CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

1.1 General Introduction
1.2 Importance and Scope of Fundamental Thermodynamic Properties
1.3 Theories of Liquids
   1.3.1 General
   1.3.2 Introduction to Various Theories
      A. Cybotactic State Theory
      B. X-ray and Solid like Theory of Liquids
      C. Hole Theory
      D. Cell Theory of Eyring
      E. Cell Theory of Lennard-Jones and Devonshire
   1.3.3 Modification to Theories
1.4 Types of Intermolecular Forces
1.5 Specific Interactions
   A. Charge Transfer Interactions
   B. Contact Charge Transfer Interactions
   C. Hydrogen Bond Interactions
1.6 Characteristics and Industrial Importance of Solvents and Solutes under Study
1.7 Literature Survey
1.8 Objectives of present study
1.9 Present Work
   References
CHAPTER 1

INTRODUCTION

1.1 General Introduction:-

In the recent years, much importance has been given to the behavior of mixed solvents rather than a single solvent because of their wide range of applications in many chemical, industrial and biological processes. The physico-chemical data are often required in many industrial processes (flow, mass transfer or heat transfer calculation, polymerization, solvolysis, etc.) and also leads to the formulations of a large number of methods for correlating or predicting the physical properties. Therefore in view of practical importance of mixed solvents, a deeper knowledge of their solution structure and intermolecular interactions between component molecules at molecular level thus becomes essential. Recently researchers in this field have been focusing their interest more sharply on the molecular structure along with some representative macroscopic property that serves to characterize it. The composition and temperature dependence of volumetric, acoustic, transport and surface properties of associated liquid system provides substantial information of the molecular influence on the intensity of the intermolecular interactions among component molecules and can be used as a powerful tool for studying intermolecular interactions in these systems.

Science of solution chemistry is very complex. It requires for its clarification, investigation and understanding of some thermodynamic information and the help of many branches such as mechanics, electrostatics and hydrodynamics. Under real use conditions involving various processes such as separation of chemicals or chemical reactions, common practice is that several liquid components that differ in chemical nature and polarity, mixed together. This situation results in a very complex fluid state, the understanding of which becomes very difficult.

Most of techniques to know molecular interactions are based on spectroscopic investigation. But majority difficulties found in such techniques due to, intrinsic insensitivity of
spectroscopic investigation and weak molecular interactions. Hence instead of such techniques one can have a better idea about molecular interactions by investigating and monitoring thermodynamic properties which includes, volumetric, transport and ultrasonic properties.

From the basic and fundamental thermodynamic properties like density, viscosity and ultrasonic velocity we can derive number of parameters like excess molar volume, acoustic impedance, intermolecular free length, viscosity deviation, molecular association and many more. Such type of derived thermodynamic parameters helpful to understand the strength of molecular interactions, hydrogen bonding phenomenon which based on polarity and size of molecules of two liquids in a solution in definite composition and over a fixed temperature range. Properties of liquid-liquid binary mixtures are very important qualitatively and quantitatively as a part of studies of thermodynamic, acoustic and transport aspects. Compositional dependence of thermodynamic properties has proved to be a very useful tool in understanding nature and extent of pattern of molecular aggregation resulting from interactions. This study is a powerful means of characterizing various aspects of physicochemical behaviors of liquid mixtures and molecular interactions.

Mixing volume effects are also important from theoretical as well as practical point of view. These properties found many applications in paints, varnishes, cleaning products, antioxidant agents, inks, adhesives, dispersion for textiles, papers, polystyrene, etc. where volume effects are also involve in conversion of formulation from gravimetric to volumetric analysis. Properties like molar volume and their deviations from ideality and variation with temperature and composition of binary mixtures are useful to design engineering processes in chemical and biological industries. Also, volumetric and ultrasonic properties have practical importance in understanding interactions and physicochemical behavior. The mixing of different compounds gives rise to solutions that generally don’t behave ideally. Deviation from ideality may be expressed by many thermodynamic variables, particularly by excess properties. Excess properties of mixtures correspond to difference between actual and properties if system behaves ideally and thus are useful in study of molecular interactions and arrangements. In particular, they reflect interactions that take place between solute-solute, solute-solvent and solvent-solvent species.

Thermodynamic properties are also important in designing industrial equipments with better precision. There has been an increasing interest in the study of molecular interactions and
a number of experimental techniques have been used to investigate the interactions between the components of binary liquid mixtures. Traditional theories of solutions dwell exclusively on two aspects of liquid mixtures. One of these is the entropy associated with dispersion of the two molecular species or of their constituent elements in case of complex molecules, among one another. A lattice model often serves as the device for estimating this “combinational entropy”. The other aspect relates to the interactions between unlike and like neighbors. Treatment of the properties of liquid mixtures has progressed little beyond the level of interpretation possible within the framework supported by these two considerations alone [1, 2]. There are two principal reasons for the great amount of experimental and theoretical work on the properties of liquid mixtures. The first is that they provide one way of studying the physical forces acting between the two molecules of different species, and second for the study of mixtures, is the appearance of new phenomenon (interactions) which are not present in pure liquids. The most interesting of these are, new types pf phase equilibrium which arise from the extra degree of freedom introduced by possibility of varying the properties of components.

The equilibrium properties of a liquid are strongly dependent on what may be loosely called its local structure, often expressed in terms such as packing density, free volume or more exactly in terms of the radial distribution function. In as such as, this local structure depends on the forces between molecules and volume of the molecules; in general, it will change with the composition. This change in turn will be reflected in the thermodynamic properties of the mixture. Contributions of this nature have either been ignored altogether, or correction to a state of null volume change on mixing has been adopted as a means of compensating for the effects referred. It will be apparent, however that, adjustment of one thermodynamic quantity (e.g. volume in this manner) will not in general, affect a simultaneous correction of others (e. g. the free energy of that part of it relating to the local structure) to their linearly interpolated values. The choice of volume as the property to be conserved is arbitrary and there is assurance that nullity of volume change obviates consideration of other characteristic properties of the liquid.

Investigations in the liquid state pose a fascinating and challenging problem to both the theoreticians and experimentalists. The molecules in liquid can not be studied as free molecules as in gas or the structurally fixed crystalline arrangements of solids. In short liquid can be considered as distorted crystal or a condensed gas. It is unfortunate that both the theory and practice of the study of liquid mixtures have often been divorced from the study of pure liquids.
Although researchers have studied the liquid state for centuries, surprisingly the first published theory on liquid structure did not appear the early 1930’s.

1.2 Importance and Scope of Fundamental Thermodynamic Properties:

Studies on thermodynamic properties of liquid-liquid binary mixtures are gaining a lot of attention these days owing to their relevance in understanding the nature and extent of molecular interactions between the components of the liquid mixtures in developing the new theoretical models and carrying out engineering applications in the process industry. The knowledge of thermodynamic and physical properties of liquid-liquid systems is of considerable importance due to their wide range of applicability as solvent media in various physicochemical studies, in processing and product formation in many industrial applications. Measurements of some of the bulk properties like density, viscosity and ultrasonic velocity of liquids provide an insight into the investigation of the intermolecular arrangement of liquids and help to understand the thermodynamic and acoustic properties of the liquid mixtures. The study of thermodynamic properties involves challenges of interpreting the excess quantities as a means of understanding the nature of intermolecular interactions among the mixed components. The interactions between molecules can be established from a study of characteristic departure from ideal behavior of some physical properties like density, volume, viscosity, compressibility and dielectric properties [3, 4].

Accurate knowledge of thermodynamic properties of binary liquid mixtures has great relevance in theoretical and applied area of research. These data are needed for design process in chemical, petrochemical and pharmaceutical industries. Usually, for non-ideal mixtures, direct experimental measurements are performed over the entire composition range. Many times predictive methods for the excess quantities could be more useful than the direct experimental measurements especially when quick estimate are needed. Most empirical approach for calculating the excess properties attempts to explain solution non idealities, in terms of specific or non-specific intermolecular interactions.

Volume properties and evaluation of thermodynamic properties gives the better knowledge of the processes that occur in the mixture [5-7]. In addition, the better understanding of these kinds of properties of fluids is essential in designing processes involving heat transfer,
mass transfer and fluid flow. The more information of magnitudes such as excess molar volume of a given component of a mixture, the more efficient the design of engineering processes in which these magnitudes are involved. However, during the mixing process new effects can affect the volume behavior, such as changes in the structure of components, repulsion or attraction between unlike molecules these effects can make. So a better understanding of the excess molar volume of a system is of considerable physicochemical interest. Binary liquid mixtures rather than single component liquid system are widely used in processing and product formulations in many industrial applications. Among the various properties considered in process and product design and optimization excess molar volumes is the most important. Although a number of predictive equations are available for estimating thermodynamic excess properties (excess volume, excess enthalpy, excess Gibb’s free energy, etc.) of multi component systems.

Study of viscous behaviour of liquid mixtures is of strategic importance in understanding the in-depth of their transport behavior. Recently, it has been applied in the study of mass transfer in a rotating packed bed with viscous Newtonian and non Newtonian fluids [8], on breakage parameters of quartz [9], on liquid-solid fluidization [10], diffusion and the mesoscopic hydrodynamics of super cooled liquids [11], in the use of nanoliter viscometer for analyzing blood plasma and other liquid samples [12], in the flow of viscous shear thinning fluids behind cooling coil banks in large reactors [13], on shear viscosity relaxation of liquid n-alkanes [14], etc. Besides this previous work, recently a large amount of work has been reported on the experimental measurements of viscosity of single components and that of binary liquid mixtures. Density and viscosity are important basic data used in process simulation, equipment design, solution theory and molecular dynamics [8, 9]. Knowledge of viscosity is widely used in processing and product formulations [10] in many industrial applications.

Ultrasonic velocity measurement of liquid mixtures of non electrolytes provides an excellent tool to investigate inter and intermolecular interactions between unlike and like molecules. Alcohols exist in the form of aggregates. When they are mixed with other non electrolyte molecules, the aggregates of alcohol dissociate and form intermolecular complexes with unlike molecules.

The velocity of sound is very important for liquids to study molecular interactions and to elucidate internal structure of liquid mixture. The knowledge of sound velocity in liquids has been found very helpful in the study of high velocity interpartical collisions [15], ultra
spectrometry for liquids [16], in multiphase flows [17], crystal growth from solutions [18], aqueous fluids [19], convective flow electrochemistry [20], desorption of metal ions from activated carbon [21], gas phase RTD measurements in gas and gas-solid reactors [22], acoustical absorption spectrometry study [23], sonochemical removal of nitric oxide from flue gases [24], shear impedance spectrometry [25], ultrasonic spectrometry of polystyrene latex suspensions [26], structural isomerization and molecular motions of liquid n-alkanes [14]. Density and ultrasonic velocity are important basic data used in process simulation, equipment design, solution theory and molecular dynamics [15, 16].

1.3 Theories of Liquids:

1.3.1 General:

The structure of liquid is one of the important unsolved problems. A natural approach for depicting a liquid would be one, which consider it, to be derived from a gas, since the transition from the gaseous state to liquid state through critical point is essentially continuous with little destination between the two phases. The tendency for gas molecules to remain together for a significant period of time after colliding becomes greater as the temperature is lowered. This results in the formation of clusters consisting of one or more molecules. As temperature decreases, the size and number of clusters increases. Increased pressure also increases the number of clusters because the available space is decreased. The mathematical development by Mayer [27] led to satisfactory description of the condensation of a saturated vapour into a liquid. Other investigations have added to his work, among them Green [28], who has outlined the improved theory in his book on fluids. The theory states that during condensation, the individual clusters of a vapour coalesce and loose their identity. The liquid which results may be, simply considered as one giant cluster that is many neighboring molecule about any given molecule.

