CHAPTER: 1

INTRODUCTION
1.1 **INTRODUCTION**

When potential difference is applied to insulator no electric current flows, even then their behavior in fields is very important because the presence of the field may change behavior of an insulator. The insulators whose behavior gets modified in the electric field are called dielectrics.

Dielectric materials are mainly used for electric insulation. Without insulation no electrical system can operate, be it a simple electric iron, a complex power transmission substation, or a sophisticated weather satellite.

Understanding the phenomena occurring in dielectric materials in the presence of electric fields is a pre-requisite for advance in technology. This has been and still is the driving force for many research groups concern with the study of electrical properties of dielectric materials.

The state of the matter refers to the group of matter with the same properties. In other words, we group the objects together according to their properties. In solids, since the atoms are closely packed, the particles perform relatively small oscillations about their equilibrium positions governed by the temperature. This explains rigid shape and size of solids. In liquid state; intermolecular interaction are less than solid. As a result of this, the molecules of liquid can move about inside the liquid. From the statistical mechanics, different theories for the equilibrium properties of liquids are developed. Different theories [1-4] have been proposed for various types of liquids.

The substances called insulators which do not have free electrons, the electrons are tightly bound to the atom. When the potential difference is applied to insulator no electron current flows, even then their behaviour in fields may change. The insulator whose behaviour gets modified in the electric fields is called as dielectrics [5]. When the change in behaviour of the dielectric is independent of the direction of applied field, the dielectric called as isotropic, otherwise the change in behaviour of the dielectric depends on the direction of the applied field, and the dielectric is called 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 particles of each molecule are displaced from their equilibrium positions in
opposite directions. The overall effect of the charges is called polarization and the dielectric is said to be polarized.

The molecules of dielectrics are classified into two classes

1. Polar molecules.
2. Non-Polar molecules.

In general, polarity refers to the dipole-dipole intermolecular forces between the slightly positively-charged ends of one molecule to the negative end of another or the same molecule. Molecular polarity is dependent on the difference in electronegativity between atoms in a compound and the asymmetry of the compound's structure.

A molecule with a permanent electric dipole moment is called a polar molecule. When electric field is applied to dielectric, the molecular charges get displaced. The total charge passing through unit area within the dielectric perpendicular to applied field is called polarization. A molecule is polarized when it carries an induced dipole. The physical chemist Peter J. W. Debye [2] was the first scientist to study molecular dipoles extensively, and dipole moments are consequently measured in units named debye in his honor. A permanent electric dipole moment, that is although the total amount of positive and negative charge on the molecule are equal, so that the molecule is electrically neutral, the distribution of two kinds of charges are different, so that the positive and negative charges are centered at points separated by distance of molecular dimensions known as electric dipole. When two centers of gravity coincide in a molecule, the molecule as a whole possesses no result charge and is said to be non-polar.

There are three types of polarization; (i) Orientation polarization, (ii) Electronic polarization, and (iii) Atomic polarization. In electronic polarization the electrons in each atom are displaced from their usual positions, giving each molecule a small dipole moment. Contribution of electronic polarization to the dielectric constant of the liquid is numerically equal to square of refractive index. In atomic polarization there is relative change in the mean positions of the atomic nuclei within the molecules. It occurs at radio frequencies. In the case of orientational polarization, the molecules are partially aligned by the field and contribute heavily to the polarization. The orientational polarization is additional to electronic and atomic polarization for polar molecules. Therefore the polar materials have higher permittivity than non-polar materials. For example, the dielectric constant of a non polar liquid such as hydrocarbon is about 2, which is of a weakly polar
liquid, such as chloroform or ethyl ether, are about 5, while those of highly polar liquids, such as ethanol and water range from 25 to 80. The orientation polarization falls off rapidly with rising temperature, because the increasing thermal motion reduces the alignment of the permanent dipoles caused by the electric field. For this reason the permittivity of a polar material falls more rapidly with rising temperature.

