 %
Power: 50 %
Engrave Direction: Top-Down
Image Dithering: Standard

Options
☐ Auto Focus
☐ Center-Engraving
Center-Center

Piece Size (inches)
Horizontal: 8.50
Vertical: 11.00

Vector Setting
Speed: 50 %
Power: 50 %
Freq.: 2500 Hz
☑ Vector Sorting: Optimize
☐ Frequency Automatic

Fig. 2.7 Software settings

Before I start going into the processes of vector cutting and rastering, I want to quickly cover the settings you will encounter. A laser cutter has four primary settings, as listed and described below. While power and speed apply to both vector cutting and rastering, frequency only applies to vector cutting and resolution only applies to rastering. The settings need to be changed based on your material in the laser cutter "Print

Properties" dialogue box before you "print" your job (remember, laser cutters connect to computers like normal printers). Based on the material you are cutting through or rastering on: for example, harder, thicker materials require higher power and lower speed so that the laser can actually be strong enough and move slows enough to successfully cut all the way through the material, while thinner, weaker materials can be cut with lower power and higher speed.

Power: How strongly the laser fires. A high power will cut through stronger, thicker material, but may end up burning thinner, more flammable stock. A low power may not be strong enough to get all the way through the material. During rastering, higher power will burn more layers off of the material, creating a darker image.

Speed: How fast the head of the laser cutter moves along its gantry. A high speed will cut faster, but may not cut all the way through if you have thicker or stronger materials. A low speed will definitely cut through, but has the potential to burn or melt the edges of the material as it slowly cuts. During raster operations, the laser moves back and forth very quickly, so a high speed on a large piece may wear out the gantry.

Frequency (only for cutting)**:** Determines how fast the laser pulses during a cutting operation. The laser turns on and off rapidly when it makes cuts, so a higher frequency will create a cleaner cut, but if the material is flammable it may end up catching fire, so a lower frequency would be preferable.

Resolution (only for rastering)**:** Determines the resolution and quality of the raster operation. A higher resolution will produce a better, darker image, but if there is too much heat concentrated in one area, it may severely melt, burn, or damage the work piece.

2.8 Advantages

- very high reliability
- there is no tool wear – no mechanical action of the process;
- high speed;
- flexibility and changeovers;
- processing of lamellae with complex configuration because of the possibility of the laser radiation to transported by fiber and finely to focus in small work spot;
- a rapid implementation at new constructive solutions, shortening the time of execution (from creating a new drawing to cutting of lamella with new sizes and shapes) ; there is no necessity of production a new punching tool, as it stands in conventional technology;
- reducing the tooling costs;
- reducing the setup times of the technological system;
- lower production costs and higher productivity;
- high accuracy of the obtained dimensions;
- Good quality (no burrs, a small HAZ, etc.).

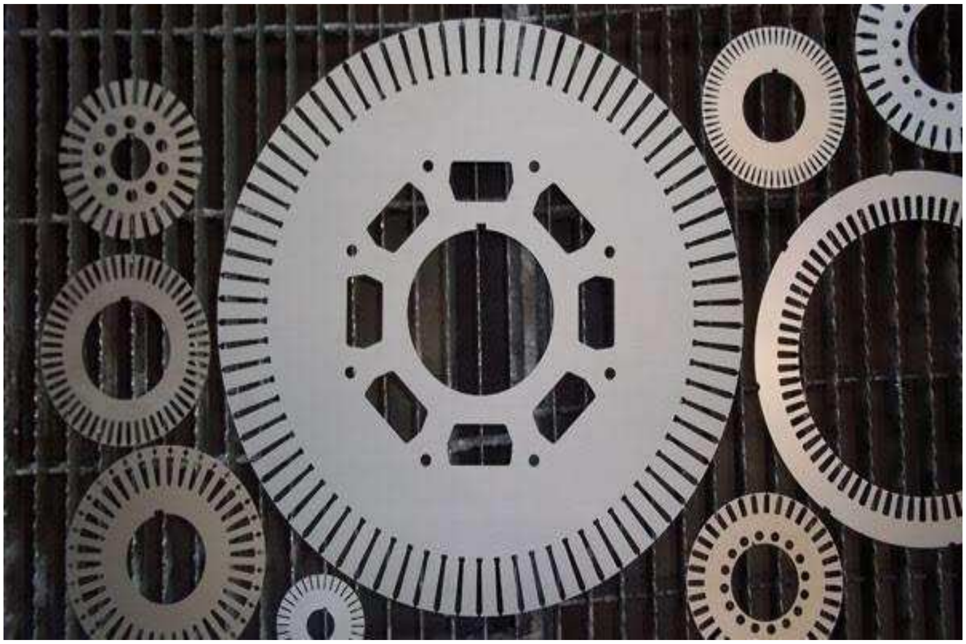


Fig. 2.8 Lamellae with different geometry

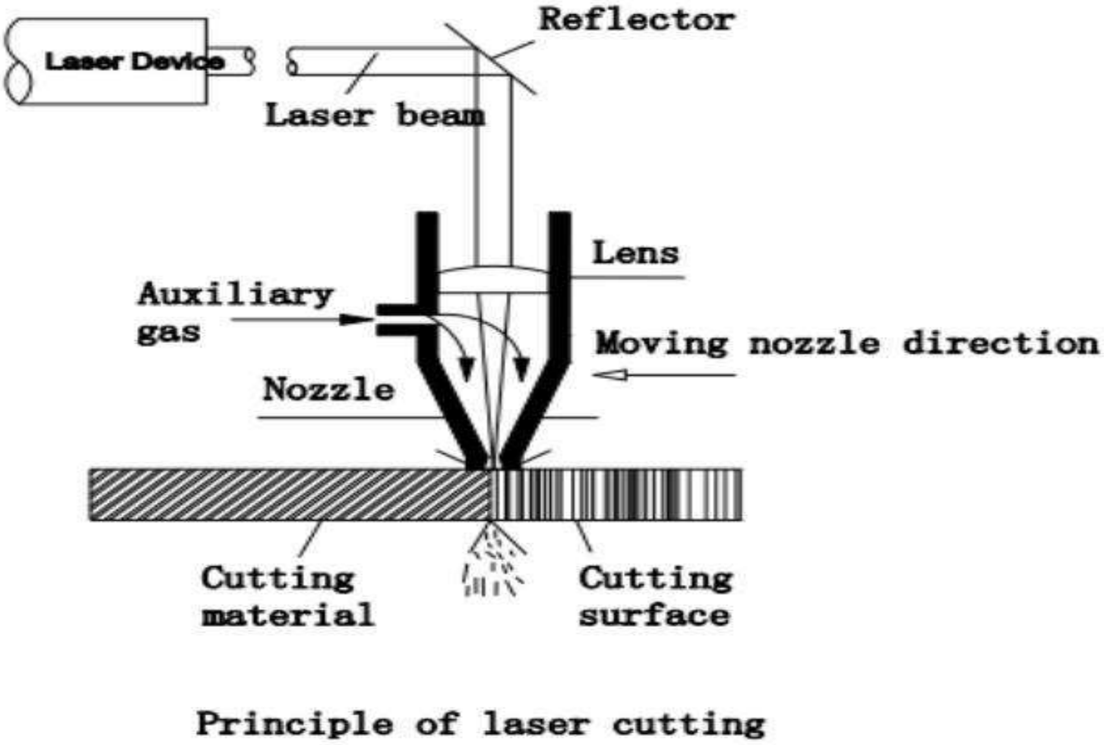


Fig. 2.8.1 Principal Schema for laser cutting

A principle schema for a technological laser system is shown on in it are included the following basic modules:

- laser source
- supply block (26 kVA); remote system; cooler system;
- working table;
- cutting head for moving along x, y and z axis;
- an optical cable for laser beam transporting to the working table;
- focusing system;
- Auxiliary gas supply system – nitrogen.