1.3.2 Introduction to Various Theories:

In 1887, an organized theoretical and experimental investigation of conducting solution was begun. van’t Hoff [29] predicted that solutions which readily conduct electric current possess freezing points, boiling points, osmotic pressure, vapour pressures, characteristics of a special class of a system and the simultaneous and even more important discovery of Arrhenius [30] that such systems contain electrically charged particles or ions. The powerful methods of
thermodynamic were for the first time applied by van’t Hoff to solutions in a systematic manner. His treatment, however, lacked the generality which might have been achieved at that time if the system of thermodynamics developed by Gibb’s [31] ten years earlier had been employed. Gibb’s great treatise provided all the essential basic principles required for the thermodynamics of solutions.

The first systematic attempt in this direction was made by Young [32] by pooling large amount of data on the thermodynamic and mechanical properties of liquid mixtures. A systematic theoretical study [33-36] has also been made by many scientists on the liquid mixtures. In view of these facts, the thermodynamic of binary mixtures of non electrolytes is of great importance in the field of solution chemistry as it provides a valuable tool to understand the nature of molecular interactions amongst the constituents of the liquid mixtures. These quantities represent the deviation of the real properties of the mixtures from those of an ideal mixture. Examples are given by Douheret [37-41].

A. Cybotactic State Theory:

Stewart [42] studied the X-ray patterns of several different liquid alcohols consisting of rod like or straight chain molecules and found evidences for two distinct intermolecular distances. One value was essentially constant for all the different alcohol series; the other varied linearly with the length of the alcohol molecule. The constant quantity was interpreted as representing the perpendicular distance between more or less parallel, rod like molecules. This idea suggested some degree of order in the way the alcohol molecules are arranged. The other quantity was related to the number of carbons in the chain, in that it showed a specific increase with each CH₂ group added to the molecule. There was little resemblance between the X-ray patterns of these liquids and those of the corresponding solids, however, which indicated that the scattering results for liquids don’t arise from crystal fragments, but rather from temporary molecular space-array units. Stewart called these units as cybotactic groups. The remaining molecules between these groups are distributed in a random fashion. Since molecules randomly leave and re-enter the cybotactic group, the overall picture is one of the essentially random structure. Because this behaviour was found only in rod like molecules and has not been observed in other types, it is not a general property of liquids. Considerable effort has been expended in attempts to develop the idea of cybotactic state into a general theory for liquid
structure, but these have met with little success. X-ray scattering not only provide the essential information for the development of this theory but also play an important role to explain the nature of liquids. Since X-ray patterns of liquids exhibit features somewhat like those crystalline solids, some investigations infer that there are solid-like aspects to liquids.

B. X-rays and Solid Like Theory of Liquids:

During the early experiments on the diffraction of X-rays by crystalline solids, investigators used amorphous materials for contrast to show the variation in X-ray patterns provided by different classes of materials. Liquids were among the amorphous substances they used and although no distinct patterns were observed, the intensity of the scattered X-rays was not uniformly distributed as would be expected for substances devoid of structure. Both Debye and Ehrenfest thought this non-uniformity in X-ray patterns was the result of somewhat definite spacing of the molecules in liquids. Following this proposal many suggestions were made in attempts to relate the structure of liquids to that of solids. Keesom and deSmeldt appear to have been the first to suggest an incipient crystalline structure for liquids. At about the same time, Joff’s published his concept of irregularities in crystalline solids and shortly thereafter Frenkel considered the possibility of vacancies in liquids. Zernike and Prince in 1927 assumed a statistical regular arrangement of molecules in the liquid state. These discoveries and suggestions all point to an ordered arrangement of molecules in liquid. Debye was among the first investigators to use X-ray in the elucidation of the structure of matter. He and Menke carried out a classic study to provide experimental information about the nature of radial distribution function (W). This effort made by Debye and Menke [43] encouraged investigators to try to develop a model for liquids, which incorporates solid-like characteristics. Prior to this, the consensus was that liquids should more logically be related to gases; this study, however, have given impetus for the study of solid-like aspects of liquids.

C. Hole Theory:

An interesting reversal to the cluster and group theories of Mayer and Stewart start from the postulation of holes in a liquid. Such holes logically arise if structure existed in the make up of a liquid. One of the early suggestions involving such holes or vacancies in liquids was made
by Frenkel [44]. This model involving spaces in the structure of liquids is somewhat indefinite but the basic idea has been applied in several modifications and extensions of the hole theory.

**D. Cell Theory of Eyring:-**

More sophisticated treatments [9, 45] of liquid mixtures derive their conceptual basis from
(I) The cell model for liquids
(II) The postulation of a universal form for the intermolecular potential expressed by

$$\varepsilon_{ij} = \varepsilon^{*ij} \phi \left( \frac{r_{ij}}{r^{*ij}} \right),$$

where $r_{ij}$ is the distance between centers of molecules $i$ and $j$, $\varepsilon^{*ij}$ and $r^{*ij}$ are characteristic parameters for the pair and $\phi \left( \frac{r_{ij}}{r^{*ij}} \right)$ is a universal function of its argument. The corresponding states approach, including conformal theory, proceeds from the latter of these premises [45]. In so far as giving account of experimental result is concerned, these approaches have failed to establish decisive advantage over treatments recalled in the preceding paragraphs. Reasons, therefore, undoubtedly relate to limitations of the cell model and to severe departures from propositions (II) above for component molecules, which differ appreciably in size, shape or composition. The definition of the cell, consisting of neighbour molecules in fixed array about the central ‘wanderer’ erroneously, ascribed as crystal like characteristics to the liquid. Each molecule is required to perform duel, mutually inconsistent rolls. It must function both as a fixed neighbour and as the wanderer within its own cell. Thus, not only the cell model incorporates the acknowledged deficiencies of the Einstein model for solids, but it also takes account of those features, which set a liquid apart from a solid. These short comings of the cell model have been stressed by Hildebrand [1, 2].

In 1936, Eyring [46] used the idea of hole theory to initiate the first structure that would make possible the calculations of various physical quantities. He progressed from a hole structure to a ‘fluidized, cellular model’. He considered the vacancies to be smeared out, fleeting and fluidized as a result of the conflict between the tendency to cell formation and the rapid motion of molecules as they jump into the holes and distort the cell. By determining the energy needed for a molecule to occupy a vacancy, it is possible to arrive at an evaluation of the physical properties and to relate these properties to the molecular behaviour of the liquid. In the cell theory a single molecule is considered to be entrapped in each cell, which consists of 8-12 symmetrically, arranged molecules. The number of molecules around the entrapped one, in a cell is called the coordination number. The cohesion between molecules may be described in terms of
the potential energy and it is believed that the attractive potential varies inversely with the sixth power of distance of separation. Eyring postulates that the potential field is uniform within the cell and that a molecule therein may be considered to have the freedom of motion of ideal gas molecules. The space available for the movement of the entrapped molecule is called the free volume. This is not the same as the entire cell volume because the enclosed molecule can move only until it touches a cell molecule and this leaves regions, which cannot be occupied.

**E. Cell theory of Lennard-Jones and Devonshire:**

By computing the mean intermolecular energy for a set of molecules in perfect array, each being assigned to the center of its cell, the cell model prescribes a dependence on the volume, which is too great. This error can be seen to be an inevitable consequence of the order implied by this model and would follow for any acceptable representation of the intermolecular energy for a pair of molecules. That, the energy (E) and volume (V) relationship according to the cell model is at variance with experiment, has been abundantly shown \[2, 47\]. The intermolecular energy is usually discussed on the basis of the familiar Lennard-Jones potential \[2\] operating between molecular centers. Even in comparatively simple polyatomic molecules e.g. CH\(_4\) or CCl\(_4\), the acentric distribution of polarizable electrons necessitate fairly drastic modifications of this potential. Kihara \[48\], Hamann-Lambert \[49\] and Pitzer \[50\] have offered modified intermolecular potential for poly atomic (globular) molecules, especially those approximating spherical symmetry in form. Pitzer replaces each molecule with a smooth distribution of interacting elements (electrons), these being distributed uniformly either on the surface of a spherical core or throughout the volume of the core. In either case Lennard-Jones interaction is ascribed to each pair of elements, one from the distribution for each of two neighboring molecules and the total interaction is obtained by integrating over the receptive cores. The form of the potential is modified considerably by acentricity irrespective of which of the two models is used. Both the attractive and the repulsive terms are rendered more steeply dependent on the distance between molecular centers \[49, 50\], but to a degree, which is highly dependent on the particular molecule.

An extension of considerations which suggests itself as basis for treating the intermolecular energy in liquids consists of integrating the interactions of elements of the core of one molecule with the elements of all surrounding molecules, these later being treated as a
continuum, occupying the space outside the cavity reserved for the molecule in question. The result obtained departs markedly from the form of intermolecular energy according to the theory Lennard-Jones and Devonshire [10] which covers dense gases, critical phenomenon and liquids. They attempted first to evaluate the thermodynamic functions for a single component fluid in terms of intermolecular energy parameter. They used a free volume or cell model. For a ratio of core to cavity diameters greater than 1/5, the energy is approximately proportional to the density; it depends also on a simple function of the cavity diameter. In as much as the form of the potential depends on parameters peculiar to the molecular species, it does not lend itself to reduction to a parametric expression such as is required to sustain a law of corresponding states [10]. Limitations [51] of the corresponding states scheme advanced by Prigogine [9] are probably related to considerations of this nature. Proceeding along the same lines Lennard-Jones and Devonshire developed their mathematical cell theory, which provided a semi quantitative picture of liquids.

1.3.3 Modifications to above theories:-

Interest in the thermodynamic properties of binary liquid mixtures extended over most of the 19th century. Binary liquid mixtures are often used as solvents for chemical equilibria and for media in which to carry out chemical reactions. Binary liquid mixtures can be broadly classified into simple mixtures and associated mixtures. Simple mixtures are defined as those in which the nominal components are identical with the actual species in the pure liquids as well as in the mixtures. The associated mixtures are defined as those in which there is an evidence for the association of at least one of the components either with each other (self association) or with those of other components. It is possible to approach the description of such mixtures in terms of the properties of the components in a formal thermodynamic manner or with respect to the molecular interactions, such as dipole interactions, hydrogen bonding and coordinative bond formation, etc. Different theories which describes thermodynamics of binary liquid mixtures are based on either the radial distribution function or on the choice of some suitable physical model. Theories of perturbation type have been extended to the liquid mixtures from the problems of pure liquids where it showed its successful applications.

Prigogine and Garikian [52] extended the above model to the liquid mixtures. Random mixing of components was their main assumption that can be used if the molecules have similar
sizes. Prigogine and Bellemans [53] developed a two fluid version of the cell model. They got the results that while $V^E$ was negative for mixtures of molecules of same size but they found large positive $V^E$ of solutions with molecules having small difference in their molecular size. Longuet Higgins [54] gave a new approach with his theory of conformal solutions, which is based on the principle of corresponding states as developed by Pitzer. He used a simple perturbation approach to show that the properties of mixture could be obtained from the knowledge of intermolecular forces and thermodynamic properties of the pure components. Recently, Rowlinson [45, 55-56] worked towards reformulations of average rules for van der Waal’s mixtures and calculated values are found in much better agreement with the experiment from their approach even when one fluid theory is applied. One more recent independent effort is the perturbation theory of Baker and Henderson [57]. In this approach, the attractive part of intermolecular potential is treated as perturbation on hard sphere potential.

A more successful approach is due to Flory who also makes the use of certain features of cell theory and assumes an empirical equation for the dependence of energy on volume. Flory [58] have explored the application of a comparatively simple partition function suitable for liquids comprising chain molecules to homologues of the normal paraffin hydrocarbon series, H-(CH$_2$)$_n$-H with $n > 5$. A coherent correlation of the properties of the pure hydrocarbons has been achieved which, as it involves relationships expressed in algebraic form, is much to be preferred over the various corresponding states schemes which have been propounded [9, 51]. Flory has developed a statistical mechanical theory for predicting the excess functions of binary mixtures from the equation of state, properties of pure liquids along with adjustable parameters. This theory was developed originally for nonpolar liquids only; however, the use of adjustable parameters makes it applicable to components whose molecules interact in a specific manner. This is the only theory that can be applied to mixtures of realistic interest in which the component molecules may differ considerably in size and shape.

