1.1 Introduction

We know that 75% area of earth covered by water and nearly 70% of human body is composed of this unique liquid. As considering this fact, study of properties of liquids and their structures are important. There are large numbers of liquids available, every liquid have unique properties which is decided by its compositions. The slightly change in composition and environmental conditions leads to changes in physical and chemical properties. There are different theories [1-4] and techniques developed for this purpose. The first systematic attempt in this direction was made by Young [5] by pooling large amount of data on the thermodynamic and mechanical properties of liquid mixtures.

The interaction of electrical energy with matter is determined by the electromagnetic properties of the material. On a macroscopic scale under steady state conditions, these properties are conventionally described by the permittivity and permeability of materials. A fundamental contribution to understand the dielectric behaviour was made by Peter Debye in 1912, who developed the theory of dielectric polarization, assuming the existence of permanent electric dipoles resulting from a space distribution of charges in molecules.

An investigation in the liquid state becomes a fascinating and challenging problem to both the theoreticians and experimentalists. The molecules in liquid can’t 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 practical of the study of liquid mixtures have often been divorced from the study of pure liquids.

1.2 Scope of Thermodynamic Properties

The study of thermodynamic properties of liquid-liquid systems 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 industries process. Therefore, it is apparent that knowledge of thermophysical properties such as density, refractive index, viscosity and related
parameters are useful for full understanding of the non-ideal behavior of mixtures, caused by molecular interactions and intermolecular force occurring when two or more components are mixed, particularly when polar components involved. In this respect, the evaluation and the prediction of these properties of solvent mixtures as functions of temperature and composition are of theoretical and practical importance [6,7].

Density of liquid mixtures and related volumetric properties such as excess molar volume are required for theoretical calculations as well as applications. For the practical purpose (tank design, pipe lines etc), the knowledge of volume of liquid mixture is important than the corresponding density value. The sign and magnitude of excess molar volume gives good estimate of strength of unlike interactions in binary mixtures. The refractive index, excess refractive index etc. are used to explain the nature of solute-solvent interactions. The refractive index along with density values of mixtures are used to test the accuracy of available refractive index mixing relationships in predicting binary refractive index data.

1.3 Scope of Dielectric Properties

From the point of view of electrical conduction, all naturally occurring materials can be divided into three basic groups: dielectric (insulator), semiconductor and conductor. The substance having free electrons to conduct current is known as conductor while substance do not possess free electrons (the electrons are tightly bound to the atom) to conduct current is called as an insulator or bad conductor. Those insulators whose behaviour gets modified under the influence of external electric field are called as dielectrics [8]. If this behaviour depends on direction of electric field, then dielectric is called anisotropic and behaviour independent on direction of electric field is known as isotropic dielectric. When a dielectric is placed in an electric field, electric charges do not flow through the material, as in a conductor, but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This creates an internal electric
field that partly compensates the external field inside the dielectric. If a dielectric is composed of weakly bonded molecules, then molecules not only become polarized but also reorient so that their symmetry axis aligns in the direction of the field.

The dielectric spectroscopy is the nice probe to access information about molecular structure, molecular interaction between components of solution, dynamics and kinematics of the solution. Hence, this technique has grown tremendously over the past few years and is now being widely employed in field of physics, chemistry, biochemistry, pharmaceutical, materials science and engineering. The measurement of dielectric properties has gained importance because it can be used for non destructive monitoring of specific properties of material undergoing physical or chemical changes [9]. The static permittivity is a central solvent property which determine and reflects the magnitude of solute-solvent interaction. It strongly depends on the composition of the solution, temperature and frequency of applied electric field [10]. One can understand the structural changes in liquid due to changes in amount of hydrogen bonding by using dielectric spectroscopy.

Dielectric relaxation study deals with ability of material to store electric energy in the form of polarization. If the system consisting of macroscopic charged particles and when this system is subjected to time dependent electric field, the particles will exhibit time delayed response termed as relaxation, if changes in applied field are fast compared to relaxation times of rearranging constituents. Applied electric energy causes change in redistribution in dielectric material, which will build up induced polarization.

Information of static dielectric constant of pharmaceutical solutions is also important because it is directly proportional to the solubility of a drug in the solvent which influences its rate of disassociation in the body [11]. The range of potential applications of dielectric spectroscopy is quite broad. Virtually any physical process changes leads to changes in dielectric and thermodynamic properties of samples [12].

Study of solute solvent interaction of polar-polar liquids through dielectric properties
According to charge distribution in molecules, molecules are classified into two types: (1) Polar molecule (2) Non-polar molecule. The molecule possesses a permanent electric dipole moment (large difference in electronegativity) which is known as a polar molecule. The molecule having zero dipole moment (zero difference in electronegativity) is known as a nonpolar molecule.

The magnitude of the dipole moment depends on size and symmetry of the molecule. The dipole moment, usually represented by the symbol $\mu$ and its order of magnitude is $10^{-18}$ e.s.u. The unit $10^{-18}$ e.s.u. is called a Debye and dipole moments are commonly measured in Debye (D). The molecules having a centre of symmetry such as Methane and Carbon tetrachloride are non-polar (having zero dipole moment) while molecules having no centre of symmetry are called polar. The dipole moment of the molecule of substance influences its permittivity (or dielectric constant) and studies of permittivity (in particular in temperature dependence) can be used to measure the dipole moment of the molecule.