Implementation of the method of laser cutting of thin materials from electrical steel for achieving higher quality in manufacturing process of electric motors is a cause for increasing in the competitiveness of various countries. The positive economic and social effect by the introduction of such innovative laser technologies has been connected not only with increasing of the production, but also they created new technological areas, opened new horizons and thereby a large number of jobs; as it leads to improve quality and increase the competitiveness of the products on world markets; intellectualization of the engineering work, resulting in improved working conditions, while increasing the educational level of working staff and ultimately increases the standard of living in countries applying innovative solutions and procedures.

3 PUNCHING MACHINE

3.1 Principle

A CNC punching machine is basically programmed to move a sheet of metal in an X and Y direction so as to accurately position the sheet under the punching machine ram under to punch a hole or form. By using a combination of single hits or overlapping geometries, complex sheet or metal components shapes can be produced. Computer numerically controlled (CNC) punching is a sheet metal manufacturing process that is carried out by CNC punch presses. These machines can be either a single head and tool rail (Trumpf) design or multi-tool turret design. The CNC punching machine is basically programmed to move a sheet of metal in an x and y direction so as to accurately position the sheet under the machine's punching ram ready to punch a hole or form.

The processing range for most CNC punch presses is 0.5mm to 6.0mm thick in a range of materials including steel, zintec, galv, stainless steel and aluminum. The choice of hole punched can be as simple as a circle or rectangle right through to special shapes to suit a specific cut out design. By using a combination of single hits and overlapping geometries, complex sheet metal component shapes can be produced. The machine may also punch 3D forms such as dimples, taptite screw thread plunges, and electrical knockouts etc on either side of the sheet, which are often employed in sheet metal enclosure design. Some modern machines may have the ability to tap threads, fold small tabs, punch sheared edges without any tool witness marks making the machine very productive within the component cycle time. The instruction to drive the machine to create the desired component geometry is known as the CNC program.

CNC Programming sheet metal components on a CNC punch press

CNC programming is the computer aided manufacturing (CAM) side of the CAD/CAM cycle. Information about a design may be presented in a 2D format such as DXF or DWG files or a 3D file format. This information is then used to create the flat sheet metal pressing and assign the correct tooling to create the desired component. The software can also be used to establish the most efficient layout of components from a given size of sheet metal, known as the CNC nest. Obviously, the more components that can be produced from a panel of sheet metal the cheaper each CNC punched component will become. Modern software packages such as Radon can help to automate this process to achieve the maximum yield from a given sheet metal panel. As a designer of components that will be CNC punched, you do not need to know the exact details of how this may be achieved but it may be useful to bare the following in mind when designing a component that is to be CNC punched from sheet metal.

This AMADA ARIES 255 Turret Punching Machine was manufactured in Japan in 1997, and has a working record of 54000 production hours. Operated through an AMADA AMNC-PC control unit, the machine stands in good working conditions and has handled mainly mild steel of up to 2 mm of thickness. Moreover, the model offers easily available spare parts.

3.2 Overview

- BRAND: AMADA
- YEAR: 1997
- MODEL: ARIES 255
- PRODUCTION HOURS: 54000
- APPLICATION TYPE: PUNCHING
- MACHINE TYPE: TURRET PUNCHING MACHINE
- CONTROL UNIT BRAND: AMADA

3.3 MACHINE DESCRIPTION

TECHNICAL INFORMATION

GENERAL DATA

- MEASUREMENTS WIDTH: 3500 MM
- MEASUREMENTS DEPTH: 4100 MM
- MEASUREMENTS HEIGHT: 2050 MM
- MACHINE WEIGHT: 10400 KG
- BRAND: AMADA
- MODEL: AMNC-PC
- PUNCHING FORCE: 200 KN
- MAXIMUM SHEET THICKNESS: 3 MM
- X-AXIS MOVEMENT: 1250 MM
- Y-AXIS MOVEMENT: 1290 MM

- WORKPIECE X: 1250 MM
- WORKPIECE Y: 1250 MM
- NUMBER OF INDEX: 2
- NUMBER OF STATIONS: 30
- MAX TOOL DIAMETER:88.9 MM
- STEEL: 6 MM
- STAINLESS STEEL: 4 MM
- ALUMINUM: 4 MM
- MAIN ELECTRONIC CONNECTION: 200 V
- POWER CONSUMPTION: 14 KVA
- AIR PRESSURE: 5.5 BAR

High - rigidity double construction frame

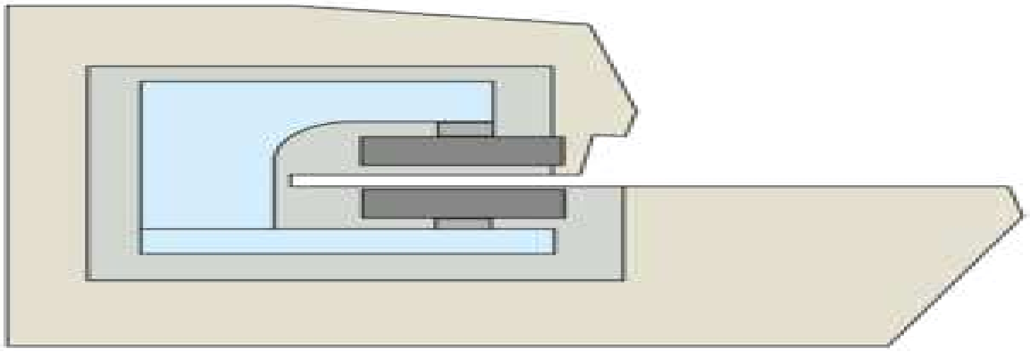


Fig. 3.3 Punching machine with double construction frame

The ARIES series utilizes a double construction frame which combines a high-rigidity main frame with a high-rigidity turret tool holder. Since the striker which punches a tool is installed to the main frame and the tool is held at right angles to the work piece at all times ,the press load does not affect the tool. The ARIES series can thus sustain high-precision working for a long period and ensures a long tool life.

Fig. 3.3.1 ARIES -255 Punching machine

Fig. 3.3.2 Punching machine

The ARIES series is designed to allow the clamps to pass through between the upper and lower turrets, in order to minimize the portion that cannot be punched (dead zone). The clamps, however, may be punched if punching is done when the clamps come under the punch. To ensure that the work clamps are not punched, the override detection device monitors the positions, and if the clamps move intoacritical zone, the machine will automatically stop. In addition, the ARIES series features a mechanism to detect the dead zone for each individual tool size. If the clamps are located under the punch, the sensor automatically detects it, thereby completely eliminating the possible damage to the tool and clamps as the tool will never punch the clamps even if the override button is pressed. Once the override is turned to the "OFF" position, it is not required to ascertain the override from the first work sheet. Simple tooling replacement them use of standard ‘tools sets’ minimizes setting time and eliminates the need for tool alignment.

Fig. 3.3.3 Punching machine with punched sheets

The ARIES-255 adopts a newly developed low-noise type double cam mechanism for its driving system. This mechanism is designed for a production cycle that provides a slow momentary speed when a work piece is punched in order to reduce the cause of noise and then resumes the speed again after punching. This system in combination with the above frame construction design has successfully helped decrease the noise and vibration as much as 20%(comparison using our own machines) without any reduction in productivity. This is the first machine of this type among mechanical systems. The low-noise machine has brought about a great improvement in the factory environment.