A dielectric material is one which contains either permanent or induced dipoles which when placed between two electrodes acts as a capacitor, i.e. the material allows charge to be stored and no dc conductivity is observed between the plates. The polarisation of dielectrics arises from the finite displacement of charges or rotation of dipoles in an electric field and should not be confused with conduction which results from translational motion of the charges when the electric field is applied. At the molecular level polarisation involves either the distortion of the distribution of the electron cloud within a molecule or the physical rotation of molecular dipoles. The investigation of dielectric properties provides an important approach to understand the structure of matter.

The permittivity of a material, \( \varepsilon \), is a property which describes the charge storing ability of that substance irrespective of the sample’s dimensions. The dielectric constant or relative permittivity is the permittivity of the material relative to that of free space. Dielectric studies involve the measurements of dielectric permittivity, dielectric loss at different frequencies and temperature. Understanding of static dielectric constant (low-frequency dielectric constant) is useful in determination of dipole moments of molecules. The measurements of dielectric permittivity and dielectric loss can be used to determine relaxation time and distribution parameters. These parameters then can be used to investigate the molecular motions, which depend on molecular structure, size, shape, and intra molecular forces.

The distribution of two kinds of charges in molecule is not symmetric; the positive and negative charges are centered at points separated by a distance, forming an electric dipole. In a dielectric material, these charges can’t move freely through the medium but can be displaced. The magnitude of the dipole moment depends on the size and symmetry of the molecule. Molecules having center of charge symmetry are non-polar, while molecules having no center of symmetry, are polar. Thus, the dipole moment indicates electronic structure of molecule. The dipole moment of the molecule
influences its permittivity and therefore studies of permittivity can be used to measure the dipole moment of the molecules.

The behavior of dielectric under the influence of high frequency field is different from the static behavior [3, 4, 6, 7]. The frequency of the externally applied alternating field is such that there is an observable lag in the attainment of equilibrium. This lag is commonly referred to as relaxation, which, in general, may be defined as the lag in the response of a system to change in the forces to which it is subjected [8]. Dielectric relaxation is 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 its original value, 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 [9]. When the polar molecules are very large in size, or the frequency of the alternating field is very high, or the viscosity of the medium is very great, the rotary motion of the molecules is not sufficiently rapid for the attainment of equilibrium with the field. The dipole moments are not able to orient fast enough to keep in alignment with the applied electric field and the total polarizability falls from \( \alpha_t \) to \((\alpha_t - \alpha_0)\); where \( \alpha_t \) is the total polarizability given by:

\[
\alpha_t = \alpha_0 + \alpha_e + \alpha_a ,
\]

where, \( \alpha_0 \) is orientational polarizability;

\( \alpha_e \) is electronic polarizability;

\( \alpha_a \) is atomic polarizability.

This fall in polarizability, with its related reduction of permittivity, and the occurrence of 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 frequencies 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), and that for 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.
Dielectric Behaviour And Molecular Association In Monoalkyl Ethers Of Diethylene Glycol Molecules With Amides Using Time Domain Reflectometry Technique

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[10], because of discrete energy levels. On the other hand, the dipolar orientation process gives rise to relaxation, both the frequency and shape of the dielectric loss characteristic depend 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 group, result in frequency dependent polarization in the radio frequency and microwave region.

From Maxwell’s theory of Electromagnetic waves, the relative permittivity of material is equal to square of its refractive index measured at the same frequency. If the square of refractive index is measured at frequency of the D lines of Sodium, this gives permittivity, a means for 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 D lines is mainly due to the permanent dipole moment.

1.2 APPLICATIONS OF DIELECTRIC STUDY

1.2.1 Agriculture:

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. This variation is used to get an idea of the moisture contents in seeds.