When the dielectric material is under influence of an external electric field then the molecular charges inside the material are displaced, due to which new dipoles are formed. The newly formed or existing dipoles are oriented along the direction of the applied electric field. The total charge passing through unit area within the dielectric perpendicular to applied field is called polarization. There are three types of polarization: (i) Electronic polarization (ii) Atomic polarization and (iii) Orientation polarization.

(i) Electronic Polarization ($\alpha_e$): The electronic polarization occurs due to the displacement of electrons with respect to the atomic nucleons. This type of polarization is observed in all dielectrics.

(ii) Atomic Polarization ($\alpha_a$): The atomic polarization occurs due to the mutual displacement of atoms or group of atoms. It occurs at radio frequencies.

The electronic and atomic polarizations together known as distortion polarization ($\alpha_d$), because it is caused due to the displacement of charges in atom with respect to each other in the direction of applied external electric field. When there is redistribution of charges in response to applied field, it possesses dipole...
moment called induced dipole moment. The magnitude of induced dipole moments depends on the field strength and polarizability of the dielectric material. The induced dipole moments retain so long as the electric field is present. The induced dipole moments do not depend on the temperature of the dielectric material.

(iii) Orientation Polarization ($\alpha_o$): In absence of external electric field, permanent dipole moments are randomly orientated. When dielectric material subjected to external electric field, the molecular dipoles orient in the direction of the external electric field. Thus polarization occurs due to the rotation of permanent dipoles of dielectric material is known as orientation polarization. The time required to occur this polarization is in the order of $10^{-12}$ to $10^{-10}$ second which are corresponds to the period of microwave frequency region.

Thus, total polarization of dielectric material is

$$\alpha_t = \alpha_o + \alpha_e + \alpha_a$$

The material’s polarization does not respond instantaneously to an applied external electric field. The response must be always arising after the external applied field which can be represented by a phase difference and it depends on frequency of external electric field. For this reason permittivity is often treated as a complex (since complex numbers allow specification of magnitude and phase) function of the angular frequency ($\omega$) of the applied field. At low frequency the field changes slowly and enough to allow dipoles to reach to equilibrium state before the field has measurably changed. The response of dielectric under the influence of high frequency field is different from the static behavior [3, 4, 13, 14]. The frequency of the externally applied field is such that there is an observable lag to attain equilibrium state. This lag is commonly referred as relaxation, in general which can be defined as the lag in the response of a system to change in the force to which it is subjected [15]. Dielectric relaxation is directly proportional to the exponential decay of polarization with time when an externally applied field is removed. The relaxation time may be defined as the time in which this polarization is reduced to $1/e$ times of its original value, where ‘e’ being the...
natural logarithmic base. Under the influence of ac field, the polar molecules of a system rotate toward an equilibrium distribution in molecular orientation with a corresponding polarization [16]. When the polar molecules having very large in size and high viscosity medium subjected to the very high frequency of the alternating field, the rotational motion of the molecules is not sufficiently high for the attainment of equilibrium with the field. The dipole moments are not able to orient fast enough to keep alignment with the direction of applied electric field and the total polarizability of medium falls from $\alpha_i$ to $(\alpha_i - \alpha_0)$.

Thus fall in polarizability is related to decreases in permittivity. This is due to corresponding energy absorption take place by the sample. The energy absorption is referred to as dielectric relaxation, or dispersion. The frequency at which this fall occurs can vary from very low $10^{-1}$Hz and below for large hindered macromolecules to frequency up to $10^{12}$Hz for small molecules. In this region, $\alpha_e$ and $\alpha_a$ remain unchanged, since the dispersion due to the fall-off of the atomic polarization occurs at frequencies comparable with the natural frequencies of vibration of atoms in a molecule (i.e. infrared spectrum around $10^{14}$ Hz). The electronic polarization occurs at still higher frequencies corresponding to electronic transition between different energy levels in the atom (i.e. visible, UV, and X-ray). The frequencies at which electronic and atomic dispersions occur are determined by the internal properties of the molecules or atoms and hence have the form of resonance dispersion [17] because of discrete energy levels. On the other hand, the dipolar orientation process gives rise to relaxation who’s both the frequency and shape of the dielectric loss characteristic depends mainly on the immediate environment of the molecular dipole and the corresponding changes in permittivity are very different from that of the resonance dispersion. The rotational motions of molecules or molecular groups result in frequency dependent polarization in the radio frequency and microwave frequency region.

According to Maxwell’s theory of electromagnetic waves, the permittivity of material is equal to square of its refractive index measured at the same frequency. If refractive index is measured at frequency of the sodium of D lines,
this gives permittivity, by means of finding what proportion of the polarizability is still effective at this frequency. This will be approximately the electronic polarizability. In polar molecules [1], the difference between the static permittivity and permittivity at frequency of sodium D lines is mainly due to the permanent dipole moment or induced dipole moment.

1.4 Intermolecular Forces

The mobility of liquids show that their molecules are free to move as like gas molecules, but the restricted volume of a liquid shows that the molecules must exert forces on each other, 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 smaller than that of gas molecules.