The partition function has been adapted to mixtures of straight-chain hydrocarbon [58]. Thermodynamic properties of these mixtures are thus related to parameter obtained from equation of state characteristics of the pure component hydrocarbons. The peculiar patterns of the excess chemical potentials and the excess enthalpies for these systems are well explained by the theory. Especially striking is the excellent agreement between calculated and observed chemical potentials for a variety of systems at different temperatures with arbitrary choice of a
single parameter for all. The previous formulations [58, 59] were addressed specifically to chain molecules and to mixtures of unrelated type. One of the merits of the theory is its adaptability to mixtures of molecules differing in size and shape. Calculations performed to date encourage the expectation that it may be broadly applicable to mixtures of homopolar molecule [60]. Patterson and Delamas [61] combined both Prigogine and Flory theories and presented a general. Unified theory from which one is able to identify various contributions such as free volume, interaction, internal pressure, etc. in the excess thermodynamic quantities.

Recently, the thermodynamic properties of associated mixtures using association model and Flory equation of state contribution were described by Benson and Treszeznowicz [62], Heintz [63, 64]. The thermodynamic properties were expressed as the sum of chemical terms described by an associated model and a physical contribution given by the Flory equation of state theory. This model is known as extended real associated solution (ERAS) model.

1.4 Types of Intermolecular Forces:

The mobility of liquids shows that their molecules like those of gases are free to move but the limited volume of a liquid shows that the molecules must exert forces on one another those being probably the resultant of attractive and repulsive short range forces. The mean free path of liquid molecules if it exists must be much shorter than that of gas molecules. The forces existing between different molecules are called intermolecular forces and are different in degree and kind from the forces that hold the atom together. Intermolecular forces have been classified into four categories [65],

A. Gravitational force,
B. Electromagnetic force
C. Strong nuclear force
D. Weak nuclear force

Since the gravitational force is of extremely long range and as the molecular dimensions are of the order $5 \times 10^{-1}$ nm, the gravitational potential energy is much less [65] than the intermolecular forces. Therefore, intermolecular forces must have an electromagnetic origin and must be due to charged particles (electrons and protons) that make up an atom or molecule. The strong nuclear forces are responsible for binding the neutrons and protons inside the nucleus and
are significant [65] over a distance of $10^{-4}$ nm. On the other hand, weak nuclear forces involve short range repulsive and long range attractive forces.

The short range repulsive forces [65] arise when molecules approach each other sufficiently close enough together to cause their electron clouds to overlap so that Pauli’s exclusion principle prohibits some electrons from occupying the overlap region thereby producing a nodal plane in this region. The nuclei are thus incompletely shielded from each other and consequently repel each other. Short range forces are usually repulsive but this is not always the case of closed shells. If it were so, chemical combinations would have been impossible. Further even among physical interactions there are two forces, which are attractive rather than repulsive, one is the hydrogen bond and other is the Mulliken charge transfer complexes. The long range attractive components [65] of intermolecular forces are significant when the overlapping of electron clouds of the approaching molecules is small. The various contributions to the long range forces are due to,

A. Electrostatic contribution

B. Induction contribution

C. Dispersion contribution

The electrostatic contribution to the intermolecular energy results from the interactions between charges, dipole moments; quadruple moments etc. in the molecule and are attractive in nature.

The inductive contribution [65] to the potential energy arises when a charged particle interacts with a neutral molecule. The electric field arising from the permanent moments of one molecule will induce moments in the neighboring neutral molecule and interaction between the permanent and induced moments will leads to attraction between the two. This is induction contribution to long range forces. The induction contribution can be large for interacting ions or molecules, with large dipole moments, but it is small for nearly spherical molecule like CH$_4$ and SF$_6$, because they have low order moments. It will be zero for inert gas atoms since they have no moments of any order. The induction contributions to the potential energy are attractive in nature and are not pair additive.

The dispersion contribution to the intermolecular potential energy is present in all molecular interactions known as London dispersion forces. Fritz London [66] gave these forces a theoretical explanation. According to Rowlinson [45], the dispersion forces are also additive and
are usually the most important negative term in the potential. Very little is known about the dependence of these forces on the orientation of non-spherical molecule.

1.5 Specific Interactions:

Specific interactions arises mainly due to,
A. Charge transfer interaction
B. Polar nature of components
C. Hydrogen bond formation
D. A difference in the positive and the negative character of the components leading to the formation of molecular complexes.

It has been proposed [67] that, all molecular species necessary have ionic structure of the type B^+A^- and that the low ionization potential of B and high electron affinity of A favors the formation of stable complex. But Brackmann [68] has attributed molecular complex formation to quantum mechanical resonance between a no bond structure and structures having a bond between two species A and B. None of these views are correct. Mulliken [69] has however developed a quantum mechanical theory, which assumes that charge transfer forces operate in more or less localized fashion in much the same way as in solids and they are of the same order of magnitude as dispersion forces. This theory has revised by Glyn [70] in 1952.

A. Charge Transfer Interactions:

Such type of interaction arises from the formation of charge transfer complexes between the acceptor molecule ‘a’ and donor molecule ‘d’. The intermolecular complexes are thus stabilized by a net transfer from ‘d’ to ‘a’. Excited states of such complexes often have as a main term; an excited state of ‘d’ type charge transfer complex formation can be discussed in case of benzene and iodine. Benzene is a sacrificial donor i.e. the electrons are donated from a bonding molecular orbital. Iodine is a sacrificial acceptor. Thus on entering into charge transfer complex the bond length of I_2 is expected to increase, indicating weaker I-I bond. Although both benzene and iodine are individually in less stable states in the charge transfer complex, there is always a
net gain of stability in the charge transfer complex as a whole. Intervalent donors and acceptors can also be present where a lone pair is donated or accepted e.g. $\text{NH}_3$ (donor) or $\text{SnCl}_4$ (acceptor). A wide variety of phenomenon [71] from ion pairing to even covalent compound formation can also be treated under their formalism. These types of interactions may exist between both like and unlike molecules. However, these interactions are usually weaker for like molecules. These forces may often share with dispersion forces in accounting van der Waal’s cohesive forces between molecules especially in systems containing more than one component. The charge transfer forces may often be of the same order as dispersion forces but the former predominance in solution and other systems in which molecules of different kinds are present together. Dispersion forces predominate where interactions between the like molecules occur. The dispersion forces of attraction tends to be maximum in those orientations that bring maximum polarizibilities to play, while the orientational properties of charge transfer forces are governed by considerations of quantum mechanical symmetry of molecular wave function.

B. Contact Charge Transfer Interactions:-

These types of interactions have been explained by Orgel and Mulliken [72]. The contact charge transfer absorption can occur whenever the donor and acceptor molecules are in contact. According to Mulliken the absorption bands corresponding to intermolecular charge transfer transitions should occur when donor-acceptor complex is formed and applied equally well to the pairs of molecules when in contact or when sufficiently close to each other. It does not depend upon the ability of charge transfer forces that overcome exchange between the components but on repulsion, the existence of nonzero overlap integral between donor and acceptor orbital.

C. Hydrogen Bond Interactions:-

In the systems where the intermolecular energy is exceptionally large, the hydrogen bond is the most important constituent of the liquid state. Hydrogen bond interactions are important in number of cases, configuration of polymers especially coiled polymers, folded polymers or coiled coil polymer, globular particles depends on hydrogen bonds. It plays a major role in solvent solute interactions in several cases. Generally, hydrogen bond formation [73] is believed
to involve three types of interactions viz. dipole-dipole, charge transfer and $\pi$-electron interactions as shown below,

$$U_{\text{H-bond}} = U_{\text{dipole-dipole}} + U_{\text{charge transfer}} + U_{\pi \text{-electron interactions}}$$

$U_{\text{charge transfer}}$ accounts for the donor-acceptor interactions, dipole moments, x-ray, neutron diffraction and infra-red spectral studies have been employed to study hydrogen bonding, proton magnetic resonance studies in relatively non interacting solvents, have also provided a powerful tool to study these interactions.

1.6 The Characteristics and Industrial Importance of Solvents and Solutes under Study:

Attempts have been made to probe the liquid structure through evaluation of density, viscosity and ultrasonic velocity data. Literature survey reveals that such type of study has been carried out for several liquid-liquid systems over the entire range of composition but at a limited range of temperature. We have thus undertaken the thermodynamic study of binary liquid-liquid systems containing many polar and non-polar liquids to investigate the molecular interactions.

Alcohols are a class of compounds with polar character. The dipole-dipole type van der Wall’s forces are present. In addition to dipole-dipole forces alcohols are hydrogen bonded and thus involve strong intermolecular interactions. Alcohols are protic and have relatively high dielectric constants and are self associated with hydrogen bonding. Degree of association in them decreases with increasing carbon chain length; from hexanol to dodecanol. Alcohols serve as simple example of biologically and industrially important amphiphilic materials.

Alkanes are an important series of homologous, non-polar solvent. They have often used in study of solute dynamic because their physicochemical properties as a function of chain length are well-known. They are also employed in a large of chemical processes.

1-Hexanol is slightly soluble in water, but miscible with ether and ethanol. It is used in the perfume industry1-hexanol is believed to be a component of the odour of freshly mown grass. Alarm pheromones emitted by the Koschevnikov gland of honey bees contain 1-hexanol.

1-Heptanol is a clear colorless liquid that is very slightly soluble in water, but miscible with ether and ethanol. Heptanol is commonly used in cardiac electrophysiology experiments to
block gap junctions and increase axial resistance between myocytes. Increasing axial resistance will decrease conduction velocity and increase the heart's susceptibility to reentrant excitation and sustained arrhythmias. 1-Heptanol has a pleasant smell and is used in cosmetics for its fragrance.

1-Octanol occurs naturally in the form of esters in some essential oils. The primary use of octanol is in the manufacture of various esters (both synthetic and naturally occurring), such as octyl acetate, which are used in perfumery and flavors. Other uses include experimental medical applications utilizing octanol to control essential Tremor and other types of involuntary neurological tremors.

1-Octanol and water are immiscible. The distribution of a compound between water and octanol is used to calculate the partition coefficient 'P' of that molecule (often expressed as its logarithm to the base 10, log P). Water/octanol partitioning is a relatively good approximation of the partitioning between the cytosol and lipid membranes of living systems.

1-Decanol is a straight chain fatty alcohol and a colorless viscous liquid that is insoluble in water and has a strong odour. Decanol is used in the manufacture of plasticizers, lubricants, surfactants and solvents.

Dodecanol, also known by its IUPAC name 1-dodecanol or dodecan-1-ol and by its trivial name dodecyl alcohol and lauryl alcohol, is a fatty alcohol. Dodecanol is a colorless, water insoluble solid of melting point 24 °C and boiling point 259 °C. It has a floral odour. It can be obtained from palm kernel or coconut oil fatty acids and methyl esters by reduction. Dodecanol is used to make surfactants, lubricating oils and pharmaceuticals. In cosmetics, dodecanol is used as an emollient. It is also used to form a detergent called as sodium lauryl sulphate. This can be used in soft, hard water as well as in acidic solutions. It is also used in synthesis of mercaptant which finds applications in rubber processing and as an intermediate for various chemical derivatives. Highly refined graded 1-dodecanol used in tuberose violet and rose perfumes.

2-Hexanol has a chiral center and can be resolved into enantiomers.