3.4 Special Punching Programs

For faster programming of work pieces the following extra programs are available:

- Nibbling
- Divided Circle
- Hole Circle
- One-sided and double-sided notching
- Horizontal and vertical mirroring
- Chamfering corners up to 20 mm
- Rounding corners with R_{max} = 25 mm (wider radiuses on request)
- Copy and modification programs
- Radiused cutting with R_{max} = 30 mm (wider radiuses on request)
- Angular cutting
- Embossing
- Countersinking
- Embossing buttons
- Embossing digits and/or characters
- User-own macro programming

3.5 Advantages

- Continuous Use: Unlike manual labor, CNC machinery (barring any malfunction or maintenance issue) can work continuously over any period of time without a break. This greatly increases productivity and efficiency.
- Consistency, Precision and Redundancy: With computer software, the design of any given product only needs to be programmed once. The CNC machine can then perfectly replicate that design, for any order quantity.
- Low Skill Requirement: CNC machine operators require little training and skill when compared to manual machine operators.
- Fewer Personnel: Because computer software controls the machinery, fewer technicians are needed for operation and oversight, cutting overall expenses.
- Flexibility: The software can be reprogrammed quickly and easily to produce different parts, allowing operations to keep up with shifting customer demands.
- Capability: This technology uses computer precision to go beyond the limitations of manual capabilities. More complex and intricate operations are possible with CNC machining.

4. BENDING MACHINE

4.1 Principle

A bending machine is a forming machine tool (DIN 8586). Its purpose is to assemble a bend on a work piece. A bend is manufactured by using a bending tool during a linear or rotating move. Bending is a manufacturing process that produces a V-shape, U-shape, or channel shape along a straight axis in ductile materials, most commonly sheet metal. Commonly used equipment includes box and pan brakes, brake presses, and other specialized machine presses.

Fig. 4.1 Bending machine

Bending machines represent a wealth of experience and pioneering innovation. The extensive portfolio includes machines for die and panel bending technologies as well as large format bending machines and fully automated solutions. There is a wide range of options available for each bending technology to suit your specific application. Use TruBend machines to produce simple and complex parts in any format precisely and cost-effectively. You always benefit from high-quality parts, increased flexibility, innovative tools, sophisticated automation solutions and intelligent software all from a single source. We focus on operability and ergonomics to ensure the machine supports operators in their work.

4.2 Types of bending machine

Die bending

In die bending or edge bending processes, the sheet metal is bent through a controlled downward movement of the press beam. The flat sheet is pressed by an upper tool into a V-shaped lower tool (die) and reshaped in a straight line. The back gauges ensure that the work piece is positioned accurately.

Panel bending

Panel bending is ideally suited to complex bending applications with radius bends, short sides, or narrow profiles. TRUMPF panel benders contain a bending frame comprised of a C profile onto which the lower and upper bending tools are mounted. When the sheet metal is bent, the C profile moves up or down and performs a small elliptical movement (the swivel)

Die bending with the Bend master

With innovative gripper technology and handling equipment, the Bend master can be used to process small and large parts weighing up to 100 kg. Its practical modular system gives you the flexibility to match the best grippers to your applications.

Tool Master

The Tool Master quickly takes care of set-up processes for you – an invaluable advantage, particularly for small lot sizes. The Tool Master can be retrofitted to many **TRUMPF** bending machines and is also compatible with your existing standard tools.

Fully automatic panel bending

Bend any part with greater productivity using the fully automatic bending center TruBend Center 7030 from TRUMPF. The innovative rotary part manipulator secures the blank and, when necessary, rotates it to the required position. Every bend is fully automatic. It becomes unbeatable when combined with the patented 2-axis part manipulator: It gives you endless possibilities such as negative bending.

Noise levels

Energy-efficient, fast and exceptionally quiet – every TRUMPF press brake works this way. Energy-efficient, fast and exceptionally quiet – TRUMPF bending machines work this way, for example, with the on-demand servo drive. It noiselessly performs upcoming tasks while effectively protecting the operator.

Magic Shoe

Operators have the freedom to trigger the stroke by foot from any position in front of the machine. The Magic Shoe intelligent sensor technology makes this possible.

Touch point Bend

The Touch point Bend makes operating TRUMPF bending machines even easier and more intuitive by combining the benefits of modern multi-touch technology and industrial controls.

Tube Bender and Grinder

A bending machine is primarily used for forming a bend on the work piece. The machine makes use of a bending tool for this process. Different types of bending machines are available, namely- Metal sheet bending machine, Busbar bending-cutting-punching machine, hydraulic and mechanical Profile bending machine, Hydraulic hand, hydraulic hand/motorized pipe bending machine, sheet folding machine, sheet metal bending machine, pipe bending machine, etc. The sheet bending machine is chosen for creating a bend on the sheet metals. Metal pieces are first fixed on to the clamping device that holds them during the entire operation. The robust nature of this bending machine is due to the fact they are manufactured using high-grade raw materials.

A sheet folding machine is an instrument used to bend objects at an angle. This profile bending machine is also known as pipe bending machine as it is used to bend pipe objects also. This machine is suitable to use when it comes to bending objects like pipe, tubes, etc. These profile bending machines are used due to their high precision quality and preferred among most of the people.

Sheet folding machine

Sheet folding machines assist you in curving and folding different materials to achieve the desired outcome. In the metal industry, manufacturers are required to bend metal sheets at an angle to achieve the desired result. Sheet folding machines uses tension and compression to create a sophisticated product. Additionally, the machine enables the manufacturers to set-up multiple parts that are otherwise hard to work with.

Sheet folding machines offer businesses an innovative opportunity to mold the raw materials into sophisticated products as per their needs. These machines are popular since they can be customized with different accessories and cater to the needs of various industries.

Pipe bending machine

Pipe bending machines help in bending pipes and tubes of different materials. Industries such as automotive, plumbing, architecture, and others consistently use the pipe bending machine for curving pipes and other industrial purposes. Whether you are working on bending a small piece of pipe or a large one, this equipment works perfectly without using any high-level energy or force. If you are looking for an ergonomic solution for bending hard material pipes such as steel, aluminum, or others, then a pipe bending machine is the ideal solution.

4.3 Bending equipment

Bending equipment is a class of machine tools and automatic systems for shaping base metal in a solid-drawn way without the use of welding works. Industrial and automatic machines and other equipment for bending are used for manufacturing products from stainless steel, iron, copper, aluminum and various alloys.

Metal bending technologies fall into two categories: cold and hot bending. Steelwork done from a solid plate through bending is notable for higher durability, monolithic structure and corrosion resistance. Cylinders, closed-loop components and complex and irregular parts can be produced on bending equipment.

4.4 Applications

Machine industry, aircraft and ship construction (production of tubes, cylinders and other metal parts);

- Production of pipes and pipe-line parts (both for engineering communication and oil-and-gas industry);

- Production of construction materials (roof and facade non-standard precast components, weatherings, moulding);
- Production of parts for buildings, constructions, reservoirs, gas holders, shelters, plate structures of blast-furnace departments;
- Production of elements and components for machines and aggregates of various purpose;
- Production of furniture and interior objects (shelves, nooks, furniture legs, hangers, hooks);
- Production of footing for stands signs, billboards and road signs.

Aside from rolling and bending machines, there are models for bending metal fittings, wire, fen or steel sections. Metal bending machines can be manual, mechanical or fully automated (including models with in-built CRM). There are as well both, universal types of machines and field-specific equipment, which is targeted at producing specific items - from bucket handles to welded and gas pipes.

4 .5 Types of bending equipment

- Sheet bending presses, automatic and mechanical
- Multi-functional equipment for laser-cutting, forming and bending
- Rotary (rolling press) sheet bending machines
- Hydraulic/electromechanical folder machines
- Hydraulic/electromechanical profile bending machines
- Pneumatic bending equipment
- Pipe-bending machines
- Machines for bending wire and fittings.

5 CONCLUSION

The study of machineries and metal tools is one the most fascinating experience. The reason from being a raw material a quite substantial amount of material is removed in the form of chips in order to achieve the final required shape. And also lot of energy is put up on material removal. Machine technology is undergoing continuous changes along with the process in various technological fields. During the course of this field work project whatever machine or equipment is described here is practical information such as specification operating parameters and designing process has been highlighted. Each and every process is explained in simple illustrations. And in this report I have incorporated various machines, their types and advantages. It helped me to find a balanced approach dealing with machine technology and Physics, that direct towards concepts and applications. “There is no science without experiments”, there is no technology without physics. This field work report has provided an insight to look deep into more and more physics concepts which is the mother of all technology. This also helped me to understand the nuances of the process as a student. Learning something new is a knowledge enriching experience, this filed report on machineries has inspired me to learn more and more about machines and their emerging science behind it.