All matter is held together by force. The forces of attraction which hold an individual molecule together (for example chemical bonds, the covalent bonds) are known as intramolecular force. The forces existing between different molecules are called intermolecular forces. Intermolecular forces are weaker forces compared to the intramolecular forces. For example, the covalent bond present within Hydrogen Chloride (HCl) molecule is much stronger than the forces present between the neighboring molecules.

Intermolecular forces are responsible for most of the physical and chemical properties of materials. The first attempt to explain intermolecular forces was made by Keesom (1912) based on the interaction between permanent dipoles. Debye in 1920 extended the dipole theory, he has taken into account the induction effect in which a permanent dipole induces a dipole moment in another molecule and a mutual attraction results. This interaction depends on the polarizability and dipole moment of the molecule. The cause of the attractive forces between neutral molecules is the dispersion interaction; the quantum mechanical treatment of this interaction was given by London in 1930. These different works furnished much very interesting information were based on the potential energies of the Lennard-Jones type, and were very often limited to isolated molecules.
This link gives an excellent introduction to the interactions between molecules. These forces are believed to exist between molecules when they are sufficiently close to each other. The different types of intermolecular forces are shown in table 1.1 with example.

Table 1.1: Different intermolecular forces with model and example

<table>
<thead>
<tr>
<th>Intermolecular forces</th>
<th>Model</th>
<th>Basis of attraction</th>
<th>Energy KJ/Mole</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-Dipole</td>
<td></td>
<td>Ion charge-Dipole charge</td>
<td>40-600</td>
<td>![Na+⋯O]</td>
</tr>
<tr>
<td>H-bond</td>
<td></td>
<td>Polar bond-H dipole charge, High electro negativity N, O, F</td>
<td>10-40</td>
<td>![H⋯H]</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td></td>
<td>Dipole charges</td>
<td>5-25</td>
<td>![Cl⋯Cl]</td>
</tr>
<tr>
<td>Ion-induced dipole</td>
<td></td>
<td>Ion charge-Polarizable e– clouds</td>
<td>3-15</td>
<td>![Ba2+⋯O₂]</td>
</tr>
<tr>
<td>Dipole-induced dipole</td>
<td></td>
<td>Dipole charge-Polarizable e– clouds</td>
<td>2-10</td>
<td>![H⋯Cl]</td>
</tr>
<tr>
<td>London dispersion</td>
<td></td>
<td>Polarizable e– clouds</td>
<td>0.05-40</td>
<td>![F⋯F]</td>
</tr>
</tbody>
</table>
1.4.1 Types of Intermolecular Forces

Some important intermolecular forces are discussed below.

1. Dipole-Dipole force

Dipole-dipole interactions are electrostatic interactions between permanent dipoles in molecules. The positive end of a one polar molecule will attract the negative end of the other molecule and cause them to be arranged in a specific arrangement. They are much weaker than ionic or covalent bonds and have a significant effect only when the molecules are close together. Polar molecules have a net attraction between them. For example HCl and chloroform (CHCl₃)

\[
\begin{align*}
\delta^+ & \quad \delta^- \\
H & \quad Cl & \quad H & \quad Cl
\end{align*}
\]

The molecules have dipolar groups within them, but have no overall dipole moment. This occurs, if there is symmetry within the molecule (e.g. tetrachloromethane), causing the dipoles to cancel each other.

2. Hydrogen bonding

Hydrogen is unique among the elements because it has a single electron. When this electron is hogged by another atom in a polar covalent bond, a significant fraction of the hydrogen nucleus becomes uncovered and the bare nucleus desperately seeks to be covered by electrons from other atoms.

A hydrogen bond is the attractive interaction between two closed shell species that arises from the link of the form A-H-B, where A and B are highly electronegative elements. Normally, hydrogen bonds only exist when atoms A and B are Nitrogen, Oxygen and Fluorine.

The hydrogen bond is often described as a strong electrostatic dipole-dipole interaction. It is directional, stronger than a Van der Waals interaction.
Intermolecular hydrogen bonding is responsible for the high boiling point of water (100 °C). It plays an important role in the structure of polymers, both synthetic and natural.

3. London dispersion force

The dispersion contribution to the intermolecular potential energy is present in all molecular interactions known as London dispersion forces (named after Fritz London who first suggested how they might arise)[18]. It is also known as quantum-induced instantaneous polarization or instantaneous dipole-induced dipole forces.

To understand London dispersion forces, think the presence of the electrons in a molecule as a constantly changing cloud. In a nonpolar molecule, the electrons are distributed equally over the molecule, but occasionally one side or the other will gain a small excess of electron density. When this situation occurs, then molecule has instantaneous dipole, one side of the molecule has a slightly positive charge and the other a slightly negative charge. When another molecule approaches the first, it can feel this dipole. The electrons around the second molecule can then rearrange so that there is a favorable interaction between the two molecules. These forces dominate in the interaction of non-polar molecules and also play a less significant role in Van der Waals forces than the molecules containing permanent dipoles or ionized molecules.