2-Octanol is nature colorless aromatic odour from the liquid fuel easily. It is used in polyethylene plastic used plasticizers, synthetic finishes, emulsifier’s toxicity of raw materials and low toxicity, slightly bactericidal. It has some unpleasant odour.
n-octane is used in organic syntheses, calibrations, and azeotropic distillations and is a common component of gasoline and other petroleum products. The engine fuel antiknocking properties of an isomer of n-octane (2,2,4-trimethylpentane or isooctane) are used as a comparative standard in the octane Rating System. Octane” is colloquially used as a short form of "octane rating" (named for the ability of octane’s branched-chain isomers, especially isooctane, to reduce engine knock), particularly in the expression "high octane." However, components of gasoline other than isomers of octane can also contribute to a high octane rating, while some isomers of octane can lower it, and n-octane itself has a negative octane rating.

n-decane is used as a solvent in organic synthesis, as a hydrocarbon standard in jet fuel research, in the manufacturing of paraffin products, in the rubber industry, in the paper-processing industry and in cleaning agents. n-decane is also found in several widely used petroleum distillates, such as Stoddard solvent and jet fuel. n-decane also represents 7.6-11% of white spirits, a mixture of saturated aliphatic and alicyclic, and alkyl aromatic C_{7}-C_{12} hydrocarbons. Stoddard solvent, a form of white spirit, contains 30-50% of linear and branched alkanes (ATSDR, 1995a; World Health Organization, 1996). The source used to prepare the jet fuel JP-4 apparently affects the amount of n-decane present. N-decane was found at percentages of 11.25 or 2.24 in JP-4 fuel when the source was shale or petroleum, respectively.

n-dodecane is used as a solvent, in organic synthesis, distillation chaser, in jet fuel research, standardized hydrocarbon, manufacture of paraffin products; rubber industry, paper processing industry, and as a component of gasoline may result in its release to the environment through various waste streams. In recent years, n-dodecane has garnered attention as a possible surrogate for kerosene-based fuels such as Jet-A, S-8, and other conventional aviation fuels. It is considered a second-generation fuel surrogate designed to emulate the laminar flame speed, largely supplanting n-decane, primarily due to its higher molecular mass and hydrogen to carbon ratio which better reflect the n-alkane content of jet fuels.

n-Tetradecane is both a naturally occurring and an anthropogenic compound which is used as a solvent and a synthetic intermediate.
1.7 Literature Survey:-

In recent years, enormous amount of work has been done in the investigation of thermodynamic properties of binary liquid-liquid systems. These properties have been used as means of interpreting nature of intermolecular interactions present amongst the mixing components. It is beyond the scope of this thesis to give an entire coverage of the published literature. The variations of molar volumes, viscosities and their excess values of binary and multi component liquid of protic, aprotic and associated liquids with changing mole fractions of one of the components have been investigated by some of the researchers. The trends of changes either positive or negative have been interpreted in terms of differences in size of molecules and strength of specific or non-specific interactions taking place between the components of the mixtures. In order to investigate depolymerisation of these alcohols in the in the presence of other non electrolyte molecules, extensive studies of ultrasonic, volumetric and viscometric measurements through binary liquid mixtures with alcohols as one of the components have been reported in the literature.

Viscosities were determined [74-75] for the binary mixtures dimethyl carbonate (DMC) + hexane, + heptane, + octane, and + cyclohexane and diethyl carbonate (DEC) + hexane, + heptane, + octane, and + cyclohexane at (293.15, 298.15, 303.15, and 313.15) K and dynamic viscosities for the binary mixtures diethyl carbonate + methanol, + ethanol, + 1-propanol, + 2-propanol, + 1-butanol, + 2-butanol, and + 1-pentanol at (293.15, 298.15, 303.15, and 313.15 K). From these experimental data, the interaction parameters (\(\text{CH}_3^{-}\text{OCOO}\)), (\(\text{CH}_2^{-}\text{OCOO}\)), and (\(\text{CH}_2\text{-CH}_2^{-}\text{OCOO}\)) were determined for their application in the UNIFAC–VISCO method, based on contribution groups, to predict the dynamic viscosities of the binary mixtures. Root-mean-square deviations are also gathered.

Speed of sound for the binary mixtures hexane + 1-chlorohexane, hexane + 1-iodohexane, and 1-chlorohexane + 1-iodohexane were examined as a function of composition and temperature along the saturation line between 293.15 K and 373.15 K by Bolotnikov and Neruchev [76]. Nonlinear behavior is observed with temperature and concentration.

Piñeiro et.al [77] investigated the density and speed of sound at 298.15 K for the ternary mixture methyl tert-butyl ether (MTBE) + 1-butanol + decane and for the binary 1-butanol +
decane. Experimental data were also used to test several empirical expressions for estimating ternary properties from experimental binary results.

Garabal et. al. [78] presented excess volume and excess enthalpy data for the ternary system (butyl butyrate + 1-octanol + dodecane) at the temperature 308.15 K and atmospheric pressure. The ternary system results were correlated using the Cibulka equation. Experimental values were compared with the predictions obtained by several group contribution models. The prediction of some empirical equation was also tested.

Densities, viscosities, and refractive indices of the binary mixtures of 1,4-dioxane + ethanediol, hexane, tributylamine, and triethylamine [79] and 1,4-dioxane + 1,2-dichlorobenzene, ethyl acetate, trichloroethylene, 2-chloroethanol, dimethyl acetamide, diethylmalonate, and 1-butanol [80] were measured at (298.15, 303.15, and 308.15) K, while the speed of sound data are measured at 298.15 K. These data was used to discuss the mixing behavior of the components.

The results of densities, viscosities, and refractive indices at (298.15, 303.15, and 308.15) K and speed of sound at 298.15 K in the binary mixtures of tri-n-butylamine with triethylamine, tetrahydrofuran, tetradeceane, tetrachloroethylene, pyridine, and trichloroethylene were observed by Nayak et.al [81]. These results have been discussed to study the type of mixing behavior between the mixing molecules.

Baragi and co-worker systematically calculated the experimental values of density, viscosity, and refractive index at $T = (298.15, 303.15, \text{and } 308.15)$ K while the speed of sound at $T = 298.15$ K in the binary mixtures of methylcyclohexane + n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, iso-octane [82] and methylcyclohexane + ethanol, propan1-ol, propan-2-ol, butan-1-ol, 2-methyl-1-propanol, 3-methyl-1-butanol [83] over the entire mole fraction range of the binary mixtures.

Density and refractive index at (298.15, 303.15 and 308.15) K for the binary liquid mixtures of acetylacetone with n-Nonane, n-Decane and n-Dodecane [84] were reported over the entire mole fraction range of binary liquid mixtures. Using these data, excess molar volume and deviation in molar refraction were calculated. The computed quantities were fitted to Redlich–Kister polynomial equation to derive the coefficients and estimate the standard deviation values. These quantities have been discussed in terms of intermolecular interactions.

Rahbari and co-worker [85] computed the densities and viscosities of solutions of poly(ethylene glycol) (PEG) in water and ethanol and solutions of poly(propylene glycol) (PPG)
in ethanol were measured at (293.2, 308.2, 313.2, 318.2, 328.2, 333.2, and 338.2) K. The number-average molecular weights for PEG were 200, 300, and 6000, and that for PPG was 2025. The density and viscosity data were fitted by second- and third-order polynomial equations, respectively, with respect to mass fraction of polymer at each temperature.

The surface tensions and liquid densities of mixtures of cyclohexane + heptane, cyclohexane + propanone, and toluene + propanone [86] were determined at a normal pressure of 1 bar over the temperature range from 287 K to 317 K. The high precision pendant drop apparatus allows accurate measurements of the interfacial tension in systems with liquid–liquid phase separation. The resulting data were parametrized using polynomial and Wegener expansion type equations.

In a series of papers H Iloukhani et al. systematically investigated the thermodynamic properties of N, N-dimethylformamide (DMF) with , + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol + 1-hexanol [87s], formamide with + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol, and + 1-hexanol [88], 1-heptanol +1,2-dichloroethane, +1,1,1-trichloroethane, +1,1,2,2-tetrachloroethane, +trichloroethylene, + tetrachloroethylene [89], pure toluene, cyclohexane, and n-hexane and those of their binary and ternary mixtures [90], methylcyclohexane with + n-pentane, + n-hexane, +n-heptane, +n-octane, +n-nonane, + n-decane [91-92], methylcyclohexane (MCH) with + ethanol, +2-propanol, +2-butanol, +2-pentanol, +2-hexanol, +2-heptanol, +2-octanol [93], toluene + n-pentane, + n-hexane, + n-heptane, +n-octane, + n-nonane, + n-decane [94], acetonitrile with +2-propanol, +2-butanol, +2-pentanol, +2-hexanol + 2-heptanol [95], acetophenone with + 2-propanol, +2-butanol, +2-pentanol, +2-hexanol, +2-heptanol [96], ternary systems of 1-butanol (1) + 2-butanol (2) + 1,2-butanediol (3) and the binary systems of 1-butanol (1) + 2-butanol (2), 1-butanol (1) + 1,2-butanediol (3), and 2-butanol (2) + 1,2-butanediol (3) [97] The experimental on the constituted binaries were analyzed to discuss the nature and strength of intermolecular interactions in these mixtures. The experimental results were used to test the applicability of the Prigogine–Flory–Patterson (PFP) theory. The results obtained for viscosity of binary mixtures were used to test the semi-empirical relations of Grunberg and Nissan, Tamura and Kurata, Hind et al., Katti and Chaudhri, McAllister, Heric, Kendall, and Monroe.

N. V. Sastry and co-worker [98-99] examined the densities and sound speeds of ternary mixtures of methyl acrylate (1)+1-propanol (2) or 1-butanol (2)+n-hexane (3), +n-heptane (3),
+cyclohexane (3), +benzene (3), and +toluene (3) and methyl methacrylate (MMA) + 1-alkanols (1-butanol, 1-pentanol, 1-heptanol) + aromatic organic solvents (benzene, toluene, p-xylene, and ethylbenzene) or + cyclohexane at T/K = (298.15 and 308.15).

V. Vyas [100-101] was interpreted the densities and speed of sound of three ternary liquid systems viz. Toluene + n-heptane + n-hexane (I), Cyclohexane + n-heptane + n-hexane (II) and n-hexane + n-heptane + n-decane (III), at 298.15 K. The theoretical predictions of excess molar volumes of these systems were carried out with the help of Flory's statistical theory. The theoretically computed values of excess molar volume were compared with the experimentally evaluated values. Computed values of isothermal compressibility were compared with Flory statistical theory.

Binary mixtures of tripropylamine [102] with n-hexane, n-octane, n-decane, n-dodecane, n-hexadecane, dimethylsulfoxide (DMSO) [103] with alkane, benzene, toluene, 1-alkanol, or 1-alkyne, methylobalanine [104] with methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol, dibutylether [105] with 1-heptanol, or 1-octanol, or 1-decanol were investigated by J.A. González et.al. The extended real associated solution (ERAS) model was applied to 1-alkanol + secondary amide [106] mixtures. González et.al were also investigated the 1-Alkanol + linear alkanolate [107] mixtures in the framework of the DISQUAC model. Simultaneous analysis of the experimental excess volumes and of the excess enthalpies reveal that free volume effects were important in systems formed by tripropylamine and longer alkanes, as well as in those involving tripropylamine or tributylamine and the shorter alkanes. The ERAS model is applied to 1-alkanol + N-methylobalanine, and 1-alkanol + diethylamine systems. The ERAS parameters confirm that the strongest interactions between unlike molecules are encountered in solutions with methanol.

A.Ali et.al presented the densities, and viscosities, for pure N,N-dimethylacetamide (DMA) [108], 1-hexanol, 1-heptanol and their 18 binary mixtures with DMA as a common component, densities and ultrasonic speeds in binary mixtures of tetrahydrofuran (THF)[109] with alkanols (1-hexanol, 1-octanol and 1-decanol), acetonitrile [110] with alkanols (1-hexanol, 1-octanol and 1-decanol) and densities, \( \rho \), ultrasonic speeds, \( u \) and viscosities, \( \eta \) of pure benzyl alcohol, 1-propanol, 2-propanol [111] over the whole composition range at various temperatures.
Viscosities, densities and speed of sound for 2-propanol [112] and 2-butanol [113] with octane, decane, dodecane over the whole composition range at several temperatures $T= (293.15, 298.15, 303.15)$ K were computed by B. González and co-workers.