STUDY ON TELEVISIONS

A field work report submitted to

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

Affiliated to

MANONMANIAM SUNDARANAR UNIVERSITY,
TIRUNELVELI

In partial fulfilment of the requirements for the award of

MASTER OF SCIENCE IN PHYSICS

Submitted by

H. SRI VIDHYA

Reg. No: 20SPPH15

Under the guidance of

Ms. A.VALENTINA M.Sc., M.Phil.,

DEPARTMENT OF PHYSICS

ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI

(Re-accredited with 'A+' Grade by NAAC)

2020-2021

CERTIFICATE

This is to verify that this field work report entitled **"STUDY ON TELEVISIONS"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** in partial fulfilment of requirements for the award of **MASTER OF SCIENCE IN PHYSICS** and is a record of work done during the academic year **2020 -2021** by **H. SRI VIDHYA** (Register No: 20SPPH15)

Signature of the Staff – in - Charge

Signature of the Co-Ordinator

Joyce

Signature of the Director

Director
Self Supporting Courses
St. Mary's College (Autonom
Thoothukudi - 628 001.

Lucia Rose

Signature of the Principal

Principal
St. Mary's College (Autonomous)
Thoothukudi - 628 001.

17/4/21

Signature of the Examiner

DECLARATION

I hereby declare that the field work report entitled, **"STUDY ON TELEVISIONS"** is submitted to **ST.MARY'S COLLEGE (AUTONOMOUS), THOOTHUKUDI** affiliated to **MANONMANIAM SUNDARANAR UNIVERSITY, TIRUNELVELI** for the award of the Degree of Master of Science in Physics is my unique work and no part of this field work report has been submitted for any Degree, Diploma or other similar titles.

H. Sri vidhya

Station: Thoothukudi **Signature of the Student**

Date: 10.04.2021 (H.SRI VIDHYA)

ACKNOWLEDGEMENT

On the very outset of this report, I would like to extend my sincere and heartfelt obligation towards all the personages who have helped me in this endeavour.

I wish to record our profound gratitude to our Principal Rev. Dr. Sr. A. S. J. LUCIA ROSE M.Sc., PGDCA., M.Phil., Ph.D., for her motivation.

I sincerely thank our Director of SSC, Rev. Dr. Sr. F. MARY JOYCE BABY M.A., M.Phil., Ph.D., for her encouragement and support.

I wish to thank Rev. Dr. Sr. JESSIE FERNANDO M.Sc., M.Phil., Ph.D., HOD & Associate Professor for her inspirational work to complete this work.

I owe a great deal to Mrs. P. PADMAVATHI M.Sc., M.Phil., SET., SSC Co-ordinator for supporting me throughout this field work.

I am indebted Ms. A. VALENTINA M.Sc., M.Phil., for her guidance and support for the successful completion of this field work report.

It's my pleasure to thank Mr. S. KARPAGARAJ, the Proprietor, Venuka Electronics, Thoothukudi for all the facilities provided to me in the pursuit of this field work.

I am deeply grateful to all the staff members of Department of Physics (SSC) for supporting us in all aspects.

CONTENT **Page.no.**

1 INTRODUCTION

Television is a system for transmitting visual images and sound that are reproduced on screens; it is used to broadcast programs for entertainment, information, and education. The television set has become a commonplace in many households, businesses, and Institutions. It is a major vehicle for advertising. The word **television** is derived from Latin word **tele** which means far and Latin word Visio means sight.

2 RADIO

Radio with Pictures

Fig.2 Radio with Pictures

The basic idea of television is "radio with pictures". In other words, where radio Transmits a sound **signal** (the information being broadcast) through the air, television sends a picture signal as well.

3 TELEVISION

Television has a three parts. They are **TV Camera**, **TV Transmitter**, **and TV Receiver**.

- The TV **camera** that turns a picture and sound into a signal.
- The TV **transmitter** that sends the signal through the air.

- The TV **receiver** (the TV set in your home) that captures the signal and turns it back into picture and sound.

3.1 TV Camera

Fig. 3.1 TV Camera

- We can see things because they reflect light into our eyes. An ordinary "still" camera photographs things by capturing this light on light-sensitive film or using electronic light detector (in the case of a digital camera) to make a snapshot of how something appeared at a particular moment.
- A TV camera works in a different way: it has to capture a new snapshot over 24 times per second to create the illusion of a moving picture.
- An old-fashioned TV camera works exactly like this when it turns a picture into a signal for broadcasting, only it copies the picture it sees a line at a time. Light-detectors inside the camera scan across the picture line by line, just like your eyes scanning from top to bottom of the picture in an art gallery. This process, which is called **raster scanning**, turns the picture into 525 different "lines of colour light" (in a common TV system called NTSC, or 625 lines in a rival system known as PAL) that are beamed through the air to your home as a video (picture) signal.