All molecules (including ions, polar molecules, and nonpolar molecules) have dispersion forces. In general, they are quite weak and their effects do not show up in molecules that are held together by stronger forces such as network covalent bonds or large permanent dipoles. Since the strength of dispersion forces depends on the electron cloud around the molecule being able to move.
4. **Dipole-induced dipole force or Debye forces**

The induced dipole forces appear from the induction (also known as polarization), which is the attractive interaction between a permanent multipole on one molecule with an induced multipole on another. This interaction is called Debye force after Peter J. W. Debye.

1.5 **Applications of Dielectric Study**

1.5.1 **Agriculture**

Dielectric properties of agricultural products are interested for several reasons. It is found that, the dielectric constant increases with increasing moisture content in the seeds and decreases with increasing frequency. At high moisture level and low frequency range the magnitude of variation in dielectric constant were large. It is used for rapid measurement of moisture content in grain and in considering potential dielectric heating applications. Dielectric properties data for grain, insects and fruit are presented that relate to applications for selective heating of insects in grain, potential maturity and quality sensing in fresh fruits and vegetables.

1.5.2 **Soil**

Dielectric constant of soil is an important parameter because the variation of dielectric constant depends on mineral composition of soil and soil moisture. Soil moisture can be an important factor for land managers to consider when making decisions concerning livestock grazing patterns, crop planting, irrigation scheduling and soil stability for machinery traffic.

1.5.3 **Pharmaceutical and Medicine**

Pharmaceutical solutions are important because the solubility of a drug in the solvent directly influences its rate of disassociation in the body, which in turn impacts bioavailability. Dielectric properties such as the dielectric constant of solutions have been used to study the solubility of cosolvent systems, reaction rates of pharmaceutical solutions and drug stability.

The interest of microwaves increased due to biological effects. The controlled dose of microwaves can be made useful for medical diagnosis, therapy
and human comfort. Physical therapy of microwave radiation has been found effective in curing inflammation, piles, and injury etc. There has been a surge of interest in the last few years in the use of microwave diathermy for effective cancer treatment. This is expected to burn away the damaged tissues so that the spread of cancer can be controlled.

1.5.4 Electrochemical supercapacitors

Recent advertisement in the electro-chemical capacitors have resulted in new type of capacitors known as ‘supercapacitors’ or ‘ultra-capacitors’. These have capacitance (energy capable of being stored) of several hundred farad (generally, the capacitance of normal capacitors is in the range of fractions of a farad). When a metal is brought in contact with a solid or liquid ionic conductor, a charge accumulation is achieved electrostatically on either side of the interface, leading to development of an electrical double layer, which is essentially a molecular dielectric. No charge transfer takes place across the interface and the current observed during this process is a displacement current due to the rearrangement of charges [19].

1.6 Literature Survey

There are many research groups working in dielectric field. To study dielectric properties of liquids, different groups used different developed method. Microwave research group of Physics department of Dr. Babasaheb Ambedkar Marathwada University, Aurangabad has developed experimental setup and computer programs required to study dielectric properties of pure liquids as well as binary mixtures using TDR method. We also develop TDR simulation software for analysis of experimental data. From last two decades our research group used TDR method to study molecular interactions between various functional groups in organic compounds and biological samples. The molecular interactions in aqueous solutions of associative compounds such as Ethylene Glycol [20], Hexamethylphosphameride [21], Dimethysulphoxide [22], tert-Butyl alcohol [23], Acetone and Tetrahydrofuran [24], N,N Dimethylformamide [25], N-Methylformamide [26], Primary alcohols [27-29] was reported earlier. Similarly
an aqueous solution of non-associative solute Acetonitrile was reported by Helambe et.al [30]. The solute solvent interactions between long chain polymeric structures in alcohols with nonpolar molecules such as Benzene and n-Octane [31] and non associative polar solutes such as Aniline [32,33], p-Flourophenylacetonitrile [34], n-Nitriles [35] was studied previously. The dielectric relaxation study of binary mixtures of primary alcohols and polar solutes such as Methyl acetate [36], Dimethylformamide [37], Dimethylsulphoxide [38], Tetrahydrofuran [39] and 2-Nitroacetophenone [40] was reported earlier. The binary mixture of Ethanol with one –OH group and Ethylene Glycol with two –OH group was reported by Puranik et.al [41]. The binary mixtures of biological samples such as Methanol-Algae [42], Honey-Water [43], Glucose-Water [44], Glycine and Valine-Water [45] were studied by our group. Pure biological samples such as Albumin and Yolk of avian egg [46] and Mammalian milk [47] were studied by Lokhande et.al using TDR technique. The dielectric relaxation study of electrolyte Ca(NO$_3$)$_2$-4H$_2$O in aqueous solution of Urea was reported by Mehrotra et.al [48]. The dielectric relaxation study of Chlorobenzene with Dimethylformamide and Dimethylchloride with Ethanol has been reported by Pawar et.al [49,50]. The dielectric relaxation study of Ethanol with Nitrobenzene and Nitrotoulene has been reported by Chaudhari et.al [51]. N,N-Dimethylacetamide with Ethanolamine and Formamide with N,N-Dimethylaminoethanol has been reported by Undre et.al [52-53]. Alkyl Methacrylate with alcohols has been reported by Sivagurunathan et.al [54-60]. Many other research workers in various fields carried out structural dynamics in different type of pure liquids and binary mixtures [61-76] by using different experimental techniques.