1.2.2 Medicine:

The interest of microwaves increased due to biological effects. Exposure to microwaves results in thermal stresses both deep inside the body and also on the surface. Excessive exposure may cause damage but controlled exposure may result in therapy and human comfort. 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. microwave treatment of cancer has also been studied. 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 is controlled. Human comfort and physical health depend upon the energy exchange between man and surrounding. Normally heat is generated in the human body by metabolism in the body. Incident microwave energy can help the heat generation metabolism in the body.
1.2.3 Electrochemical super-capacitors [11]:

Recent advertisement in the electro-chemical capacitors have resulted in new type of capacitors known as ‘super-capacitors’ or ‘ultra-capacitors’. These have capacitance (energy capable of being stored) of several hundred farads (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.

1.3 TIME DOMAIN SPECTROSCOPY

Time Domain Spectroscopy (TDS) probes the interaction of a macroscopic sample with a time-dependent electric field. The resulting polarization, either expressed by the frequency-dependent complex permittivity characterizes amplitude and time scale (via the relaxation time) of the charge-density fluctuations within the sample. Such fluctuations generally arise from the reorientation of the permanent dipole moments of individual molecules or from the rotation of dipole moments in flexible molecules, like polymers. The time scale of these fluctuations depends on the sample and on the relevant relaxation mechanism. Relaxation times range from several Picoseconds in low-viscosity liquid, such as water, to hours in the case of glasses [12]. Probably TDS is the technique with the most extensive coverage of dynamical processes. The corresponding measurement frequencies range from $10^{-14}$ Hz to $10^{12}$ Hz, which requires a variety of instruments for complete coverage. However, it is generally sufficient to concentrate on a smaller frequency range adapted to the sample properties.

In contrast to conventional spectroscopic methods, like NMR spectroscopy, TDS is especially sensitive to intermolecular interactions. TDS includes, Time Domain Reflectometry (TDR) and Time Domain Transmission (TDT) method. TDS is able to monitor cooperative processes and thus provides a link between molecular spectroscopy, which monitors the properties of the individual constituents, and techniques characterizing the bulk properties of the sample, especially the viscoelastic and rheological behavior. The time scales covered by these processes range from milli to picoseconds, so that experiments must be conducted in the range of radio to microwaves.
Precise spectra over a broad frequency range are necessary for a meaningful deconvolution. E.g. water peaks at 20 GHz - already in a frequency range difficult to access, such limited investigations do not only forbid a characterization of the solvent response, but also hamper a precise separation of the solute contribution or of specific cooperative relaxation processes [13-15].

1.4 TIME DOMAIN REFLECTOMETRY

The Time Domain Reflectometry is a measurement concept having great usefulness in the analysis and synthesis of wide band systems. The development of Time Domain Reflectometry by Cole et. al., [16-19] gives dielectric relaxation study over a wide range of frequency.

The basic TDR system consists of fast rising pulse generator, sampling unit and a wide band, digitizing oscilloscope. A step voltage pulse produced by tunnel diode is detected at the sampler and displayed on the oscilloscope. This voltage pulse is propagated through a coaxial line. The cell, which holds the sample, is placed at the end of coaxial line. When the voltage pulse reaches the air-dielectric interface, a part of pulse is reflected and the rest is transmitted through the dielectric sample. The reflected part is recorded and reflection coefficient is determined. This reflection coefficient, after analysis provides the dielectric parameters. The access to structural changes is through relative changes in dielectric parameters. The relative changes in dielectric parameters over broad range of frequencies and wide range of concentrations at various temperatures can readily be measured using TDR method.