3.2 TV Transmitter

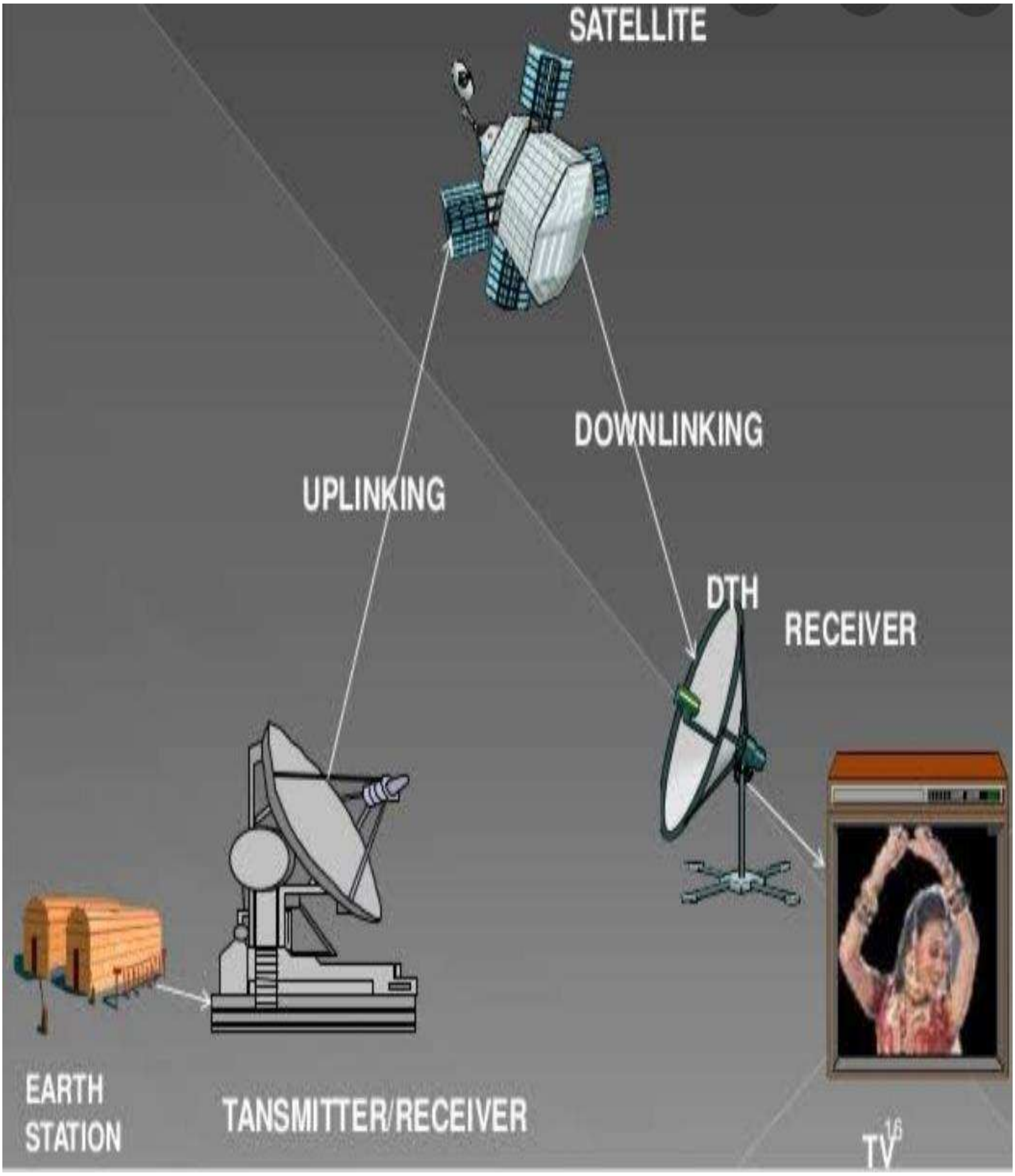


Fig. 3.2 TV Transmitters

3.3 TV Receiver

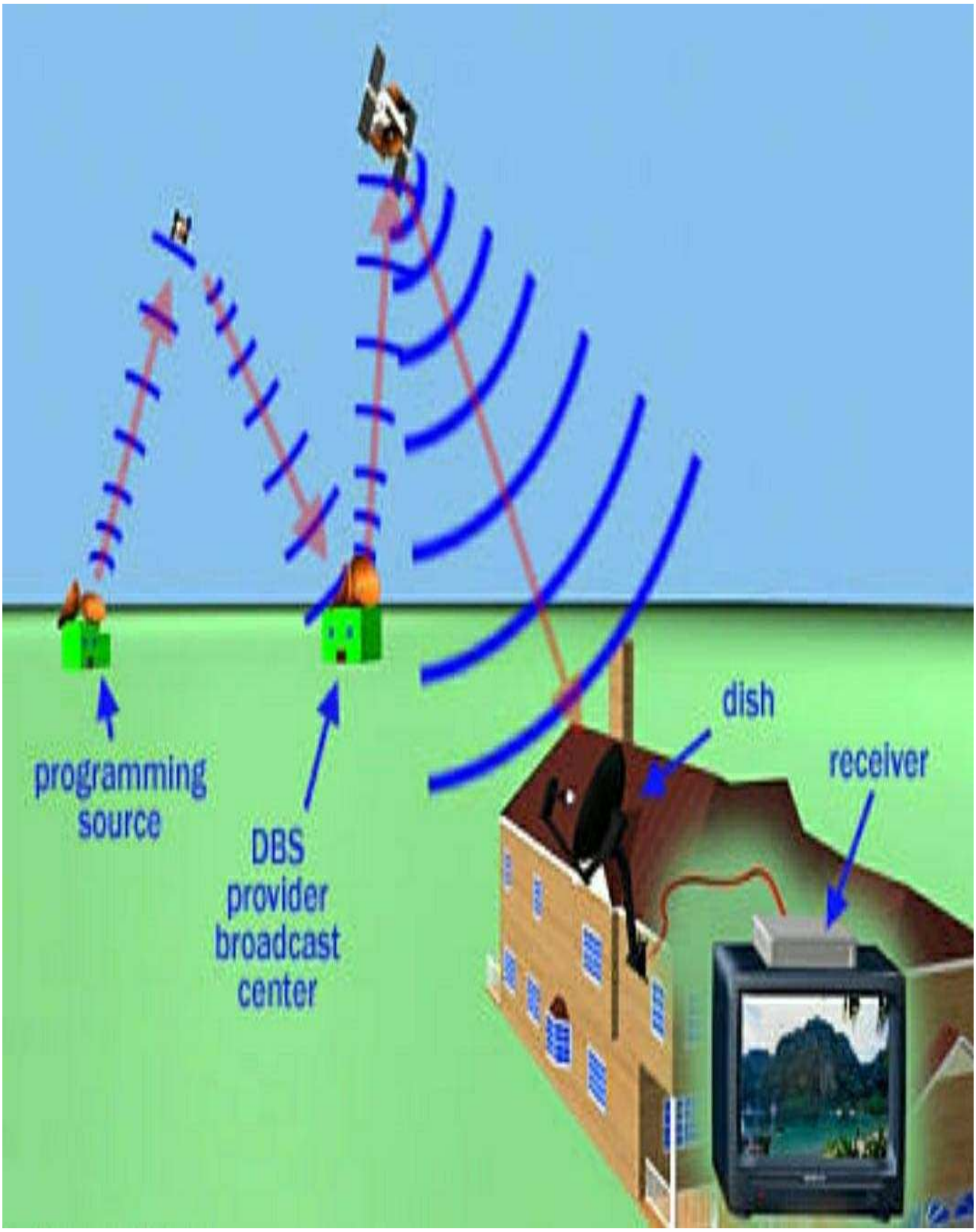


Fig. 3.3 TV Receiver

4 TYPES OF TELEVISIONS

- Quantum Light Emitting Diode
- Organic Light Emitting Diode (OLED) Display
- LED TVs
- Liquid Crystal Display (LCD)
- Digital Light Processing (DLP)
- Plasma Display Panels
- Direct TV

4.1 Quantum Light Emitting Diode

Fig. 4.1 Quantum Light Emitting Diode

- QLED stands for Quantum Dot Light Emitting Diode.
- Quantum dot LED (QLED) uses quantum dots to produce superior colour range and brightness.
- QLED television screens can be larger and they will also have a longer life.

4.2 Organic Light Emitting Diode (OLED) Display

Fig. 4.2 Organic Light Emitting Diode (OLED) Display

- OLED stands for organic light emitting diode and organic materials like carbon to create light when supplied directly by an electric current.
- OLED screens can be super thin and crucially, flexible.

4.3 LED TVs

Fig. 4.3 LED TVs

- LED use the same technology as an LCD TV, but instead of being illuminated by a florescent bulb from behind, they are lit by an array of LEDs (light emitting diodes).
- LED can be broken up into two further major categories Direct (Back-lit) LED and Edge-lit LED.

4.4 Liquid Crystal Display

Fig. 4.4 Liquid crystal Display

- LCD's are thin displays, normally used in laptop computers and TV screens.
- The term 'LCD' Stands for 'Liquid Crystal Displays'.
- A liquid crystal display is a special flat panel that can block light, or allow it to pass.
- The panel is made up of segments with each block filled with liquid crystals.

- The colour and transparency of these blocks can be changed by increasing or reducing the electrical current.
- LCD crystals do not produce their own light, so an external light source like a florescent bulb is needed to create an image.

4.5 Digital Light Processing

Fig. 4.5 Digital Light Processing

- Digital Light Processing (DLP) is a display technology developed by Texas Instruments.
- It is based on an optical semiconductor, called a Digital Micro-mirror Device (DMD), which uses mirrors made of aluminum to reflect light to make the picture.
- DMD can be combined with image processing, memory, a light source and optics to form a DLP system capable of projecting images with better colour fidelity and consistency than current technology.
- It provides all-digital projection displays that offer superior picture quality in terms of resolution, brightness, and contrast.

4.6 Plasma Display Panels

Fig. 4.6 Plasma Display Panels

- A plasma display is a computer video display in which each pixel on the screen is illuminated by a tiny bit of plasma or charged gas, somewhat like a tiny neon light.
- Plasma displays are thinner than cathode ray tube (CRT) displays and brighter than liquid crystal displays (LCD).
- A plasma displays panel (PDP) is a type of flat panel displays common to large TV displays 30 inches (76 cm) or larger.

4.7 Direct TV

Fig. 4.7 Direct TV

Direct view televisions are known as 'cathode ray tube' television or CRT.