Buta Singh [77] has studied the relative permittivity of aliphatic ketones (2-Hexanone, 3-Hexanone, 3-Methyl2-Pentanone, 3-3Dimethyl-2-Butanone, 2-Pentanone, Heptanal and Cyclohexanone) in dilute solution of Cyclohexane, Decalin and 1,4–Dioxane at 10 GHz frequency. He has concluded that dipole reorientation occurs mainly by an intramolecular relaxation process in the ketones.
and Heptanal. Celiano et al. [78] studied the dielectric constant of mixtures Acetone with Methanol, Ethanol, 2-Propanol, 2-Methyl 2-Propanol and p-Dioxin at 25 °C. Crossley [79] reported the dielectric constant and dielectric loss for a number of aliphatic and aromatic ketones in Cyclohexane, n-Hexadecane, Decalin and Paraffin oil-Cyclohexane mixtures up to ten frequencies between 1 and 145 GHz at 25 °C. Dharne et al. [80-82] reported dielectric relaxation measurements of Allyl Chloride with Dimethylformamide and alcohol using the Time Domain Reflectometry. Prakash et al. [83] reported densities, viscosities and sound velocities of o-Chlorophenol with Acetone and Ethyl Methyl ketone systems at 25°C. Krchma et al. [84] reported dielectric constant of binary mixtures of Carbon Tetrachloride with Benzene, Toluene, Chloroform, Ethyl ether, Methyl Acetate, Ethyl Acetate, Acetone, Ethyl alcohol, iso-Amyl alcohol using electrical resonance method. Ghosh et al. [85] reported the dielectric relaxation and free energy of activation of pure ketones in ultra high frequency region. Jeyaraj et al. [86] reported the dielectric relaxation study of Allyl Bromide and Allyl ether in dilute solution of Benzene in the microwave frequency region at different temperature. Madhurima et al. [87] studied the steric hindrance of ketones (Acetone, 2-Butanone and 3-Pentanone) in dielectric relaxation of Methanol and ketone mixtures. Awwad et al. [88] reported the density, refractive index, permittivity and related properties for N-Formylmorpholine with Ethyl Acetate and Butanone systems at 298.15 K. Lomte et al. [89] studied the densities and viscosities of binary liquid mixtures of 2-Butanone with branched alcohols at different temperature.

Kinart et al. [90] reported the excess molar volume and viscosity deviations for 2-Methoxyethanol with Acetone mixtures. Peng and Chein Tu [91] studied densities and viscosities of Acetone, Diisopropyl ether, Ethanol and Methyl Ethyl ketone with a five-component hydrocarbon mixtures from 288.15 K to 308.15 K. Ouyang et al. [92] studied excess molar volume and surface tension of Xylene with Acetone or 2-Butanone at 298.15 K. He was found that excess molar volume of mixtures is negative. Gonzalez et al. [93] studied dynamic viscosities of the
binary systems of Cyclohexane and Cyclopentane with Acetone, Butanone, or 2-Pentanone at temperature 293.15, 298.15 and 303.15 K. The excess molar volume was found to be positive whereas viscosity deviation is negative. The variation in viscosity deviation was discussed in the light of intermolecular interaction.

Rangra et al. [94] studied dielectric relaxation of Acetone with N-Methylacetamide in Benzene using standard standing wave microwave technique. It is found that dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) vary linearly with weight fraction of solute in Benzene mixtures. This shows that there is no change in the nature of rotating molecular entities in Benzene solution. Dielectric evidence for Acetone hydrate was studied by Wilson et al. [95]. Johari [96] studied dielectric constant, density and viscosity of Acetone with 1-Propanol and 2-Hexane. He reported that addition of Acetone in 1-Propanol produce considerable structure breaking effect and consequently decreases and increases in dielectric constant of mixtures consistent with the mixture rule. Moshen–Nia et al. [97] studied dielectric relaxation of Water, Methanol, Ethanol, Butanol and Acetone by new set up based on low pass filter method. Menaut et al. [98] reported excess molar volume of ternary mixtures of 2-Butanone, 2-Pentanone with 1-Chloroalkane + n-Octane at 25 °C. Alonso et al. [99] studied density and speed of sound of ketone with Amine and Aniline mixtures. Excess properties show the strong ketone-amine interaction which are more easily created in mixtures with aniline. Fabio-Comelli et al. [100] reported the excess molar volume of Diethyl Carbonate with linear ketones at 298.15 K. This mixture shows regular increase in excess molar volume with ketone chain length. Liang-Sun Lee et al. [101] reported the positive excess molar volume of Cyclohexane with ketone mixtures. Clara et al. [102,103] studied density, viscosity, refractive index and related excess properties of 2-Butanone with Chloroform and 1-Butanol, negative excess molar volume for all temperature and composition shows the interaction between different molecules are stronger than interaction between molecules of pure liquids. Pico et al. [104] reported excess molar volume of 2-Pentanone with
Chapter 1

Study of solute solvent interaction of polar-polar liquids through dielectric properties