1.5 LITERATURE SURVEY

Many research groups to study molecular interactions in liquids have used TDR method. Microwave group at 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. Our group has been studied interactions between various functional groups in organic compounds and biological samples has very effectively used this method. The molecular interactions in aqueous solutions of associative compounds such as Ethylene Glycol [20], Hexamethylphosphoramide [21], Dimethylsulfoxide [22],
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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], Dimethylsulfoxide [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 groups was reported by S.M. 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 S.C. Mehrotra et. al., [48]. The dielectric relaxation study of Chlorobenzene with Dimethylformamide and Dimethylchloride with Ethanol has been reported by V. P. Pawar et. al., [49-50]. The dielectric relaxation study of Ethanol with Nitrobenzene and Nitrotolenene has been reported by Ajay Chaudhari et. al. [51]. N,N-dimethylacetamide with ethanolamine and Formamide with N,N-dimethylaminoethanol has been reported by Prabhakar Undre et. al. [52-53]. Alkyl methacrylate with alcohols has been reported by P. 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 [61-89] by using different experimental techniques.

1.6 INTRODUCTION TO PROBLEM

Dielectric study of binary mixtures is a sensitive tool for detecting molecular interactions. The complex permittivity of polar-polar compounds can be related to molecular structure,[90] It provides valuable information about the molecular interactions and intra and intermolecular relaxation processes. Dielectric relaxation study through TDR makes it possible to determine complex permittivity over wide frequency range in a single measurements [91,92].
The dielectric properties of Monoalkyl ethers of diethylene glycol molecules are of great interest because changes in properties are chiefly related to chain length and molecular size [93-96]. Monoalkyl ethers have wide range of applications and are used as industrial solvents, surfactants, detergents and wetting agents. Due to great industrial applications of these molecules, it is interesting to investigate the molecular dynamics of these short-chain molecules. These short chain molecules have end –OH group and they can enter either into intra- and intermolecular hydrogen bonding. Intermolecular hydrogen bonding in the liquid state plays an important role in relaxation phenomenon. This interaction retards the molecular reorientation since breaking and reforming of hydrogen bonds is required for molecular rotation in an alternating electric field.

Amide is defined as any compound derived from ammonia by substitution of an acid radical for hydrogen, or from an acid by replacing the -OH group by -NH₂ [97-100]. Amides can participate in hydrogen bonding as hydrogen bond acceptors and donors. Amide plays a role in the synthesis of some condensation polymers, such as nylon and Aramid (Twaron / Kevlar). Amide generally represented by the formula: R₁ (CO) NR₂R₃, where either or both R₂ and R₃ may be hydrogen. It can also be regarded as a derivative of a carboxylic acid in which the hydroxyl group has been replaced by an amine.

The mixing properties of these liquids have not been studied and hence it is planned to study the interaction among Monoalkyl ethers of diethylene Glycol and Amides using time domain reflectometry technique at various temperatures and compositions. Information at molecular level can be gained from a study of dielectric behaviour.

In the present work an attempt has been made to study the dielectric relaxation behavior of Monoalkyl ethers of diethylene glycol with Amids at different temperatures.

All the chemicals used for present investigation are of spectroscopy grade. The systems chosen for the present work are as follows.
Pure Liquids

**Monoalkyl Ethers Of Diethylene Glycol**
1. Diethylene glycol monomethyl ether (DGME).
2. Diethylene glycol monoethyl ether (DGEE).
3. Diethylene glycol monobutyl ether (DGBE).

**Amides**
1. Formamide (FMD).
2. N,N-dimethylformamide (DMF).
3. N,N-dimethylacetamide (DMA).

**Monoalkyl Ethers Of Diethylene Glycol – Amides**

A) DGME + Amides
1. Diethylene glycol monomethyl ether + Formamide
2. Diethylene glycol monomethyl ether + N,N-dimethylformamide
3. Diethylene glycol monomethyl ether + N,N-dimethylacetamide

B) DGEE + Amides
1. Diethylene glycol monoethyl ether + Formamide
2. Diethylene glycol monoethyl ether + N,N-dimethylformamide
3. Diethylene glycol monoethyl ether + N,N-dimethylacetamide

C) DGBE + Amides
1. Diethylene glycol monobutyl ether + Formamide
2. Diethylene glycol monobutyl ether + N,N-dimethylformamide
3. Diethylene glycol monobutyl ether + N,N-dimethylacetamide