5 BY SCREEN TYPE

- Flat screen
- Curved screen

5.1 Flat Screen

Fig. 5.1 Flat Screen

A flat screen television is a television with a flat, narrow screen. Flat screen displays are thin and lightweight.

5.2 Curved screen

Fig 5.2 Curved screen

It is a special type of TV. The screen is used as curved so it is called curved TV.

6 COMPONENTS OF TVs

- Cathode ray tube
- Light valve
- Logic board
- Capacitors
- Screen and surround

6.1 Cathode Ray Tube

Fig. 6.1 Cathode Ray Tube

- Most televisions used today utilize a cathode ray tube (CRT) inside of the TV to display images.
- The CRT is a display screen which produces images in the form of the video signal.
- It is a type of vacuum tube which displays images when the electron beams through electron guns are strikes on the phosphorescent surface.
- In other words, the CRT generates the beams, accelerates it at high velocity and deflects it for creating the images on the phosphorous screen so that the beam becomes visible.

Components of CRT

They are three main components

- Electron Gun
- Electron Beam
- Screen

Working of CRT

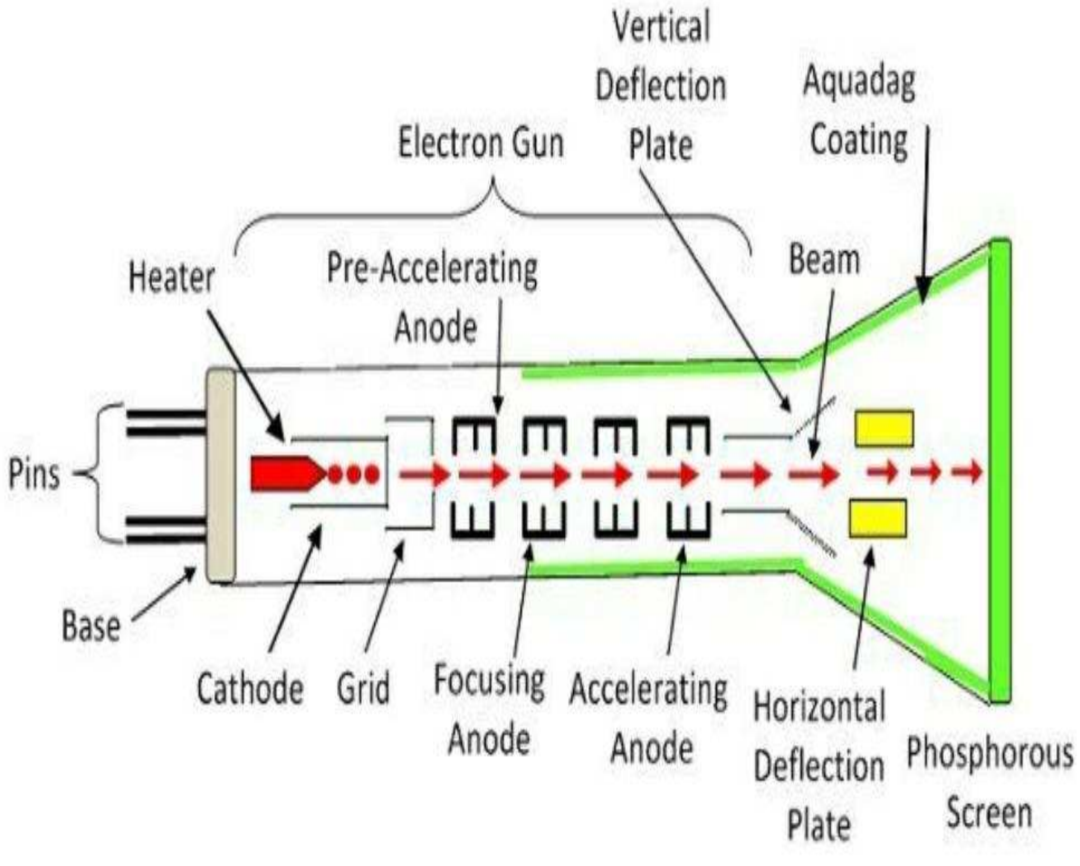


Fig. 6.1.1 Cathode Ray Tube

- The working of CRT depends on the movement of electron beams. The electron guns generate sharply focused electrons which are accelerated at high voltage.

- The high velocity electron beam when a strike on the fluorescent screen creates luminous spot.
- After exiting from the electron gun, the beam passes through the pairs of electrostatic deflection plate.
- These plates deflected the beams when the voltage applied across it.
- The one pair of plate moves the beam upward and the second pair of plate moves the beam from one side to another.
- The horizontal and vertical movement of the electron are independent of each other, and hence the electron beam positioned anywhere on the screen.
- The working parts of a CRT are enclosed in a vacuum glass envelope so that the emitted electron can easily move freely from one end of the tube to the other.

Features of CRT

The features of CRT can be split into four main sections.

- Electrons gun
- Deflection system
- Fluorescent screen,
- Glass Tube and Base

Types of CRT

- CRTs were produced in two major categories, **picture tubes** and **display tubes**.
- Picture tubes were used in TVs while display tubes were used in computer monitors.