1-Chloroalkanes are positive at temperature 298.5 K and 308.15 K. Krishna et.al [105] studied density and speed of sound for binary liquid mixtures of Thiolane-1, 1-Dioxide with Butanone, 2-Pentanone and 4-Methyl 2-Pentanone. Begoa Gonzalez et.al [106] reported dynamic viscosity of binary system of Cyclohexane and Cyclopentane with Acetone, Butanone and 2-Pentanone. Baraldi et.al [107] studied density, refractive index and related properties of 2-Butanone with n-Hexane at various temperature. Ming Jer Lee et.al [108] studied density and viscosity of 2-Butanone with Dibutyl ether and 2-Picoline binary mixtures. Adhikhari et.al [109] studied volumetric behaviour of the binary mixtures of 2-Butanone (Methylethyl ketone) with n-Hexane, Cyclohexane and Benzene at different temperature. Tang et.al [110] studied density and viscosity of 2-Butanone with Chlorinated Polypropylene at different temperature. Roy et.al [111] reported the excess molar volume and viscosities deviation of 2-Butanone with 1,3 Dioxolane and 1,4 Dioxane. Urszula Ska et.al [112] studied densities, excess molar volume and excess molar enthalpies of N-Methyl -2-Pyrrolidinone with ketones. Hsu-Chen Ku et.al [113] studied densities and viscosities of binary and ternary mixtures of Ethanol, 2-Butanone and 2,2,4-Trimethylpentane at temperature 298.15 K, 308.15 K and 318.15 K. Sukhmehar Singh et.al [114] studied viscosities, densities and speeds of sound of binary mixtures of o-Xylene, m-Xylene, p-Xylene and Isopropylbenzene with 2-Butanone at 298.15 K. Holgado et.al [115] reported negative excess molar volume and viscosity deviation of 2-Butanone with 2-Methoxyethanol for entire concentration range. Gilani et.al [116] reported the nonlinear variation of dielectric constant of 2-Butanone with 2-Butanol and Cyclohexane. This is due to hetero interaction present between mixing components. Dutkiewicz [117] studied non-dielectric of Acetone with benzene system and effective intermolecular interaction leads to formation of dimmer. Madhurima et.al [118] studied dielectric and $^{13}$C NMR of hydrogen bonded of binary systems of Methanol and ketones. Conformational analysis of Methanol with ketone systems with variation of hydrogen bonded angle studied by Madhurima [119] and results are compared with experimentally
determined dipole moments. Maharolkar et.al [120] reported the dielectric constant, density, viscosity and refractive index of Allyl Chloride with n-Butanol. The dielectric relaxation of binary N,N-Dimethyl Acetamide and Acetone dissolved in Benzene is studied by Sahoo et.al [121]. Ortega et.al [122] reported positive excess molar volume of 2-Hexanone with n-Alkane due to rupture of strong dipole-dipole interaction between 2-Hexanone molecules. Venkatesu et.al [123] studied excess molar volume of ternary mixtures of N,N-Dimethylformide, 2-Pentanone and 1-Alkanols and also binary mixtures of 2-Pentanone with 1-Alkanols. Wang et.al [124] studied volumetric and viscosities of 1-n-Butyl-3-Methylimidazolium Tetrafluoroborate ionic liquid with 2-Butanone, Acetonitrile, Dichloromethane and N,N-Dimethylformide. Celda et.al [125] reported the dynamic viscosities of n-Alkanes with 2-Butanone binary mixtures at temperature 20 °C. Topallar et.al [126] reported density and viscosity decreases as addition of Acetone to sunflower seed oil. Yergovich et.al [127] reported the density and viscosity of aqueous solution of Methanol and Acetone from freezing point to 10 °C.

1.7 Objective of the Present Work

The dielectric constant of solvents is an index of its polarity. In series of solvents, increasing polarity will show a similar increase in dielectric constant. Dielectric constant of molecule is strongly depends on functional group of molecule, polarity, molecule geometry. When two liquids of different functional groups are mixed together, the complex formed for different concentration show slightly change in physical and chemical properties. Dielectric properties are basic fundamental properties of polar molecule and it is functions of frequency, composition and temperature. The availability of Time Domain Reflectometry technique most benefited for study of dielectric properties of polar liquids in microwave frequency range. Density and refractive index of solvents are temperature and molecule structure dependent properties which are also gives information about intermolecular interaction between solute and solvent. Thus, knowledge of frequency dependent dielectric properties and thermodynamic
The physical and chemical properties of allyl halide are interested due to presence of double bonded carbon and attached halogen group. The different properties of Allyl Chloride and Allyl bromide are easily related to chlorine and bromine atom respectively. In carbon-halogen bond, halogens have significantly greater electronegativity than carbon. The presence of double bond will restricted to reorientation of dipole moment of molecules.

The ketones are among most important organic compound because they are central importance to organic chemistry and biochemistry. The ketones contain carbonyl group (C=O) attached to alkyl group R and R’, where R and R’ may be same or different alky group. It is generally believed that the physical and chemical properties of ketones are largely determined by the carbonyl group. Therefore solution chemistry of these compounds can be strongly influenced by the aggregation phenomenon, which can play significant role in the physical properties of these polar molecules. The reorientation of molecular dipole is influenced by terminal alky group.