S. C. Bhatia et al in a series of papers measured densities, viscosities for three ternary mixtures of squalane [114] with (hexane+benzene), (cyclohexane+benzene) and (hexane + cyclohexane), refractive indices [115], viscosities [116] of octan-1-ol with chloroform, 1,2-dichloroethane (DCE), 1,1,2,2-tetrachloroethane (TCE), densities, ultrasonic velocities of decan-1-ol [117] with 1,2-dichloroethene, 1,2-dibromoethane, and 1,1,2,2-tetrachloroethene, densities, speeds of sound, refractive indices of binary mixtures of decan-1-ol [118] with 2-methylphenol (o-cresol), 3-methylphenol (m-cresol), 4-methylphenol (p-cresol), and methyl phenyl ether (anisole). T. viscosities $\eta$, densities $\rho$, speeds of sound $u$, refractive indices $nD$ of 1-decanol [119] with o-xylene, m-xylene, p-xylene, ethylbenzene and mesitylene, densities $\rho$, speeds of sound $u$, viscosities $\eta$, refractive indices $nD$ of octan-2-ol [120] with benzene, chlorobenzene and bromobenzene, densities, $\rho$, viscosities, $\eta$, speeds of sound, $u$, refractive indices, $nD$ of 1-decanol [121] with o-chlorotoluene, m-chlorotoluene, and p-chlorotoluene, densities, $\rho$, viscosities, $\eta$, speeds of sound, $u$, refractive indices, $nD$, of binary liquid mixtures of 2-octanol [122] with 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene and densities, $\rho$, speeds of sound, $u$, of 1-nonanol [123] with o-xylene, m-xylene, p-xylene, ethylbenzene and mesitylene. The calculated excess and deviation functions have been fitted to the Redlich–Kister polynomial equations. Refractive indices were compared with those predicted by several mixing rules: Lorentz–Lorenz, Gladstone–Dale, Arago–Biot, Wiener, Heller, Laplace and Eyringman. The viscosity data were correlated using Kendall–Monroe, Grunberg–Nissan, Tamura–Kurata, Hind–Mclaughlin Ubbelohde, Katti–Chaudhary viscosity models and McAllister's three body interaction models at different temperatures. The experimental ultrasonic velocities were analyzed in terms of the ideal mixture relations of Nomoto and Van Dael, Jacobson’s free length, Schaaff’s collision factor, Flory’s statistical and Prigogine–Flory–Patterson theories and thermo acoustical parameters. The results were discussed in terms of interactions between the components of liquid mixtures, and the effects of size and shape of the components on excess properties.
Romano et al. [124] interpreted the densities and kinematic viscosities for the dimethyl carbonate (DMC) + (ethanol, 1-propanol, 1-pentanol, 1-octanol) binary systems at 288.15, 293.15, 303.15 and 313.15 K.

R.Mehra et al determined density and refractive index for binary mixtures of hexadecane and heptadecane [125] with 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol at 298.15, 308.15 and 318.15K. A comparative study of Lorentz-Lorenz,Weiner and Heller and Gladstone and Dale relation for predicting the refractive index of a liquid were determined for eight binary mixtures. Also excess parameters like excess acoustic impedance (\(Z_E^E\)), excess internal pressure (\(\pi_i^E\)) and excess enthalpy (\(H_E^E\)) were calculated from densities (\(\rho\)), sound speed (\(u\)), and viscosities (\(\eta\)) of a binary mixture of n-heptane+ 1-dodecanol [126] and diethyamine +1-decanol [127] at (293, 303, and 313) K over the entire range of compositions were computed by R.Mehra et al. Different theoretical models of sound speed are also applied to experimental sound speed to find the best fit theory for the system under investigation.

A. Tourino et al. reported experimental values of speeds of sound, densities and refractive indices on mixing of the binary mixtures n-hexane + (n-heptane, n-octane, n-nonane, n-decane, n-undecane, or n-dodecane)[128] and refractive indices of the ternary mixtures chlorobenzene + n-hexane + (n-nonane or n-decane) [129] were done at 298.15 K. Different estimation methods were applied, qualitative agreement between the experimental and theoretical values both in magnitude and sign being obtained.

The excess molar volumes \(V_{m}^E\) for binary liquid mixtures containing dipropylene glycol monomethyl ether or dipropylene glycol monobutyl ether[130] and methanol, 1-propanol, 1-pentanol and 1-heptanol and n-alkanol (methanol, ethanol, and 1-propanol)+ 1-methoxy-2-propanol, 1-ethoxy-2-propanol, 1-propyoxy-2-propanol, 1-butoxy-2-propanol, or 1-tert-butoxy-2-propanol [131] were calculated by A.Pal et.al. Also viscosities (\(\eta\)) in binary liquid mixtures of n-alkoxypropanols [132] + methanol, ethanol, or 1-propanol, densities, \(\rho\) and the speeds of sound, \(u\), for \{2-(2-hexyloxyethoxy)ethanol (C\textsubscript{6}E\textsubscript{2}) [133] + methanol, +1-propanol, +1-pentanol, and +1-heptanol and densities, \(\rho\), ultrasonic speeds, \(u\), and viscosities, \(\eta\), were computed over the whole composition range for the binary mixtures of dipropylene glycol dimethyl ether (DPGDME) [134] with ethanol, 1-propanol, 1-pentanol, and 1-heptanol were repted by A.Pal and R. Gaba. The experimental viscosity data was correlated by the methods of Grunberg–Nissan, Hind, Tamura–Kurata, Chaudhry, Auslaender, Heric, and with McAllister
correlations. The variation of these properties with composition and temperature of the mixtures were discussed in terms of molecular interactions.

Ortega et al measured the $H_m^E$ and $V_m^E$ for a set of 30 binary mixtures composed of five alkyl ethanoates (methyl to pentyl) [135] with six odd n-alkanes (C7 to C17), a set of 30 binary mixtures comprised of five alkyl propanoates (methyl to pentyl) [136] with six odd alkanes (heptane to heptadecane) and binary mixtures alkylbenzene + alkanes or + alkylethanoates [137]. To these binary systems some group contribution models were applied. A modified version of the UNIFAC model gives satisfactory results for enthalpies.

Tojo and co-worker [138-139] calculated the densities and excess molar enthalpies of the binary mixtures dimethyl carbonate with alkanes from C$_6$ to C$_{10}$ at several temperatures, and dynamic viscosities the binary mixtures of 2-pentanol with n-alkanes (n-hexane, n-octane, and n-decane) were measured over the entire composition range at 298.15 and 308.15 K. Correlations of the activity coefficients and reduced excess Gibbs energy using Wilson, NRTL, and UNIQUAC equations were good for all the binary mixtures. The best predictive results were yielded by ASOG for the binary dimethyl carbonate with nonane and by UNIFAC for dimethyl carbonate with decane. The variations of these excess parameters with composition were discussed from the viewpoint of intermolecular interactions in these mixtures.

Salgado et al [140] examined the densities and speeds of sound for {1,5-dichloropentane or 1,6-dichlorohexane} + dodecane} in the temperature interval (278.15 to 328.15) K. Some comments related to the influence of the well-known effects of {polar + long alkyl chain linear alkane} on excess properties were included.

Densities, refractive indices, and speeds of sound at 298.15 K and isobaric vapor–liquid equilibria (VLE) data at 101.3 kPa were reported for the binary mixtures containing ethyl acetate [141] + 1-pentanol and ethanol + 2-methyl-1-propanol by Resa et al. VLE experimental data were tested for thermodynamic consistency by means of a modified Dechema test and were demonstrated to be consistent.

Wen-Lu Weng reported the densities and viscosities for the binary mixtures of n-butylamine [142] with 2-hexanol, 3-hexanol, 2-methyl-1-pentanol, 2-methyl-2-pentanol, and 4-methyl-2-pentanol at 303.15 K, 313.15 K, and 323.15 K. McAllister’s three-body and four-body interaction models were also used to correlate the kinematic viscosities.

27
Densities and viscosities for the dimethyl carbonate (DMC) with + (hexane, heptane, chlorobenzene) [143], + (toluene, methanol, and 2-propanol) [144] and (1-propanol, 1-butanol, and 1-pentanol) [145] were determined by C. Yang et al. Density and viscosity measurements were used to compute the excess molar volumes, \( V^E \), and viscosity deviations, \( \Delta \eta \). The excess molar volumes, \( V^E \), and viscosity deviations, \( \Delta \eta \), have been fitted to Redlich–Kister equation.

J. Troncoso et al. [146] computed the densities and speeds of sound in the temperature interval (278.15 to 318.15) K and heat capacities per unit volume from (283.15 to 318.15) K for the dodecane + 1-butanol and + 2-butanol systems.. Results were critically compared with literature data of systems containing these butanol isomers. Differences between both systems were ascribed to the different association ability of the two alcohols.

Excess molar volumes \( V^E \) measured for the (1-propanol + 1-octene), (1-butanol + 1-octene), (1-octanol + 1-octene), and (1-decanol + 1-decene) [147] and 1-hexanol with the homologous \( \text{C}_6, \text{C}_7, \text{C}_8, \text{C}_{10} \) 1-alkenes [148] systems were reported by Treszczanowicz and co-worker. In the first series of mixtures the \( A^E_\rho \) values change from positive over the whole concentration range in the systems formed by 1-propanol and 1-butanol, to positive-negative for longer chain alkanols, the positive values occurring in the alkene-rich region. In second series of mixtures, the \( V^E \) values vary as a function of mole fraction from positive–negative “sigmoid” shaped curves exhibiting a very small positive lobe in the dilute alkanol region for the shortest chain 1-alkene to positive values over the whole concentration range for the longer chain 1-alkene.

New experimental data for \( V^E \) and \( \Delta K_s \) for binary mixtures of m-xylene [149] with 1-propanol, 1-butanol and 1-pentanol were reported at 303.15 K. \( \Delta K_s \) values exhibit an inversion in sign in all the binary mixtures of m-xylene with 1-alkanols. The experimental sound velocity data have been analysed in terms of free length theory (FLT) and Collision factor theory (CFT). The experimental results were discussed in terms of intermolecular interactions between unlike molecules.

Saheh et al. reported densities, \( \rho \), of the systems m-xylene [150] + 1-propanol, + 2-propanol, + 1-butanol and + 2-methyl-2-propanol from 303.15 to 323.15 K with an interval of 5 K. For the systems, m-xylene + 1-propanol and m-xylene + 1-butanol, sigmoid type of curves was observed, but for the systems, m-xylene + 2-propanol and m-xylene + 2-methyl-2-propanol, positive was observed for the whole range of composition.
Density $\rho$, viscosity $\eta$, and refractive index $nD$, values of \{anisole + hexane, or heptane, or octane, or nonane, or decane, or dodecane\} [151] binary mixtures over the entire range of mole fraction at temperatures (293.15, 298.15, and 303.15) K, were investigated at atmospheric pressure. The viscosity data were correlated with equations of Grunberg and Nissan, and McAllister. The refractive indices data were used to calculate the specific refractivity $R12$, and also correlated with Lorentz–Lorenz equation. While the excess molar volumes of \{anisole + hexane\} are negative, and \{anisole + heptane\} are sigmoidal S-shaped, the remaining binary mixtures are positive.

M. Gepert, et al [152] investigated the asymmetric and symmetric Flory equations describing the excess molar enthalpy, $H^E$, for 13 systems divided into four groups ((a) hexane + heptane or octane or dodecane or hexadecane; (b) dodecane + hexane or 2-methylpentane or 3-methylpentane or 2,2-dimethylbutane or 2,3-dimethylbutane; (c) hexane + cyclohexane or benzene, cyclohexane + benzene; (d) cyclohexane + cis-decalin or trans-decalin) were used. On the basis of this, the interaction parameters, $XAB$, were obtained, and next, they were used for the prediction of excess molar volumes, $V^E$, for all the mixtures under test. The Prigogine–Flory–Patterson contributions to $H^E$ and $V^E$ were established. The results obtained were compared with those found in the literature that have been calculated by the Flory’s model in the traditional way.

