1.1 Introduction

Dielectric relaxation spectroscopy in liquids is widely used for determination of the structure and associated liquid properties which are helpful to study the molecular interactions. Dielectric relaxation spectroscopy is a powerful tool for examining the underlying physics of solvent systems and for exploring the molecular dynamics of liquids characterized by inter and intramolecular structures that vary rapidly with time [1] also the determination of structure and properties of associated liquids could provide deeper insight into the phenomena of the molecular interaction [2]. The determination of intermolecular dynamics of liquids can be best understood at microwave frequency range; hence at microwave frequency dielectric relaxation is used to study the interaction of polar molecules with neighboring polar as well as non polar molecules. Dielectric relaxation is nothing but applying electric field to the atoms, molecules that results polarization through readjustment of molecules from equilibrium. The displacement of molecules on application of electric field is frequency and temperature dependent. Dielectric relaxation of liquids contains measurement of dielectric permittivity and dielectric loss at microwave frequencies.

The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment A-H in which A is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. A typical hydrogen bond may be depicted as A-H----B-C, where the three dots denote the bond A-H represents the hydrogen bond donor. The acceptor may be an atom or an anion B, or a fragment or a molecule B-C, where B is bonded to C. In some cases, A and B are the same. In more specific cases, A and B are the same and A-H and B-H distances are the same as well leading to symmetric hydrogen bonds. Water and alcohols are some of the examples of H-bonded liquids.
Water is most precious and most abundant material on earth most studied but still not fully understood. One of the reasons to its anomalous behavior is its strong hydrogen bond. Water is polar organic compound with permanent dipole moment $\mu=1.80$ D with molecular weight 18.01gm/mol. its liquid density is 0.997g/cm$^3$ and refractive index is 1.33 at 20°C. It is not a highly viscous liquid with viscosity 0.890 cP [18].

![Figure 1.1: structure of water molecule](image)

Alcohols are compounds in which hydroxyl (-OH) group is attached to saturated Carbon atom. The hydroxyl group is a functional group of alcohols. Their general formula is R-OH and these are classified as monohydric, dihydric, trihydric and polyhydric alcohols depending upon the number of hydroxyl groups. The O-H bond in alcohol is highly polar, because oxygen is highly electronegative. The polarity of O-H bond gives rise to attraction of partially positive hydrogen atoms of other molecules. Due to this, hydrogen bonding requires a great deal of energy in the form of heat to overcome these attractive forces. The H-bond has a considerable effect on the dielectric properties of the associated polar liquids. The formation of molecular structures and network structures through hydrogen bonds is the main cause of complex molecular structures in alcohols. In the presence of another H-bond, alcohol structures at the molecular level change significantly due to breaking of their
homogeneous structures and simultaneously the formation of heterogeneous H-bonds [1]: hence a prime interest has been extensively shown to study the molecular interaction in Hydrogen bonded liquids like alcohols and water through dielectric relaxation [2-16].

Butanol is a monohydric (contains one OH group) tetra carbon alcohol with formula C₄H₉OH and molecular weight 74.12 gm/mol. Butanol has several medical and industrial applications used as synthesis intermediate of fuel components, besides this it has various industrial applications such as perfume ingredient, paint remover etc. Butanol has four isomeric structures as given below (Figure 1.2 a, b, c, d) depending upon the position of OH group attached to hydrogen atom.

1. Tertiary Butyl alcohol (TBA):
2. Secondary butyl alcohol / 2-Butanol (2 stereoisomer’s):

![2-D molecular Structure of 2-Butanol](image)

**Figure 1.2 (b):** 2-D molecular Structure of 2-Butanol

3. Butyl alcohol / 1-Butanol:

![2-D molecular Structure of 1-Butanol](image)

**Figure 1.2 (c):** 2-D molecular Structure of 1-Butanol
4. Isobutyl alcohol:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH} - \text{CH}_2 - \text{OH} \\
\text{H}_3\text{C} & 
\end{align*}
\]

