Introduction:

The dielectric permittivity can be determined from different techniques [1, 2]. These techniques are based on different principles working in different frequency regions. For the complete information of dielectric one need permittivity measurements over a wide frequency range. In the microwave region the frequency domain and time domain techniques are mostly used. There are two methods of measurements in the time domain technique, (i.e.,) reflection method and the transmission method [3].

Fellner-Feldegg [4-6] introduced time domain spectroscopy (TDS) in the field of dielectric studies in 1969. He has taken fruitful attempts to modify the TDS equipments to minimise errors in measurements and increase the frequency range. Time domain methods have some advantages over frequency domain methods. In time domain reflectometry one measurement covers a wide frequency range. More over this method can measure the complex permittivity not only in the microwave frequency range but also in radio frequency range. The time domain signal usually covers a wide frequency spectrum and the transient methods are less time consuming than frequency domain methods [7].

The instrumental setup is quite simple than that used in the frequency domain technique. The sample required for this technique is only about 1 cc. This is one of the great advantages of this method. Because of these advantages the time domain methods have long been used by several researchers to investigate the dielectric properties of materials [8, 9].

1.1 DIELECTRIC POLARIZATION:

The Dielectric materials are understood [10] as the materials in which is the electrostatic fields can persist for a long time. If a non-polar molecule is placed in an electric field then charge centers of the non-polar molecule is displaced and each molecule become a dipole and is called an induced dipole. Now the molecule is said to be polarized. The displaced charge centers of a non-polar molecule is limited by strong restoring force produced by the charges configuration in the molecule when the electric field is removed, then the two charge centers again coincide with each other in turn the dipole moment of the molecule gets vanished.
If a dielectric medium consists of polar molecules (permanent dipole) then the dipoles are oriented at random in the absence of an external electric field when an electric field is applied then the forces acting on a dipole give rise to a couple whose effect is to orient the dipole along the direction of electric field. Thus the polar molecules become induced dipoles when they are oriented by the field and therefore their dipole moments get increased. This phenomenon is known as orientation polarization.

An alternating field is commonly employed for the measurement of dielectric constant and hence the molecular polarization. At low frequencies the dielectric constant is numerically equal to the value obtained when a steady field is employed. This value persists until the molecules are unable to complete follow the reversals of the field when the frequency is increased. Then they lag behind the applied field and the orientation decreases.

When the frequency is very high the permanent dipole moment of molecules cannot orient themselves sufficiently fast to align themselves with the ever changing field direction. At such high frequencies the permanent dipole moment makes no contribution to the polarization of these molecules. Since molecules require about few pico-second to rotate in a liquid, the dipolar contribution vanishes when the dielectric constant is measured at frequency above 10 GHz (microwave region). It is possible to measure the rate of molecular orientation in liquids by carrying out observation on the variation of polarization with frequency. As a matter of fact, the technique of the dielectric relaxation is based on this principle.

At microwave frequencies the orientation polarization decreases but due to the applied electric field the molecules gets stretching and bending which results the molecular distortion. This occurs in infrared region. At still higher frequencies the distortion polarization makes no contribution to molar polarization.

1.2 BRIEF LITERATURE SURVEY ON THE DIELECTRIC RELAXATION IN LIQUIDS:

Many workers [11] have studied the dielectric properties of liquids by various methods. One of the earlier works was published by Debye. He applied the langevin theory for the average orientation of permanent magnetic moment in external
fields to the electric analogue. He gave both microscopic and macroscopic models of
dielectric relaxation. Microscopic model suggest the rotation of one molecule where as
macroscopic model gives average rotation of molecules in the liquid medium. The Debye
theory has been extended and revised by a great number of scientists.

Debye macroscopic model gives relation between complex permittivity and
relaxation time. This relation is an equation of a semicircle if dielectric loss ($\varepsilon''$) is
plotted against dielectric constant ($\varepsilon'$) in a complex plane. This Debye semicircle has
been used to represent dielectric data of a large number of compounds having a single
relaxation. Some molecules having a number of ratable polar groups show deviation
from the Debye semicircle where relaxation times are distributed symmetrically around a
most probable relaxation time. Cole and Cole gave a classic equation representing such
type of behavior. Sometimes skewed behavior of Cole-Co le arc suggests unsymmetrical
distribution of relaxation time. This skewed arc behavior has been explained by
Davidson and Cole. If two or more relaxation processes occur simultaneously one
corresponds to the rotation of molecule as a whole and other corresponding to the
intramolecular motion. Their effect on $\varepsilon'$ (complex permittivity) can be added together
and the observed behavior can be used to calculate the relaxation of each process.