The densities and kinematic viscosities of the quaternary subsystems of the regular quinary [153] system toluene (1) + octane (2) + ethylbenzene (3) + tetradecane (4) + hexadecane (5) were measured over the entire composition range at 308.15 K and 313.15 K. The viscosity data reported herein were used to test the predictive capabilities of the predictive version of the McAllister model, which was reported by Nhaesi and Asfour and the Grunberg–Nissan equation.

Gascon et al [154] presented the viscosities of the ternary mixture (hexane + 1,3-dioxolane + 2-butanol) at atmospheric pressure at 298.15 and 313.15 K. To correlate the experimental data of the ternary system, extended Nissan–Grunberg and McAllister equations was used. The group contribution method proposed by Wu was used to predict the viscosity of the mixture.

Faria and coworker [155] interpreted the experimental values of the density and dynamic viscosity, obtained at 101 kPa, for binary systems containing 1-octanol, 1-nonanol, 1-decanol,
and 1-undecanol over the entire range of mole fractions and at the following temperatures: (283.15, 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K.

Molar excess volumes, $V^E$, and molar excess enthalpies, $H^E$, of 1,4-dioxane (i) + propan-1-ol, or + propan-2-ol, or + butan-1-ol, or + butan-2-ol (j) binary mixtures were measured dilatometrically and calorimetrically by V.K. Sharma and Satish Kumar [156] at 308.15 K. The analysis of $V^E$ data by the graph approach has revealed that while propan-1-ol and propan-2-ol exist as associated molecular entities; 1,4-dioxane and butan-2-ol exist as monomers and these (i + j) mixtures contain a 1:1 molecular complex. The IR spectral studies of the (i + j) mixture lend additional support to the nature and extent of interaction for the proposed molecular entity in the mixtures.

The densities and speeds of sound in the pentan-1-ol + nonan-1-ol, pentan-1-ol + dekan-1-ol, propan-1-ol + hexan-1-ol, and propan-2-ol + hexan-1-ol binary systems were measured by G.Monika and S.Barbara [157] at 298.15 K. The excess molar volumes interpreted on the basis of results of the Symmetrical Extended Real Associated Solution Model (S-ERAS).

G.Bhoj, and R.Mahendra [158] presented the viscosity deviation ($\Delta \eta$), the excess molar volume ($V^E$) and the ultrasonic speed ($u$) from viscosity ($\eta$) and density ($\rho$) measurements of binary liquid mixtures of 1,2-dimethoxyethane with methanol, ethanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol or octan-1-ol over the entire range of composition at 298.15 K.

Density, viscosity and refractive indices measurements for binary mixtures of (1,1,2,2-tetramethylbenzene + 1-pentanol, or + 1-hexanol, or + 1-heptanol, or + 1-octanol, or + 1-decanol) at $T = (293.15$ and $303.15$) K, were conducted by M.N.M. Al-Hayan, et.al [159-160]. The viscosity data were correlated with the model of Grunberg and Nissan, and McAllister four-body model. The excess molar volumes of (1,1,2,2-tetramethylbenzene + 1-pentanol, or + 1-hexanol, or + 1-heptanol, or + 1-octanol) had a sigmoidal shape and the values varied from negative to positive with the increase in the molar fraction of 1,1,2,2-tetramethylbenzene. The remaining binary mixture of (1,1,2,2-tetramethylbenzene + 1-decanol) was positive over the entire composition range. In addition, the refractive indices were compared with calculated values using mixing rules proposed by several authors, and a very good agreement was obtained.

Excess molar volumes $V^E_{\text{mix}}$ and change in refractive indices $\Delta \text{mixn}$ of the binary mixtures of (toluene + methanol), (toluene + ethanol), (toluene + 1-propanol), (toluene + iodoethane), (methanol + iodoethane), (ethanol + iodoethane), (1-propanol + iodoethane), and the ternary
mixtures of (toluene + methanol + iodoethane), (toluene + ethanol + iodoethane), and (toluene + 1-propanol + iodoethane) were measured with vibrating-tube densimeters and an Abbe-type refractometer at the temperature 298.15 K and the pressure 101 kPa by Z. Atik, [161]. The experimental $V_{m}^{E}$ and $\Delta_{mixn}$ values of the ternary systems were predicted by empirical equations using binary solution data.

Taghi et al. [162] performed to measure the density and sound velocity of the systems {poly(propylene glycol) + methanol, +ethanol, +1-propanol, 2-propanol and +1-butanol} over the whole range of composition. From these measurements, values of the excess molar volume ($V_{m}^{ex}$) and excess molar isentropic compression, $K_{s,n}^{ex}$, equal to $-(\partial V_{m}^{ex}/\partial P)_{n}$, were calculated. Expressions for $V_{m}^{ex}$ and $K_{s,n}^{ex}$ of polymer solutions were obtained for the model of Flory–Huggins and the polymer non-random two liquid (NRTL) model. These expressions were used to fit the experimental $V_{m}^{ex}$ and $K_{s,n}^{ex}$ data of the investigated systems.

New experimental data were reported for the thermodynamic investigation of the intermolecular and intra-molecular hydrogen bonding in 2-ethoxyethanol + hydrocarbons [163]. The excess enthalpies of the mixtures of 2-ethoxyethanol + n-hexane, or cyclohexane, or benzene, or n-octane at three temperatures (298.15, 308.15, and 318.15 K) were measured. The calorimetric measurements were combined with dielectric ones and the derived Kirkwood factor was used to interpret the physicochemical behavior of our systems.

M.Hasan et al. [164-168] systematically computed the thermodynamic properties of chloroform with + propan-1-ol, + butan-1-ol, + pentan-1-ol, + hexan-1-ol, methylbenzene with + hexan-2-ol, + heptan-2-ol, + octan-2-ol, + heptan-1-ol, + octan-1-ol+ decan-1-ol and propyl acetate with butan-1-ol ,+ pentan-1-ol over the entire range of composition at (303.15 and 313.15) K and at atmospheric pressure. McAllister’s three-body interaction model was used to correlate the kinematic viscosities of binary liquid mixtures with mole fraction .The Jouyban–Acree model was used to correlate the experimental values of density, viscosity and ultrasonic velocity.

Speed of sound and densities of ternary mixtures 2-propanol+ diethyl ether + n-hexane and the binary mixtures of 2-propanol + diethyl ether and 2-propanol + n-hexane were measured at 298.15 K by G.Savaroglu and E.Aral [169]. Also speed of sound of binary and ternary
mixtures were compared with calculated values from FLT, CFT, Nomato’s relation and junjie’s relation. Isentropic compressibility $k_s$, excess isentropic compressibility $\kappa_s^E$, excess molar volume $V_E$, viscosity deviations $\Delta\eta$, and speed of sound deviations $\Delta u$ for \{chlorobenzene + 1-hexanol or 1-heptanol, or 1-octanol, or 1-nonanol, or 1-decanol\} binary mixtures at temperatures ranging from (298.15 to 313.15) K and at atmospheric pressure were derived from experimental viscosity $\eta$, density $\rho$, and speed of sound $u$ data by Adel S. Al-Jimaz et.al [170]. Speeds of sound data was analyzed in term of Schaaffs’ collision factor theory and Jacobson’s intermolecular free length theory of solutions.

Densities ($\rho$) and volumetric heat capacities ($Cp/V$) were measured at 298.15 K over the whole mole fraction range for the binary mixtures \{tetrahydropyran + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol\}. From experimental data, the excess molar isobaric heat capacities ($C_P^E$) were calculated. Excess molar volumes ($V_E^E$) were reported [171] for the systems containing 1-propanol, 1-butanol, 1-pentanol, and 1-decanol. In order to assess and compare the different degrees of hetero-association in these mixtures, the corresponding negative enthalpic contributions at equimolar fraction (Hint) were calculated semiquantitatively by using the apolar homomorph concept.

G.P. Dubey et.al [171-178] in a series of papers systematically reported the densities, viscosities, and speeds of sound for the binary mixtures of \{(CH$_3$)$_2$CHCH$_2$OH\} with n-hexane, n-octane and n-decane, (butan-1-ol with hexane, or octane, or decane), (1-octanol with n-hexane, n-octane, and n-decane), (1-hexanol with n-hexane, n-octane and n-decane), (1-octanol with hexadecane and squalane), (ethylene glycol monomethyl ether with 1-hexanol, 1-octanol, and 1-decanol), (diethylene glycol monomethyl ether with 1-hexanol, 1-octanol, and 1-decanol) and (ethylenediamine with 1-hexanol, 1-octanol, and 1-decanol). The values of $V_E^E$, $\Delta\eta$, $\Delta u$ and $\Delta\kappa s$ were fitted to the Redlich–Kister polynomial equation and were used to discuss the presence of significant interactions between alcohols and alkane molecules. The viscosity data was correlated by Grunberg and Nissan, Tamura–Kurata, and Hind correlation equations. The values of $V_{E_m}^E$ have been analyzed using Prigogine–Flory–Patterson (PFP) theory. Furthermore, the theoretical values of speed of sound ($u$) and isentropic compressibility ($k_s$) have also been estimated using the Prigogine–Flory–Patterson (PFP) theory with the van der Waals (vdW) potential energy model and the results have been compared with experimental values.
The speeds of sound in heptan-1-ol, octan-1-ol, and nonan-1-ol [179] at pressures up to 101 MPa and in decan-1-ol at pressures up to 76 MPa were measured within the temperature range of (293 to 318) K. The effect of pressure and temperature on the isothermal compressibility, isobaric thermal expansion, isobaric heat capacity, and internal pressure was discussed.

Qi. Tian and H. Liu [180] investigated densities and viscosities of the binary mixtures of the tributyl phosphate + hexane and tributyl phosphate + dodecane systems experimentally determined at different temperatures and atmospheric pressure, over the entire composition range. A discussion on these quantities in terms of molecular interactions is reported.

C.-Ta Yeh and Chein-Hsiun Tu [181] determined the densities, viscosities, refractive indexes, and surface tensions for three binary systems (2-propanol + benzyl alcohol, 2-propanol + 2-phenylethanol, and benzyl alcohol + 2-phenylethanol) at T = (298.15, 308.15, and 318.15) K over the whole composition range at atmospheric pressure. The calculated quantities of \( V_m^E, \Delta \eta, \Delta nD, \) and \( \Delta \sigma \) were fitted to the Redlich–Kister equation to estimate the binary interaction parameters.

Densities, \( \rho \), and volumetric heat capacities, \( C_p/V \), were measured at 298.15 K over the whole mole fraction range for the binary mixtures \{tetrahydrofuran [182] + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, or + 1-decanol\}.

Bhuiyana et al. [183] computed the densities and viscosities for dimethylsulfoxide (DMSO) with methanol, ethanol, 1-propanol, and 2-propanol as a function of mole fraction at T = (303.15, 308.15, 313.15, 318.15, and 323.15) K and atmospheric pressure. Excess molar volumes \( (V_m^E) \) are negative for (DMSO + methanol, + ethanol) systems throughout the whole range of composition. The (DMSO + 1-propanol) system shows both positive and negative excess molar volumes and (DMSO + 2-propanol) shows positive excess molar volume, hardly any negative value is observed in alcohol rich-region.

Excess molar volumes \( V_m^E \) [184] for (1,3-dimethylimidazolidin-2-one + an alkan-1-ol from methanol to octan-1-ol) were determined from density measurements at T = (283.15, 298.15, and 313.15) K over the whole composition range. From the temperature dependence of \( V_m^E(x_1 = 0.5) \) values for the equimolar mixtures of 1,3-dimethylimidazolidin-2-one with an
alkan-1-ol, the coefficient \((\partial V^E_{\infty}(\tau = 0.5)/\overline{\partial I})_p\) was evaluated for each mixture and its dependence of \(v\) was also studied.