Rendering of colour CRT

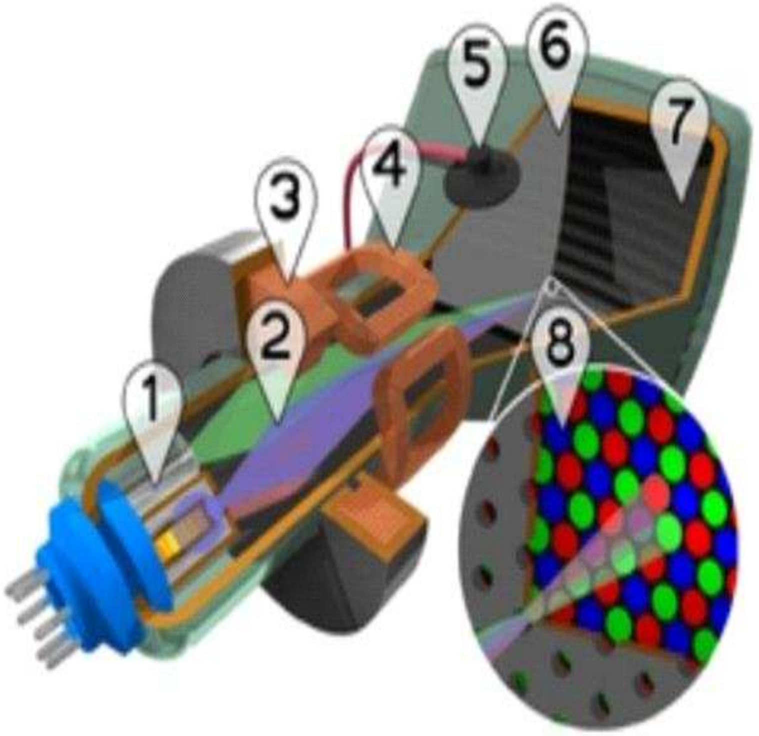


Fig. 6.1.2 Rendering of colour CRT

1. Three electron emitters (for red, green, and blue phosphor dots).

2. Electron beams.

3. Focusing coils.

4. Deflection coils.

5. Connection for final anodes.

6. Mask for separating beams for red, green, and blue part of the displayed image.

7. Phosphor layer (screen) with red, green, and blue zones.

8. Close-up of the phosphor-coated inner side of the screen.

Rendering of Monochrome CRT

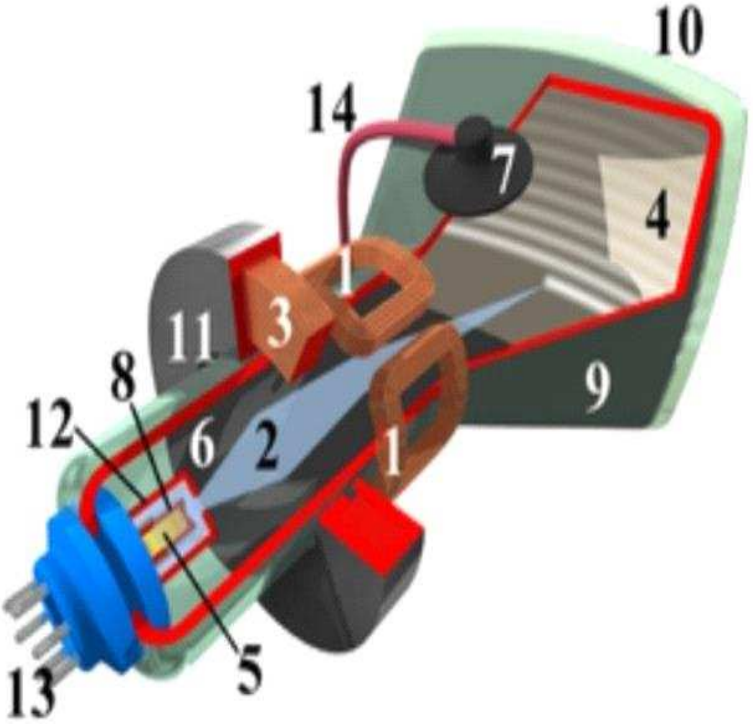


Fig. 6.1.3 Rendering of Monochrome CRT:

1. Deflection coils

2. Electron beam

3. Focusing coil

4. Phosphor layer on the inner side of the screen; emits light when struck by the Electron beam
5. Filament for heating the cathode
6. Graphite layer on the inner side of the tube
7. Rubber or silicone gasket where the anode voltage wire enters the tube (anode cup)
8. Cathode

9. Air-tight glass body of the tube

10. Screen

11. Coils in yoke

12. Control electrode regulating the intensity of the electron beam and there by the light emitted from the phosphor.

13. Contact pins for cathode, filament and control electrode

14. Wire for anode high voltage

Cathode Ray Tube (CRT) TV Works:

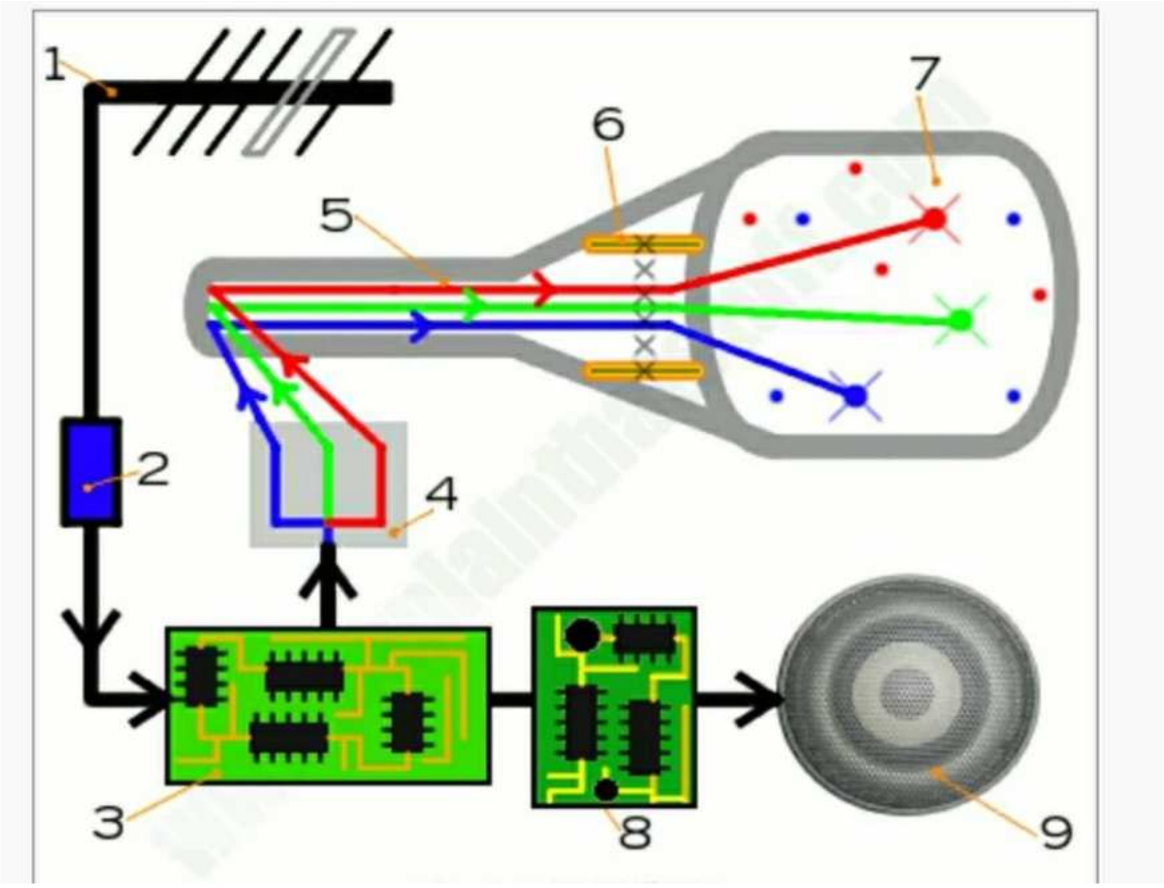


Fig. 6.1.4 Working of Cathode Ray Tube (CRT) TV Works

1. An **antenna** (aerial) on your roof picks up radio waves from the transmitter. With satellite TV, the signals come from a satellite dish mounted on your wall or roof. With cable TV, the signal comes to you via an underground fibre-optic cable.

2. The incoming signal feeds into the **antenna socket** on the back of the TV.

3. The incoming signal is carrying picture and sound for more than one station (program). An **electronic circuit** inside the TV selects only the station you want to watch and splits the signal for this station into separate audio (sound) and video (picture) information, passing each to a separate circuit for further processing.

4. The **electron gun circuit** splits the video part of the signal into separate red, blue, and green signals to drive the three electron guns.

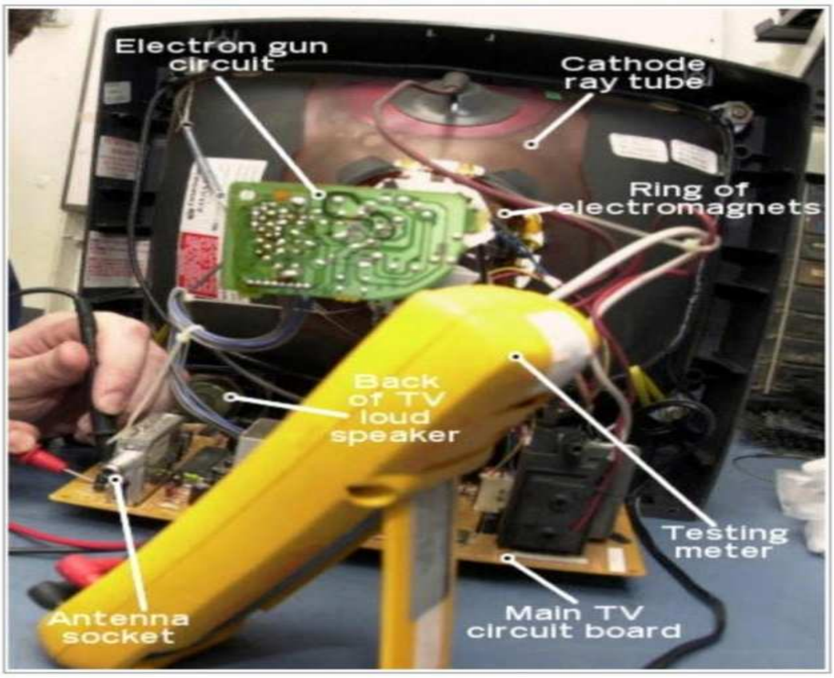


Fig. 6.1.5 Picture of Inside Part of TV

5. The circuit fires three electron guns (one red, one blue, and one green) down a **cathode-ray tube**, like a fat glass bottle from which the air has been removed.