By considering the molecular structure of Allyl Chloride, Allyl Bromide and ketones, hydrogen bonding is less possible. In pure allyl halide and ketones spatial correlation between molecules may appear only by means of dipole-dipole interactions. The dipole-dipole interaction between halogen group (-Cl or -Br) of allyl halide and carbonyl group (C=O) of ketone and also within individual molecules is playing more effective role for molecular interaction.

The dielectric and thermodynamic properties of homologous series of liquid molecules of ketones are of great interest because changes in properties are chiefly related to chain length and molecular size. The study of Allyl Chloride and Allyl Bromide are also useful because of changes in properties are easily related to Cl and Br halogen atom. Earlier in our laboratory, Dharne et.al studied dielectric relaxation of Allyl halides with amide and primary alcohol. Gilani and
Rangra have reported hydrogen bonding and dipole-dipole interaction of ketones with alcohols and amide respectively.

From literature survey, we conclude that many researchers have reported dielectric and thermodynamic properties of polar-polar or polar–nonpolar liquids. No attempt, so, far seems to have been made to study the dielectric and thermodynamic behaviour of binary mixtures of allyl halide and ketones. It is therefore appropriate to report the present work on the dielectric and thermodynamic behaviour of allyl halide and ketone molecules mixtures. The systems studied in the present work are listed as follows,

**Allyl halide-Ketone binary system**

1. Allyl Bromide (ALB) + Acetone (ACE)
2. Allyl Bromide (ALB) + 2-Butanone (2-BU)
3. Allyl Bromide (ALB) + 2-Pentanone (2-PE)
4. Allyl Bromide (ALB) + 2-Hexanone (2-HE)
5. Ally Chloride (ALC) + Acetone (ACE)
6. Ally Chloride (ALC) + 2-Butanone (2-BU)
7. Ally Chloride (ALC) + 2-Pentanone (2-PE)
8. Ally Chloride (ALC) + 2-Hexanone (2-HE)

All above binary solution are studied by preparing 11 concentrations by volume. The volume of one compound was increased by step 10 percentage and reducing the same volume percentage of other compound. The concentrations were prepared for 5 ml solution with the help of micropipette with an accuracy of 99%. The complex permittivity spectra obtained by using Time Domain Reflectometry and further used to determine static dielectric constant and relaxation time of binary mixtures. The density of binary mixtures was measured by using pycnometer with varying volume with temperature and keeping mass constant for same concentration. The refractive index of mixtures also measured for same concentration and temperature at sodium D line. Static dielectric constant ($\varepsilon_s$), relaxation time ($\tau$) are used to obtain the excess static dielectric
constant \( (\varepsilon_a^E) \), excess inverse relaxation time \((1/\tau)^E\), Kirkwood correlation factor, Bruggeman factor \((f_B)\), and thermodynamic energy parameters viz enthalpy activation \((\Delta H)\) and entropy activation \((\Delta S)\) at various temperatures. Kirkwood correlation factor is used to determine the dipole orientation while Bruggeman factor used to confirm hetero-molecular interaction. The densities are used to determine excess molar volume. The refractive index is used to determine excess molar refraction and high frequencies limiting dielectric constant \((\varepsilon_a)\). These properties are used to predicate molecular interactions. The physical constants and molecular structure of pure liquids are tabulated in table 1.2 and 1.3 respectively.

### Table 1.2: Physical properties of pure liquids

<table>
<thead>
<tr>
<th>Name of compounds</th>
<th>Mol. weight Kg/mol</th>
<th>density ( \rho ) g/cm(^3)</th>
<th>M.P. (^0)C</th>
<th>B.P. (^0)C</th>
<th>R.I. ( n_D )</th>
<th>Die. const ( \varepsilon )</th>
<th>Dipole Moment ( \mu ) D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl Chloride</td>
<td>76.53</td>
<td>0.9376</td>
<td>-134.5</td>
<td>45.1</td>
<td>1.4157</td>
<td>8.2</td>
<td>1.94</td>
</tr>
<tr>
<td>Allyl Bromide</td>
<td>120.98</td>
<td>1.3980</td>
<td>-119</td>
<td>70.1</td>
<td>1.4697</td>
<td>7.00</td>
<td>1.90</td>
</tr>
<tr>
<td>Acetone</td>
<td>58.08</td>
<td>0.7845</td>
<td>-94.7</td>
<td>56.05</td>
<td>1.3588</td>
<td>21.01</td>
<td>2.88</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>72.11</td>
<td>0.7999</td>
<td>-86.64</td>
<td>79.59</td>
<td>1.3788</td>
<td>18.56</td>
<td>2.779</td>
</tr>
<tr>
<td>2-Pentanone</td>
<td>86.13</td>
<td>0.8090</td>
<td>-76.8</td>
<td>102.3</td>
<td>1.3895</td>
<td>15.45</td>
<td>2.70</td>
</tr>
<tr>
<td>2-Hexanone</td>
<td>100.16</td>
<td>0.8113</td>
<td>-55.5</td>
<td>127.6</td>
<td>1.4007</td>
<td>14.56</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Table 1.3: Molecular structure of pure compounds