**Figure 1.2 (d):** 2-D molecular Structure of Isobutyl alcohol.

TBA is a simplest tertiary alcohol: as the alcoholic carbon is attached to three other carbon atoms (as in figure 1.2 (a)) having permanent dipole moment \( \mu = 1.66 \text{D} \) and density 0.7887 gm/cm\(^3\). It is viscous than water with 4.312cP and completely miscible with water \([17]\). 2-Butanol also called as secondary butyl alcohol (figure 1.2(b)) is secondary alcohol with alcoholic carbon attached to two other carbons having dipole moment \( \mu = 1.8 \text{D} \) with density 0.8063 gm/cm\(^3\). Its viscosity is 3.096cP and with very soluble in water \([17]\). 2-Butanol is a chiral compound as it has two stereoisomer structures (R)-2-butanol and (S)-2-butanol. 1-Butanol is a straight chain primary alcohol (figure 1.2 (c)) where the alcoholic carbon is attached to a single carbon atom with dipole moment \( \mu = 1.66 \text{D} \) and density 0.8095 gm/cm\(^3\). Its viscosity is 2.544cP and it is soluble up to 20% of its volume fraction to water \([17]\). Iso butyl alcohol is a three carbon chain with hydroxyl group attached to end carbon and one methyl group is at the middle carbon. It has very low solubility in water (less than 10%) and not considered as a system for further.
Chapter 1

Time Domain Reflectometry (TDR) has proved to be a powerful tool for the study of molecular dynamics and intermolecular interaction of liquids i.e. polar/ non polar, hydrogen bonded/ non hydrogen banded and pure/ binary mixtures of liquids. TDR technique provides reliable information in the frequency range of 10MHz to 30GHz. TDR techniques are easily grasped; even those with short experience in high-frequency measurements can quickly understand this technique. TDR measurements are based on the generation of a step-like electrical signal propagating through a coaxial cable that connects the TDR-generator with the probe and, subsequently, on the analysis of the deriving reflected signal [18]. Here TDR technique is used to study dielectric behavior of binary mixture of three aqueous alcohol systems which are hydrogen bonded as well as polar liquids. Complex permittivity spectra of a picosecond time domain measurement of the sample is carried out and by doing its Fourier transformation & using some computer analysis software’s. The following parameters were extracted from the complex permittivity spectra,

1. Static dielectric constant ($\varepsilon_0$)
2. Relaxation time ($\tau$)
3. Enthalpy ($\Delta H$) and entropy ($\Delta S$) of activation as thermodynamic parameters
4. Kirkwood correlation factor ($g_{eff}$)
5. Bruggmann factor ($f_B$)
6. Excess permittivity ($\varepsilon^E$)
7. Excess inverse relaxation time ($1/\tau^E$)

The present thesis comprises of seven chapters.
The **first chapter** gives an introduction of dielectric relaxation spectroscopy, Alcohols, the Butanol Isomers and TDR technique.

**Second chapter** describes the theories related to static and dynamic dielectric permittivity, the dielectric relaxation and different models related to the dielectric relaxation theories. The parameters like Kirkwood correlation factor, Excess dielectric properties, thermodynamic properties and Bruggeman factor are also included in this chapter.

The **chapter third** deals with experimental techniques and methodology adopted for the study including principle of time domain reflectometry, establishment and development of TDR, data analysis and calibration method used for the determination of high frequency permittivity of binary mixtures of Aqueous solutions.

**Chapter four** presents the study of dielectric relaxation in aqueous Tertiary Butyl Alcohol (TBA) solutions using time domain reflectometry technique. The values of dielectric permittivity spectra are measured at entire concentrations in the frequency range of 10 MHz to 30 GHz and at temperature range of 25°C to 10°C. using complex permittivity spectra Dielectric parameters such as Static dielectric constant \((\epsilon_0)\), Relaxation time \((\tau)\), are calculated. Thermodynamic parameters, Kirkwood correlation factor, Bruggmann factor, excess dielectric properties are also determined for aqueous TBA.

**Chapter five** deals with dielectric relaxation study of 2-Butanol with water using TDR technique. The dielectric permittivity spectra are measured over entire concentrations in the frequency range of 10 MHz to 30 GHz and at temperature range of 20°C to 0°C. Dielectric parameters such as Static dielectric constant \((\epsilon_0)\), Relaxation time \((\tau)\), are calculated. Kirkwood correlation factor, Bruggmann factor, Thermodynamic parameters, excess dielectric properties are also determined for aqueous 2-Butanol.

**Chapter six** concerns with the study of 1-Butanol aqueous solutions. The values of dielectric permittivity measured over seven different concentrations of volume fraction of 1-Butanol in the frequency range of 10 MHz to 30 GHz. Dielectric parameters such as Static dielectric constant \((\epsilon_0)\), Relaxation time \((\tau)\). The contribution of hydrogen bonds to dielectric properties of the mixture has been studied Kirkwood correlation factor, Excess dielectric constant, Thermodynamic properties are also determined.

**Chapter seven** deals with the summary and conclusion of the present study.
Chapter 1

References