6. The electron beams pass through a **ring of electromagnets**. Electrons can be steered by magnets because they have a negative electrical charge. The

electromagnets steer the electron beams so they sweep back and forth across the screen, line by line.

7. The electron beams pass through a grid of holes called a mask, which directs them so they hit exact places on the **TV screen**. Where the beams hit the phosphors (colure chemicals) on the screen, they make red, blue, or green dots. Elsewhere, the screen remains dark. The pattern of red, blue, and green dots builds up a colour picture very quickly.

8. Meanwhile, audio (sound) information from the incoming signal passes to a separate **audio circuit**.

9. The audio circuit drives the **loudspeaker** (or loudspeakers, since there are at least two in a stereo TV) so they recreate the sound exactly in time with the moving picture.

Advantages of CRT

- The cathode rayed tube can easily increase the monitor's brightness by reflecting the light.
- They produce more colours.
- The Cathode Ray Tube monitors have lower price rate than the LCD display or Plasma display.
- The quality of the image displayed on a Cathode Ray Tube is superior to the LCD and Plasma monitors.
- The contrast features of the cathode ray tube monitor are considered highly excellent.

Disadvantages of CRT

- They have a big back and take up space on desk.
- The electromagnetic fields emitted by CRT monitors constitute a health hazard to the functioning of living cells.
- CRTs emit a small amount of X-ray band radiation which can result in a health hazard.
- Constant refreshing of CRT monitors can result in headache.
- CRTs operate at very high voltage which can overheat system or result in an implosion.
- Within CRTs strong vacuum exists in it and can also result in an implosion.
- They are heavy to pick up and carry around.

Characteristics of CRT

- A CRT monitor can support many output resolutions without losing quality of the image.
- CRT monitor is bulk it’s cheap nowadays.

6.2 Light Valve

- The light valve works in conjunction with the cathode ray tube.
- It provides a fixed source of light that essentially lights up the electrons from the cathode ray tube so that they can be seen on the screen.
- Light valves have improved in quality as technology has advanced.
- High-definition TVs provide clearer and brighter pictures as a result of more sophisticated light valves.

6.3 Logic Board

- The electrical wiring within a TV set consists of transformers, coils, chokes and resistors.
- These components are secured on a logic board.
- The circuit provides the correct electrical supply and sends messages to the various components of the TV set.
- It is the brain of the TV and enables it to function.

6.4 Capacitors

- A capacitor is a device that stores an electrical charge between two metal plates and releases the energy as light.
- The capacitor in a TV set would give you a severe electrical shock if you touched it because it stores a large amount of power.

6.5 Screen and Surround

- The most obvious components of a TV are the ones you can see. These are the screen and the TV surround.
- The material the screen is made from varies.
- Traditional screens were made from glass; however, more modern units, such as LCD and plasma screens, are made from plastic.
- The surround of the TV is the outer shell which protects the internal components of the TV listed previously.
- This shell is usually made of a durable plastic

7 MAIN PARTS OF TV

There are many parts inside of televisions to make them function. Televisions are one of the primary media outlets by which people acquire information, entertainment and education. It is fascinating that a certain image and sound can be sent from distant regions of the globe and into your living room and that multiple people in different countries can watch the same exact footage at the same time, and there are many significant parts inside of a television that enable this to happen.

Main Parts are

- Anodes
- Steering Coils
- TV phosphors

7.1 Anodes

- Between the cathode and the TV a set of anodes are installed to focus the stream of electrons into a tight beam and to accelerate the electron beam.
- The accelerated electron beam is sent by the anodes through the vacuum in the tube until it hits the screen of the TV on the other side.

7.2 Steering Coils

- Steering coils consist of copper winding coils that are capable of creating magnetic fields inside the tube to direct the electron beam.
- There are two sets of coils inside of a CTR that direct the beam as to which direction to go and where to hit the screen on the other side;
- One set of coils creates a magnetic field that directs the electron beam vertically and the other set moves the beam horizontally.

7.3 TV Phosphors

- Phosphors pertain to any material that emits visible light when exposed to radiation caused by either ultraviolet light or by a beam of electrons.
- In a CTR, and thus in a TV, phosphor coats the inside of the screen, and when the electron beam strikes the phosphor, it makes the screen glow.
- To produce colour for colour TVs, three phosphors are arranged as dots that emit red, green and blue light, along with three electron beams that illuminate the three different colours together to generate and display any other colours on the light spectrum.

8 POSITIVE EFFECT OF TELEVISION

- Excitement
- Laughter
- Learn about different people and places
- Educational and Informative
- Gives families to laugh over something

Difference between the New and Old Televisions:

Old Type Television	**New Type Television**
Bulk and heavy design	Almost less than half the average old type television
Televisions will not be bigger than 36 inches in screen size	Televisions are designed to be compact, usually measuring less than 10 inches in depth
CRTs create an image by blurring pixels that can be green, blue or red	These images are clearer due to the pixels ability to be any of those colours

Growing Popularity of television over other media

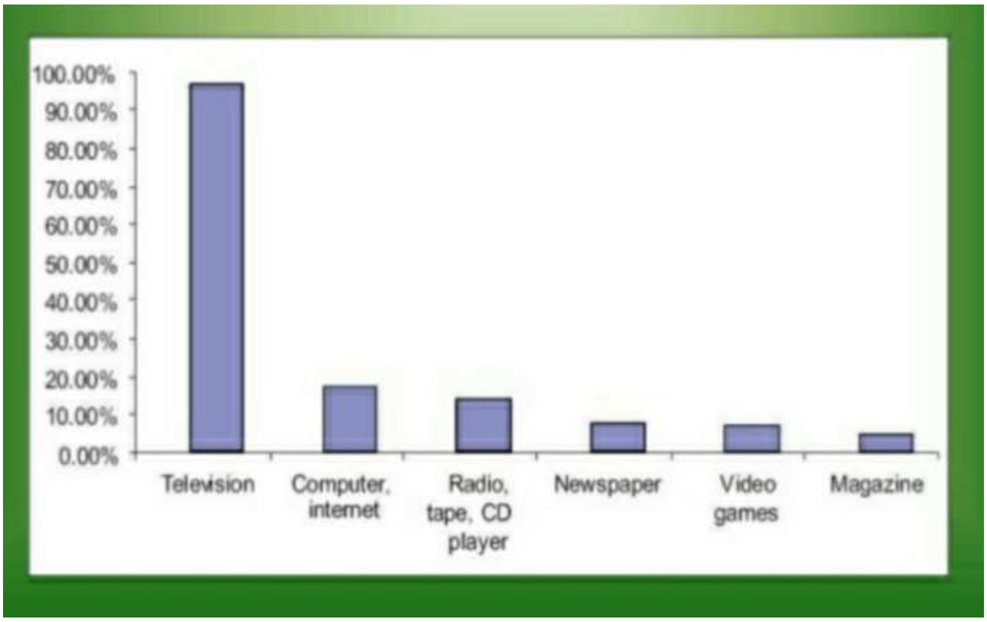


Fig. 8 Graphical representation of growing popularity of television

Evolution of Television

Fig. 8.1 Evolution of Television

9 CONCLUSION

Technology has made everything easy and simple for humankind. Television is one of the visible evidence for the development of Technological world. In olden days in 21st century the frame of television has evolved in the form of audio visual electronic device. It is not just a screen of entertainment, it also brought the whole world into a tiny box both merits and demerits through that screen. Due to this field work report, I came to know what television is all about, it helps me to understand, its parts, merits and demerits in a total different angle. Television is not just an entertainment. it also gives the tremendous knowledge about science. There is no technology without demerits, all of these technology has some disadvantage. But people have to handle it wisely. This field work report has inspire me to learn more about television and other home appliance and to find a better way to reduce its demerits.