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of compound</th>
<th>Molecular formula</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Allyl Chloride</td>
<td>C₃H₅Cl</td>
<td><img src="image1" alt="Molecular structure of Allyl Chloride" /></td>
</tr>
<tr>
<td>2</td>
<td>Allyl Bromide</td>
<td>C₃H₅Br</td>
<td><img src="image2" alt="Molecular structure of Allyl Bromide" /></td>
</tr>
<tr>
<td>3</td>
<td>Acetone</td>
<td>C₃H₆O</td>
<td><img src="image3" alt="Molecular structure of Acetone" /></td>
</tr>
<tr>
<td>4</td>
<td>2-Butanone</td>
<td>C₄H₈O</td>
<td><img src="image4" alt="Molecular structure of 2-Butanone" /></td>
</tr>
<tr>
<td>5</td>
<td>2-Pentanone</td>
<td>C₅H₁₀O</td>
<td><img src="image5" alt="Molecular structure of 2-Pentanone" /></td>
</tr>
<tr>
<td>6</td>
<td>2-Hexanone</td>
<td>C₆H₁₂O</td>
<td><img src="image6" alt="Molecular structure of 2-Hexanone" /></td>
</tr>
</tbody>
</table>

1.8 Application of Chemicals Under Investigation

Acetone is the simplest example of the ketone. It is colorless, mobile and flammable liquid. The most familiar household use of Acetone is an active ingredient in nail polish remover, paints thinner and varnishes. Acetone is a component of superglue remover residue from glass and porcelain. In the laboratory, Acetone is used as a polar aprotic solvent in a variety of organic reactions, such as S₈2 reactions.
Acetone is a good solvent for most plastics and synthetic fibers including those used in laboratory bottles made of polystyrene, polycarbonate and some types of polypropylene. It is mainly used in the production of methyl methacrylate, bisphenol A [128] and present as an excipient in some pharmaceutical products[129].

Acetone is naturally produced and disposed in the human body as a result of normal metabolic processes. Acetone and two other chemicals, Beta hydroxybutyrate and Acetoacetate are collectively referred to as “ketone bodies”. Reproductive toxicity tests show that the body naturally increases the level of Acetone in pregnant women, nursing mothers and children because their higher energy requirements lead to higher levels of Acetone production. Ketogenic diets that increase Acetone in the body are used to reduce epileptic attacks in infants and children who suffer from recalcitrant refractory epilepsy. Higher Acetone levels may be found in the blood levels of individuals or animals after strenuous exercise or prolonged dieting. Acetone production is also increased in animals in disease states such as diabetes and anorexia.

2-Butanone (methyl ethyl ketone) is a colorless liquid with a sweet, but sharp odor highly versatile organic compound and solvent properties similar to Acetone but has a significantly slower evaporation rate [130]. It is an interesting solvent widely employed in scientific studies and industrial application, especially for the solvating properties associated with its own character as an aprotic and protophilic medium [89]. It is used in processes involving gums, resins, cellulose acetate, nitrocellulose coatings and in vinyl films [131]. For this reason it finds uses in the manufacture of plastics, textiles, in the production of paraffin wax and in household products such as lacquer, varnishes, paint remover, glues and as a cleaning agent. It has largest use in the hard wood pulping industry and production of smokeless powder. It is routinely used in rubber-based industry, printing inks, cleaning fluids, other natural and synthetic resins for adhesive use and as a component of the solvent system used in producing magnetic tape.
2-Butanone is also a natural product made by some trees and is found in some fruits and vegetables. The exhausts of cars and trucks release 2-Butanone into the air. 2-Butanone is usually found in the air, water and soil of landfills and hazardous waste sites.

2-Pentanone and 2-Hexanone is used as a solvent and an intermediate in the synthesis of pharmaceuticals flavors and pesticides.

Allyl chloride is an organic compound and physically colorless liquid, insoluble in water but soluble in common organic solvents. It has a highly versatile product due to its dual reactive sites at the double bond and the chlorine atom. In the laboratory, Allyl chloride is a common alkylation agent, useful in the manufacture of pharmaceuticals and pesticides. It has also a reactant for the production of poly DADMACs (diallyl dimethyl ammonium chloride polymerized), used for flocculation and clarification of water and wastewater. It is used in the chemical synthesis of complex molecules for the pharmaceutical industry. Allyl chloride also used as a chemical intermediate in many industries [132] including the preparation of polymers, resins and other plastic materials. It is also used for the preparation and modification of catalysts and adhesives, flame retardants, chelating agents, detergents, dyestuffs, flavorings, metal brighteners and perfumes. The great majority of Allyl chloride is converted to epichlorohydrin[133].

Allyl Bromide is an industrial and research chemical with evidence of wide applications. It is a clear, colourless to pale yellow liquid and persistent smell. This chemical is highly volatile or light sensitive in nature, immiscible with water, soluble in alcohol and ether. It is an organic halide and alkylation agent which is used in synthesis of polymers, adhesives, pharmaceuticals, perfumes, biochemicals, agricultural chemicals [134,135]. It has been described as an insecticidal fumigant used in crop protection [136].
Chapter 1

Introduction

Study of solute solvent interaction of polar-polar liquids through dielectric properties

References:


Chapter 1

Introduction

[34] M. T. Hosamani, R. H. Fattepur, D. K. Deshpande and S. C. Mehrotra, J.


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