Eyring observed a dielectric relaxation based on the analogy of chemical rate
process [12] whereby through measurements of temperature dependent dielectric
relaxation times, it is possible to evaluate activation energy of enthalpy and entropy for
dipole relaxation process.

Dielectric relaxation study of liquids generally carried out on dilute solution of
polar and non-polar liquids or binary mixture in dilute solutions of non-polar liquids and
on mixtures of polar-polar liquids or simply binary mixtures.

A large amount of work has been done on dilute solutions. Difficulty arises in
measuring the dielectric absorption data in pure liquids because of its viscosity, bipolar
interactions and internal field. Therefore, dielectric properties are usually carried out in
dilute solutions of non-polar solvents. In these cases polar molecules will be quasi-
isolated state.

However, some dielectric data on polar-polar liquids have been available [13-
16] Albuquerque et.al. [17] reported the dielectric parameters for Methanol, Ethanol, 1,
2-Ethanediol, and 2-Methoxyethanol mixtures at 298.15 K. Sengwa et. al. [18] has reported the dielectric parameters for monoalkyl ethers of ethylene glycol and of dimethylene glycol and benzene mixtures at different temperatures and concentrations.

1.3 SELECTION OF THE SYSTEMS:

The study of binary liquid mixtures provides sensitive tool for detecting molecular interactions. In order to study the effect of increase of molecular size on solute-solvent interaction the series of alcohols and alkoxyalkanols are selected because no attempts have been made to study this binary system. Alcohols play an important role in many chemical reactions [19-21] due to their ability to undergo self-association with manifold internal structure and are in wide use in industry and science as reagent, solvent and fuels. Monoalkyl ethers of [22] ethylene glycol may exist in dynamic equilibrium existing in Gauche as well as open chain form. In this case monoalkyl ethers of dimethylene glycol intramolecular hydrogen bonding decreases with the increase in the size of the alkyl group. These molecules are also found to exist in both intramolecular hydrogen bonded form in equilibrium with open chain form in dilute solutions. The intermolecular association is found to be absent in dilute solutions, whereas in pure liquid state the molecule existing in open chain may form multimers. Because of such interesting facts it is decided to carry out dielectric relaxation study of Alcohols with Alkoxyalkanols.

The following systems have been selected for the present work.

1. Methanol with -2metha oxyethanol, 2-ethoxyethanol and 2-butoxyethanol

2. Ethanol with -2metha oxyethanol, 2-ethoxyethanol and 2-butoxyethanol

3. 1-Propanol with -2metha oxyethanol, 2-ethoxyethanol and 2-butoxyethanol
<table>
<thead>
<tr>
<th>Name</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>1-Propanol</th>
<th>2-Methoxy-Ethanol</th>
<th>2-Ethoxy-Ethanol</th>
<th>2-Butoxy-Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole.</td>
<td>CH₃OH</td>
<td>C₂H₅OH</td>
<td>C₂H₇OH</td>
<td>C₃H₈O₂</td>
<td>C₄H₁₀O₂</td>
<td>C₆H₁₄O₂</td>
</tr>
<tr>
<td>Weight</td>
<td>32.04</td>
<td>46.07</td>
<td>60.11</td>
<td>76.11</td>
<td>90.12</td>
<td>118.18</td>
</tr>
<tr>
<td>Density</td>
<td>0.7914</td>
<td>0.7893</td>
<td>0.8035</td>
<td>0.9647</td>
<td>0.9297</td>
<td>0.9015</td>
</tr>
<tr>
<td>Dipole Moment</td>
<td>1.7</td>
<td>1.69</td>
<td>1.68</td>
<td>2.96</td>
<td>2.1</td>
<td>2.08</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-97</td>
<td>-144.3</td>
<td>-126.5</td>
<td>-85</td>
<td>-70</td>
<td>-77</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>64.7</td>
<td>78.4</td>
<td>97.1</td>
<td>125</td>
<td>135</td>
<td>171</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>1.3288</td>
<td>1.3611</td>
<td>1.385</td>
<td>1.4024</td>
<td>1.408</td>
<td></td>
</tr>
</tbody>
</table>

* Hand Book of chemistry and physics, 64th ed., CRC Press Florida 1993
** Digest of Literature on dielectrics VOL.40 1976, national academy of science Washington, D.C. 1978
In the present thesis TDR technique has been used for the dielectric measurements. Various dielectric parameters reported here are the dielectric constant i.e static permittivity ($\epsilon_s$), high frequency limiting dielectric constant ($\epsilon_{\infty}$), relaxation time ($\tau$) in pico-second. Kirkwood correlation factor, Bruggman factor and thermodynamic parameters on the binary systems at different temperatures and at various volume concentrations.

References:


13. R.J. Sengwa, Madhavi and Sonusankhla, Physics and chemistry of liquids 2006, 1-17, preview article.