Experimental data on excess volumes, speed of sounds and viscosities at 303.15 K measured for the binary systems of methyl tert-butyl ether [185] with hexane, heptane, octane, 2,2,4-trimethylpentane, cyclohexane and benzene over the whole range of composition. The sound speeds were evaluated theoretically on the basis of Jacobson free length theory, Schaffs collision factor theory and Nomoto theory. Viscosity data was also analysed theoretically on the basis of corresponding states approach, Grunberg–Nissan treatment and Mc Allister model.

The sound speeds and densities of the 1-propanol + diethyl ether + 1-octanol ternary mixture and constituent binary mixtures, 1-propanol + diethyl ether, 1-propanol + 1-octanol, and diethyl ether + 1-octanol, were computed by G. Savaroglu [186]. By using the free length theory (FLT), Schaff’s collision factor theory (CFT), Nomoto’s relation (NR), Van Deal’s ideal mixing relation (IMR), and Junjie’s relation (JR), sound-speed values of the investigated mixtures were calculated.

Kinematic viscosities for the binary mixtures of diisopropylether, dibutylether or methyl ter-butyl ether [187] with 3-methylpentane, hexane or heptane were determined at 283.15 K, 298.15 K, and 313.15 K. The experimental values have been correlated by the McAllister equation. Using these results, new UNIFAC-VISCO parameters, Oether–CH2 and Oether–CH3, have been calculated.

A.Carrasco and co-worker [188] investigated the densities and viscosities of the ternary mixtures 2-methyl-1-propanol (or 2-methyl-2-propanol) + n-hexane + 1-chlorobutane at atmospheric pressure and 298.15 K. Excess molar volumes and viscosity deviations for the ternary mixtures were calculated from experimental data and fitted by the Cibulkka equation.

F. Yang et.al [189] interpreted the densities and viscosities of the binary mixtures of JP-10 + n-octane and JP-10 + n-decane were determined from \(T = 293.15\) K to \(T = 313.15\) K at atmospheric pressure, over the entire composition range. Conclusions were qualitatively discussed in terms of molecular interactions. The viscosity data have been correlated with several semiempirical equations, and the Grunberg–Nissan equation gives satisfactory results.

H. Kumar et.al [190-194] presented the densities, Viscosities and Speeds of sound for binary mixtures of (cyclopentane with 1-propanol, 1-pentanol, and 1-heptanol), (cyclopentane with 2-methyl-1-propanol, 3-methyl-1-butanol and 2-methyl-2-butanol) and (diethylene glycol

34
monomethyl ether and triethylene glycol monomethyl ether with 3-methyl-1-butanol and 2-methyl-2-butanol) over the whole composition range. From these densities, excess molar volumes were calculated. All the experimental excess molar volumes were fitted to the Redlich–Kister equation. Different correlations were used to correlate the viscosity data. Furthermore, a number of approximations used to obtain deviation in viscosities have been analysed. Theoretical values of the speeds of sound were estimated using theories and empirical relations.

D. R. Caudwell and co-worker [195] reported the viscosity and density of five pure hydrocarbon liquids (octane, decane, 1,3-dimethylbenzene, 1,2,3,4-tetrahydronaphthalene, and 1-methylnaphthalene) at temperatures between (298.15 and 473.15) K and at pressures ranging from 0.1 MPa to approximately 200 MPa. The densities were correlated by means of a modified Tait equation, while the viscosities were correlated both with the theory of Dymond and Assael and in terms of an empirical function of temperature and pressure.

N. M. Hussein and Abdul-Fattah A. Asfour [196] examined the densities and viscosities of ten binary mixtures of 1-propanol, 1-pentanol, 1-heptanol, 1-nonanol, and 1-undecanol were measured over the entire composition range at temperatures of (293.15 and 298.15) K. The experimental data were employed to test the predictive capabilities of viscosity models including the generalized McAllister three-body interaction model, the GC-UNIMOD model, the generalized corresponding states principle (GCSP) model, and the Allan and Teja correlation. The analysis of the models shows that the generalized McAllister three-body interaction model provided the best predictions for the 1-alcohol mixtures investigated.

U. Domańska et al [196] investigated the density and viscosity for binary mixtures containing 1-decanol and three fragrance raw materials based on cyclohexane: cyclohexyl carboxylic acid (CCA), or cyclohexyl acetate (CA), or 2-cyclohexyl ethyl acetate (2CEA) in wide range of temperatures from 300 to 340 K and atmospheric pressure. The temperature dependence of density and viscosity for these systems can be described by an empirical second-order polynomial and by the Vogel–Fulcher–Tamman equation, respectively. Comparison of the results for three binary systems elucidates the influence of the substituent at the cyclohexane ring on their physical and volumetric properties.

N.Y. Ghael et al [197] presented the excess molar volumes ($V_m^E$), viscosity deviations ($Δ\eta$), and excess Gibbs energies of activation ($ΔG^*E$) of viscous flow investigated from densities
and viscosities measurements for three ternary mixtures 1-butanol + ethyl ethanoate + cyclohexane, 1-pentanol + ethyl ethanoate + cyclohexane, and 1-octanol + ethyl ethanoate + cyclohexane and four binaries at 303.15 K. The empirical equations due to Redlich–Kister, Kohler, Rastogi et al., Jacob–Fitzner, Tsao–Smith, Lark et al., Heric–Brewer, and Singh et al., were employed to correlate $V_{m}^{E}$, $\Delta \eta$, and $\Delta G^{E}$ of ternary mixtures with their corresponding binary parameters. The results were discussed in terms of the molecular interactions between the components of the mixture. Further, the ERAS model was examined to estimate $V_{m}^{E}$ for the binary and ternary mixtures and the results are compared with the experimental data.

A. Bhattacharjee and M. Nath Roy [198] computed the densities and viscosities of eight ternary mixtures of tetrahydrofuran, dimethylsulphoxide and monoalkanols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, amyl alcohol and i-amyl alcohol The results were discussed in terms of molecular packing, specific interactions and nature of liquid mixtures. The systems studied here exhibit very strong cross association through hydrogen bonding.

Densities and speeds of sound for binary mixtures of 2-ethyl-1-hexanol with 1-pentanol, 1-heptanol, or 1-nonanol [199] were measured over the entire composition range at the temperature 298.15 K. From experimental data, the excess molar volumes and excess molar isentropic compressibilities were calculated.

M. V. Rathnam et.al [200] calculated the density, viscosity, and speed of sound data of (methyl benzoate + cyclohexane), (methyl benzoate + n-hexane), (methyl benzoate + heptane), and (methyl benzoate + octane) were determined at $T = (303.15, 308.15, \text{and} 313.15)$ K. The $V_{m}^{E}$ were fitted to the Redlich–Kister polynomial equation. The measured viscosities were correlated with Auslander and McAllister’s four-body interaction models.

M. G. Bravo-Sánchez et.al [201] presented the densities and viscosities for n-butanol, 2-butanol, isobutanol, tert-butanol, and for binary mixtures with n-butanol as a common component at temperatures between (303.15 and 343.15) K over the entire composition range. The Grunberg–Nissan equation used to correlate the experimental kinematic viscosities of the binary liquid mixtures.

Surface tensions of the ternary mixtures containing an isomer of butanol (1-butanol, 2-butanol, 2-methyl-1-propanol, or 2-methyl-2-propanol) + n-hexane + 1-chlorobutane were measured [202] at atmospheric pressure and 298.15 K. From these experimental data, surface
tension deviations were calculated and fitted by the Cibulka’s equation. Experimental results were compared to the predictions obtained by a group contribution method; furthermore, using this method, the excess surface molar compositions of n-hexane in the ternary mixtures have been also estimated.

Densities of binary mixtures of 1,3-diethyl propanedioate with methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, 2-methyl-propan-1-ol, and pentan-1-ol were measured at temperatures of (288.15, 298.15, 313.15, and 328.15) K using an Anton Paar model DMA 5000 M oscillating densimeter by Y. Wang and W. Yan [203]. Excess molar volumes were calculated from these densities. The experimental data were fitted to the Redlich–Kister equation.

O. Ciocirlan et al [204] examined the densities and refractive indices of mixing of DMSO + 1-hexanol, T = 298.15 and 323.15 K and ambient pressure. The experimental results have been used to test the applicability of the Prigogine–Flory–Patterson (PFP) theory. The agreement between theoretical and experimental results was satisfactory for DMSO + 1-hexanol systems.

Densities and viscosities of binary mixtures of {methyl tert-butyl ether (MTBE) + methanol, or +ethanol, or +1-propanol, or +2-propanol, or +1-butanol, or +1-pentanol, or +1-hexanol} were determined as a function of composition at several temperatures and atmospheric pressure. The temperatures studied were (293.15, 298.15, 303.15, and 308.15) K by H.E. Hoga, and R.B. Töres [205]. The experimental results have been used to calculate the excess molar volume ($V_m^E$) and viscosity deviation ($\Delta \eta$). Both $V_m^E$ and $\Delta \eta$ values were negative over the entire range of mole fraction for all temperatures and systems studied. Moreover, the $V_m^E$ values have been used to test the applicability of the Extended Real Associated Solution (ERAS) model.

Jingru Liu et al [206] reported the densities and the viscosities of benzene-1,3-diol in different solvents of water, ethanol, propan-1-ol and butan-1-ol under atmospheric pressure and at T = (293.15 to 333.15) K. The experimental data of densities and viscosities of benzene-1,3-diol solutions were fitted respectively using Gonzáles equation and the extended Jones-Dole equation.

Densities were measured for the binary mixtures of methanol, ethanol, 1-propanol, 1-butanol with nitromethane at temperatures (293.15, 298.15, 303.15 and 308.15) K and for 1-pentanol with nitromethane at temperatures (303.15 and 308.15) K and atmospheric pressure [207]. Excess molar volumes of mixtures studied were consistently described by the ERAS
Also The Peng–Robinson–Stryjek–Vera (PRSV) equation of state was applied, in combination with simple mixing rules.

Zorębski and E. Dec [208] measured speeds of sound for binary mixtures of 1,2-ethanediol with 1-butanol, 1-hexanol, or 1-octanol by means of pulse-echo-overlap method over the entire composition range and at temperatures ranging from 293.15 to 313.15 K. In two cases (mixtures with 1-butanol or 1-hexanol) the negative values of the excess molar compressibility’s over the whole composition and temperature range were observed. In the third case (mixtures with 1-octanol) the s-shaped dependence is observed. The rigidity in mixtures under test increases from 1-octanol to 1-butanol.

Refractive indices, and densities, ρ, at 298.15 K were measured by F. Martins and co-worker [209], for the ternary mixture methanol (MeOH)/propan-1-ol (1-PrOH)/acetonitrile (MeCN) for a total of 22 mole fractions, along with 18 mole fractions of each of the corresponding binary mixtures, methanol/propan-1-ol, propan-1-ol/acetonitrile and methanol/acetonitrile.. A thermodynamic approach to excess refractive indices, recently proposed by other authors, was applied for the first time to ternary liquid mixtures. Structural effects were identified and interpreted both in the binary and ternary systems.

Experimental values of densities (ρ), and speeds of sound (u) at T = 298.15 K in the binary mixtures of n-octane, n-decane, n-dodecane and n-tetradecane with octan-2-ol were presented by A.R.Mahajan et.al [210]. Comparisons of theoretical ultrasonic speeds, calculated by using collision factor theory (CFT), free length theory (FLT) and Nomoto's empirical equation (NOM) and the results were compared with experimental values.

M.L.L. Paredes et.al [211] presented the densities, sound velocities, and refractive indexes for this binary system of tetralin (1, 2, 3, 4-tetrahydronaphthalene), an aromatic cyclic molecule, and n-decane along with the properties of the pure components at T = (293.15, 303.15, 313.15, 323.15, 333.15, and 343.15) K. Several sound velocity mixing rules were tested, and the best result was for Nomoto mixing rule. Pure component densities and sound velocities were correlated with Prigogine–Flory–Patterson (PFP) model. This model correlated experimental densities very well and correlated reasonably well sound velocities and thermal expansion coefficient.