All above binary systems are studied for 11 different concentrations over the frequency range of 10 MHz to 20 GHz. Temperature dependent variations in dielectric parameters for four different temperatures are also reported for all the systems. The dielectric parameters i.e. dielectric constant and relaxation time have been determined. The static permittivity and relaxation time have been used to obtain the excess dielectric parameters, which give information related to molecular interaction. The Kirkwood correlation factor and Bruggeman factor for all systems have been determined. The obtained results are discussed on the basis of excess permittivity, excess inverse relaxation time, Kirkwood correlation factor, Bruggeman factor, enthalpy and entropy.
Physical Constant of Pure Liquids:

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name of Compound</th>
<th>Molecular Formula</th>
<th>Permittivity ((\varepsilon_r)) Lit. Value</th>
<th>M. W. in g/mol</th>
<th>Density in g/cm(^3)</th>
<th>Dipole Moment ((\mu)) in D</th>
<th>R. I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diethylene glycol monomethyl ether</td>
<td>C(<em>5)H(</em>{12})O(_3)</td>
<td>13.77 (308 K)(^a)</td>
<td>120.147</td>
<td>1.023</td>
<td>1.60</td>
<td>1.426</td>
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<tr>
<td>2</td>
<td>Diethylene glycol monoethyl ether</td>
<td>C(<em>6)H(</em>{14})O(_3)</td>
<td>12.58 (308 K)(^a)</td>
<td>134.174</td>
<td>0.999</td>
<td>1.60</td>
<td>1.427</td>
</tr>
<tr>
<td>3</td>
<td>Diethylene glycol monobutyl ether</td>
<td>C(<em>8)H(</em>{18})O(_3)</td>
<td>9.63 (308 K)(^a)</td>
<td>162.227</td>
<td>0.967</td>
<td>2.05</td>
<td>1.432</td>
</tr>
<tr>
<td>4</td>
<td>Formamide</td>
<td>CH(_3)NO</td>
<td>111 (293K)(^b)</td>
<td>45.0406</td>
<td>1.134</td>
<td>3.73</td>
<td>1.447</td>
</tr>
<tr>
<td>5</td>
<td>N,N-dimethylformamide</td>
<td>C(_3)H(_7)NO</td>
<td>42 (298K)(^b)</td>
<td>73.0938</td>
<td>0.9444</td>
<td>3.82</td>
<td>1.43</td>
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<tr>
<td>6</td>
<td>N,N-dimethylacetamide</td>
<td>C(_4)H(_9)NO</td>
<td>38.27 (303K)c</td>
<td>87.1204</td>
<td>0.937</td>
<td>3.7</td>
<td>1.437</td>
</tr>
</tbody>
</table>

\(^c\) Digest of Literature on Dielectrics, Vol 39, National Academy of Sciences; Washington DC, 1975
Molecular Structures of Pure Liquids:

<table>
<thead>
<tr>
<th>Molecular Structure</th>
<th>Molecular Formula</th>
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<tbody>
<tr>
<td>Diethylene glycol monomethyl ether</td>
<td>CH₃OCH₂CH₂OCH₂CH₂OH</td>
</tr>
<tr>
<td>Diethylene glycol monoethyl ether</td>
<td>C₂H₅OCH₂CH₂OCH₂CH₂OH</td>
</tr>
<tr>
<td>Diethylene glycol monobutyl ether</td>
<td>CH₃(CH₂)₃OCH₂CH₂OCH₂CH₂OH</td>
</tr>
<tr>
<td>Formamide</td>
<td>HCONH₂</td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>HCON(CH₃)₂</td>
</tr>
<tr>
<td>N,N-dimethylacetamide</td>
<td>CH₃CON(CH₃)₂</td>
</tr>
</tbody>
</table>
REFERENCES


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