Chapter 1.
INTRODUCTION
1.1 INTRODUCTION:

In substances, called insulators, which do not have free electrons, or the number of electrons are too low, the electrons are tightly bound to the atom. When potential difference is applied to insulator no electric current flows, even then their behaviour in fields is very important because the presence of the field may change the behaviour of an insulator. The insulators whose behaviour gets modified in the electric field are called as dielectrics. When the change in the behaviour of the dielectrics is independent of the direction of applied field, the dielectric called as isotropic. On the other hand, if the change in behaviour of the dielectric depends on the direction of applied field the dielectric is called as anisotropic.

If we consider a dielectric in an electric field, then the field exerts a force on each charged particle. The positive particles are pushed in one direction (direction of field) while the negative particles in the opposite direction. As a result the positive and negative parts of each molecule are displaced from their equilibrium positions in opposite directions. The overall effect is a displacement of the entire positive charge. The relative displacement of the charges is called polarisation. And the dielectric is said to be polarised.

The molecules of dielectrics are classified into two classes:
1) polar molecules, and
2) non-polar molecules.
The positive charge of the nucleus may be supposed to be concentrated at a point, say the center of the gravity of positive charge. Similarly, the negative charge due to electrons in orbit may be supposed to act at a point, known as centre of gravity of negative charge. When two centres of gravity coincide in a molecule, the molecule as a whole possesses no resultant charge and it is said to be non-polar. If two centres of gravity are displaced from each other, the molecule as a whole possesses polarity and has permanent dielectric moment and the molecule is said to be a polar molecule. A polar molecule in an electric field exhibits both permanent and induced dipole moments while non-polar exhibits induced dipole moment only.

The dielectric properties of liquids are useful to some extent to understand the liquid structure and molecular interactions therein. The study of dielectric properties of liquid materials is necessary not only to understand the liquid structure but also to provide technical data for practical uses in industry, science, medicine and engineering. For studying dielectric properties of liquids, different dielectric theories have been proposed for various types of liquids. But there is no ideal model to give satisfactory explanation of the liquid state.

Development in microwave technology and better understanding of interaction of electromagnetic fields with the matter—solids, liquids, gases and plasmas, the microwave technique is extensively proved as a technique to determine liquid structure. Hence Time Domain Reflectometry (TDR) technique has been used in present work.
to study the intermolecular interactions between solute and solvent.

1.2 A BRIEF LITERATURE SURVEY ON THE DIELECTRIC RELAXATION IN LIQUIDS:

Many workers $^{2-32}$ have studied the dielectric properties of a liquid by various methods. One of the earlier work was published by Debye $^2$. 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 suggests the rotation of one molecule whereas 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 rotatable polar groups show deviation from the Debye semicircle where relaxation times are distributed symmetrically around a most probable relaxation time. Cole and Cole $^{11}$ gave a classic equation representing such type of behaviour. Some times skewed behaviour of Cole-Cole arc suggest unsymmetrical distribution of relaxation time. This skewed arc
behaviour has been explained by Davidson and Cole\textsuperscript{10}. If two or more relaxation processes occur simultaneously, one corresponding 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 behaviour can be used to calculate the relaxation of each process.

Eyring\textsuperscript{7} observed a dielectric relaxation based on the analogy of chemical rate process 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 have been done on dilute solutions\textsuperscript{12-22}. 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 in quasi - isolated state.

However, some dielectric data on polar - polar liquids have been available\textsuperscript{24-32}
1.3 Introduction to the problem:

Different polar liquids have been studied using Time domain technique. Dimethylformamide and Dimethylsulphoxide systems have been used as solvents, because the correlation factors correspond to these systems are close to 1 i.e. there is not significant interactions among themselves. The external state molecules in these solvent may interact. The objective of the thesis is to study these interactions.

Since Dimethylformamide (DMF) and Dimethyl Sulfoxide have important applications in industry, biochemistry, pharmacy, the system have selected for our study. 2- Ethoxyethanol, Ethanol and Propanol are also chosen for our study because these liquids are also widely used in chemical industries as solvents for oils, resins and as an antifreeze for explosives.

The following systems have been selected for the present work.
1. 2-Ethoxyethanol - DMF
2. Ethanol - DMF
3. Propanol - DMF
4. 2-Ethoxyethanol - DMSO
5. Ethanol - DMSO
6. Propanol - DMSO

The physical constant of liquids under study are given in Table 1.
Table 1. Physical constants of liquids under study.

<table>
<thead>
<tr>
<th>Name</th>
<th>2-Ethoxyethanol</th>
<th>Ethanol</th>
<th>Propanol</th>
<th>DMF</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole.</td>
<td>C₂H₃OCH₂CH₂OH</td>
<td>C₂H₅OH</td>
<td>CH₃CH₂CH₂OH</td>
<td>HCON(CH₃)₂ (CH₃)₂SO</td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dipole</td>
<td>** 1.05**</td>
<td>1.69</td>
<td>1.68</td>
<td>3.82</td>
<td>3.96</td>
</tr>
<tr>
<td>Moment (debyes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mole.</td>
<td>90.12</td>
<td>46.07</td>
<td>60.11</td>
<td>73.09</td>
<td>78.13</td>
</tr>
<tr>
<td>Weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>0.8628</td>
<td>0.7893</td>
<td>0.8035</td>
<td>0.9080</td>
<td>1.1014</td>
</tr>
<tr>
<td>Melting</td>
<td>-58</td>
<td>-117.3</td>
<td>-126.5</td>
<td>---</td>
<td>18.4</td>
</tr>
<tr>
<td>Point C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boiling</td>
<td>83.4</td>
<td>78.5</td>
<td>97.4</td>
<td>177</td>
<td>189</td>
</tr>
<tr>
<td>Point C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Refractive</td>
<td>Index</td>
<td>1.3796</td>
<td>1.3611</td>
<td>1.3850</td>
<td>1.4321</td>
</tr>
</tbody>
</table>


In the present thesis TDR technique has been used for the dielectric measurements. Various dielectric parameters reported here are the dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$), static permittivity ($\varepsilon_s$), high frequency limiting dielectric constant ($\varepsilon_s$), relaxation time ($\tau$) in psec., Kirkwood correlation factor, Bruggman factor and thermodynamic parameters on the binary systems at different temperatures and at various volume concentrations.
REFERENCES:

7. A.A.Antony and C.P. Smyth, J. Am. Chem.Soc. 86/1 (1964) 156