M. S. AlTuwaim et.al [212-214]. examined the densities ρ, refractive indices nD and speeds of sound u for binary mixtures of N,N-dimethylformamide (DMF) with 1-pentanol, 1-
hexanol, 1-heptanol and 1-octanol over the entire range of mole fraction were measured at T = (298.15, 303.15, 308.15). The speeds of sound were analysed in terms of Schaaff's collision factor theory (CFT), Jacobson’s intermolecular free length theory of solutions (FLT), Nomoto relation (NM) and Van Dea ideal mixture relation (IMR). The Lorentz–Lorenz (L–L), Dale–Gladstone (D–G), Eykman (Eyk) and Arago–Biot (A–B) mixing rules were used to predict the refractive indices of the binary mixtures. Viscosity measurements of the binary systems were correlated with Grunberg and Nissan, the three-body and four-body McAllister expressions.

M. V. Rathnam and co-worker [215] calculated the densities, viscosities and speeds of sound of binary mixtures of ethyl benzoate with cyclohexane, n-hexane, heptane and octane. From these experimental values, excess molar volume (V_E), deviation in viscosity (Δη) and deviation in isentropic compressibility (ΔK_s) were calculated. The viscosities of binary mixtures were calculated theoretically from the pure component data by using various empirical and semi-empirical relations and the results compared with the experimental findings.

Second-order thermodynamic derivative properties, such as isobaric thermal molar expansions, isothermal and adiabatic molar compressibilities, and isochoric molar heat capacities of (ethanol, decan-1-ol, 2-methyl-2-butanol) + heptane mixtures at pressures up to 100 MPa and in the temperature range from 293.15 K to 318.15 K were derived from experimental speed-of-sound u(T,p), density ρ(T,p = 0.1 MPa), and isobaric heat-capacity C_p (T, p = 0.1 MPa) data using appropriate thermodynamic relations [216]. The deviations from ideality for the mixtures under test were explained in terms of the self-association of alcohols in solution which produces a strong departure from random mixing, the change in the non-specific interactions during mixing, and the packing effects.

Densities (ρ) and speed of sound (u) of the binary mixtures of tributyl phosphate (TBP) [217] and alkanes (n-hexane, cyclohexane, and n-heptane) were measured at temperatures from (298.15 to 323.15) K over the entire composition range and at atmosphere pressure. The positive or negative deviations shown by these quantities were interpreted in terms of intermolecular interactions and structure of components.

The ultrasonic speed, u of binary mixtures of methyl acrylate with 1-butanol, 1-hexanol, 1-octanol, and 1-decanol, including those of pure liquids, over the entire composition range was measured by A. K. Nain [218] at temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 318.15) K The variations of derived parameters indicate the presence of specific interactions.
between methyl acrylate and 1-alkanol molecules, which follows the order: 1-butanol > 1-hexanol > 1-octanol > 1-decanol. The values of excess parameters are found dependent on the length of alkyl chain of 1-alkanol molecules.

Values of the density for binary mixtures of propane-1,2-diol [219] with methanol, propan-1-ol, hexan-1-ol, octan-1-ol, or nonan-1-ol were measured over the entire composition range and within the temperature range from (293.15 to 318.15) K by means of a vibrating tube densimeter. The negative values of the excess molar volumes over the entire composition and temperature ranges were observed in the case of methanol and propan-1-ol. In the cases of hexan-1-ol, octan-1-ol, and nonan-1-ol, positive values of the excess molar volumes over the entire composition and temperature ranges were observed.

Blanco, A. Gayol [220] presented the analysis of different thermodynamic properties (refractive indices, excess molar volumes and ultrasonic velocity) and the temperature dependence of the ternary mixture ethanol + n-hexane + n-nonane at the range 288.15–323.15 K and atmospheric pressure. The derived properties were computed from experimental data and were fitted to the Cibulka equation.

The density and viscosity of n-heptane were simultaneously measured over the temperature range from 298 K to 470 K and at pressures up to 245 MPa using the hydrostatic weighing and falling-body techniques, respectively. The measured densities were used to develop a Tait-type equation of state for liquid n-heptane [221]. Theoretically based Arrhenius–Andrade and Vogel–Tamman–Fulcher type equations with pressure-dependent coefficients were used to describe the temperature and pressure dependences of the measured viscosities for liquid n-heptane. The measured values of the density and viscosity were compared in detail with reported data and with the values calculated from a reference EOS and correlation models for the viscosity.

M. Almasi [222] presented the densities and viscosities of binary mixtures of ethylmethylketone with 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and 2-heptanol, as a function of composition range at temperatures of 298.15 K, 303.15 K, 308.15 K, 313.15 K. For mixtures of ethylmethylketone with used 2-alkanols, \( V_{m}^{E} \) was positive and \( \Delta \eta \) was negative over the entire range of mole fraction. The ERAS-model has been applied for describing the binary excess molar volumes and also Peng–Robinson–Stryjek–Vera (PRSV) equation of state (EOS) were used to predict the binary excess molar volumes and viscosities.
M.M. Papari, et.al [223] computed densities and speeds of sound for three binary mixtures 2-phenylethanol with 1-butanol, 2-butanol and 2-methyl-1-butanol at six temperatures from 298.15 K to 323.15 K at 5 K. The results have been used to discuss the nature and strength of intermolecular interactions in these mixtures. The values of excess volumes and molar isentropic compressibilities over the entire composition range were negative. Finally the predictive power of a statistically-based equation of state for volumetric properties of the studied mixtures of alcohols was examined.

1.8 Objectives of present study: -

1. To study the effects of molecular size, shape and molecular association of normal and branched alcohols on volumetric, viscometric and ultrasonic properties of binary liquid mixture.
2. To reveal the nature and extent of molecular interactions between the component molecules in these binary mixtures.
3. To, light on the physico-chemical behavior of liquid mixtures such as molecular association and dissociation as well as strength of interactions between the components.
4. To study the dependence of thermodynamic parameters on composition and temperature.
5. To investigate depolymerisation of alcohols in the presence of other non-electrolyte molecules extensive studies ultrasonic measurements.
6. To study the effect of increasing size of carbon chain length (as we move from hexan-1-ol to dodecane-1-ol and hexan-2-ol to octcan-2-ol) on intermolecular interactions between alcohols and hydrocarbons.
7. To co-relate the experimental data with the nature of interacting components of the mixtures and to stress the factors affecting the interactions.
8. To co-relate the viscosity data with the several empirical and semi-empirical equations.
9. To study suitability of the CFT, FLT, Nomato's relation and van-Dael-Vangeel ideal mixing relation, checked by comparing theoretical and experimental values of ultrasonic speed.
10. Application and analysis of excess molar volume speed of sound and viscosity data of binary mixtures of the Prigogine–Flory–Patterson (PFP) theory, Bloomfield and Dewan
model and Prigogine–Flory–Patterson (PFP) theory with the van der Waals (vdW) potential energy model.

11. To co-relate the density, viscosity and speed of sound data with Jouyban-Acree model.

1.9 Present Work:-

In mixtures of associating molecules, alcohols and non-associating molecules, the alkanes are of particular interest from a theoretical viewpoint of the models of the hydrogen bonded system. An alcohol molecule associates manly by building up linear chain. The extent of these associations depends on a specific way on the concentration of the liquid state and on the temperature. Systematic studies of the thermodynamic excess properties of alcohols and alkanes mixtures are important from the view point of understanding the molecular liquid structure and intermolecular interactions dominated by the self-association of alkanols molecules due to hydrogen bonding. Accurate knowledge of thermodynamic mixing properties of binary and ternary mixtures has great relevance in theoretical and applied areas of research. These data are needed for design processes in chemical, petrochemical and pharmaceutical industries. From above survey one can notice that there is lack of volumetric viscometric and ultrasonic data of hydrocarbon + higher alkanols system. Also no systematic study of intermolecular interactions of higher alkanols with hydrocarbons Therefore, we have planned to study exhaustively the kind of molecular interactions present amongst the following binary systems,

The binary liquid systems under investigation are represented in four sections as follows:


From the measured data of density (ρ), viscosity (η) and ultrasonic velocity (u); derived thermodynamic functions such as excess molar volumes (V\text{E}_m), deviations in viscosity (Δη), excess isentropic compressibility (K\text{E}_s), excess intermolecular free length (L\text{E}_f), excess specific acoustic impedance (Z\text{E}_f), excess available volume (V\text{E}_a), excess energy of activation of viscous flow (ΔG\text{E}_f) and excess internal pressure (π\text{int}_E) have been evaluated and their variation with temperature and concentration is discussed. All the excess derived thermodynamic properties of these parameters at 298.15K have been represented graphically for comparison purpose. Furthermore, the excess thermodynamic properties such as excess molar volume, deviation in viscosity and deviation isentropic compressibility have been fitted to Redlich-Kister polynomial equation to obtain the binary coefficients and standard percentage deviation at all the temperatures.

Several empirical and semi-empirical relations have been used to represent the dependence of viscosity on concentration of components in binary liquid mixtures and these are classified according to the number of adjustable parameters used to account for the deviation from some average. We will consider here some of the most commonly used semi-empirical models for analyzing viscosity of liquid mixtures based on one, two and three parameters. An attempt has been made to check the suitability of equations for experimental data fitted by taking into account the number of empirical adjustment coefficients. From experimental values of viscosity various interaction parameters have been evaluated along with their standard errors using semi-empirical equations such as GrunbergNissan, Hind, Choudhary-Katti and Tamura-Kurata which were single parameter equations; Heric-Bewer, McAllister three body model which were two parameter and McAllister four body model which was three parameter empirical equations. Heric and brewer accounted for molecular interactions by dividing the free energy of activation into two parts. One part accounts for the excess free energy of activation, while the other accounts for the ideal free energy of activation. Their discussion of the effect of molecular size on excess functions gives insight into solution non-ideality and molecular interactions.

Measured values of ultrasonic velocities were compared using different types of theories proposed by Nomoto, Van deal theory, free length theory and collision factor theory. These theories have been described and used to calculate the speed of sound in the present mixtures and compared with the experimental results.

The Jouyban-Acree model was introduced to correlate the physicochemical properties of
the solution in mixed solvents including the dielectric constants, viscosity solvatochromic parameter, and density, speed of sound and more recently molar volumes. The model uses the physicochemical properties of the mono-solvents as input data and a number of curve-fitting parameters representing the effects of solvent-solvent interactions in the solution. It is basically derived for representing the solvent effects on the solubility of non-polar solutes in nearly ideal binary solvent mixtures at isothermal conditions. Experimentally measured fundamental thermodynamic properties such as density, viscosity and ultrasonic velocity were correlated using Jouyban-Acree model.

The excess molar volume data have been analyzed by using Flory and Prigogine-Flory-Patterson theories (PEP Theory) at \( T = 298.15 \, \text{K} \). The theoretical values of the speed of sound, \( u \) and isentropic compressibility \( k_s \), for both the liquid components and the liquid mixtures have been estimated using the Van der Waals (VdW) potential energy model in the Prigogine–Flory–Patterson (PFP) theory. The comparison between experimental and theoretically calculated values of speed of sound and isentropic compressibility for the studied binary mixtures at \( T = 298.15 \, \text{K} \) has been graphically represented. The values of \( \Delta \ln \eta \) have also been analyzed using Bloomfield and Dewan model. The experimental and calculated quantities are used to study the nature of mixing behavior between the mixtures.
References

28. H. S. Green, ‘The Molecular Theory of Fluids’, (Amsterdam; North Holland Publishing
Company, (1952) Chapt.4.
29. J. H. van’t Hoff, Z Physic Chem.1 (1887) 481.
32. S. T. Young, Phil, Mang, 33(1882) 153.
34. T. Boublík, I. Nezbeda and H. Hlavaty, Statistical Thermodynamics of Simple Liquids and
Their Mixtures, Elsevier (1980).
52. I. Prigogine and S. Garikian, Physica, 16 (1950) 239.
1174.


