1. Introduction

Dielectric spectroscopy also known as impedance spectroscopy, measures the dielectric properties of a medium as a function of frequency [1-8]. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. The orientation polarization decay exponentially with time; the characteristics time of this exponential decay is called relaxation time. Dielectric study of Glycols, alcohols, polar molecules and polymers in pure liquid state provides important information about molecular configurations of a system. There are several books which deal with the theory of dielectric behavior and molecular structure [9-12]. The dielectric properties of polar liquids are studied by its interaction with electromagnetic fields. When polymeric substance is subjected to electric field, a polarization phenomenon occurs. The electric field may cause a small displacement of electrons, which produce an induced electric moment in the molecules. The electric moment persists during the whole time the field is applied. The displacement of polar groups requires some time and is thus dependent on frequency and temperature, which lead to different dispersion phenomena accordingly to orientation of dipoles. At frequencies and temperatures, where dispersion occurs, some part of the electric energy is stored which is proportional to dielectric permittivity while some part of energy is lost which is proportional to dielectric loss. Dielectric studies involve measurements of dielectric permittivity and dielectric loss at different microwave frequencies. The measurements can be used to determine dielectric relaxation and distribution parameter. The dielectric relaxation studies are used to investigate the molecular and intra-molecular motions which depend on the molecular structure, size, shape and intra-molecular forces causing hindered motion.
Over the past few years, widespread theoretical and experimental studies concerning the microwave dielectric relaxation of water structure and aqueous systems have been reported. [13-21] The dynamics and physical properties of aqueous solutions have been investigated extremely by means of various techniques such as Neutron Scattering, light scattering, Nuclear Magnetic Resonance (NMR), and broadband dielectric spectroscopy.[13-21] Dielectric relaxation spectroscopy has proven a powerful tool for an investigation of H-bond rearrangement dynamics and has been widely applied for investigating super cooled and glass forming liquids.

Glycols are interesting glass forming liquid and strong tendency to form a hydrogen bonding with other molecules due to presence of hydroxyl groups. Glycols having two hydroxyl groups have intermediate properties between single hydroxyl group alcohols and three hydroxyl group glycerin. Moreover, due to longer chain and presence of two hydroxyl groups the solubility in aqueous media is more. Water constitutes the biological basic of our life having unusual properties due to its dynamics and structures which are dominated by intermolecular hydrogen bonds. The dielectric relaxation has been studied as a function of –OH group in glycols order to understand the significance of hydrogen bond interaction in glycol. Glycols are characterized by the formula H [OCH $(\text{CH}_3)$ $(\text{CH}_2)$]$_n$ OH for $n=1$ refers as Propylene glycol also called as diols with -OH groups are attached to terminal carbon atom. It is mainly used as a building block in production of some kinds of polymers by the method of condensation polymerization. Dipropylene Glycol (DPG) with $n=2$ and Tripropylene glycol (TPG) with $n=3$ has two OH groups attached to terminal carbon atoms. It is widely used in plastic industries for the production of polyester fibers, hydraulic and brake fluids and also it is used as humectants in cosmetics, food additive products, and resin solvent in the production of printing inks.
The main interest of the study is to understand the structural and dynamical behavior of aqueous glycols using Time Domain Reflectometry (TDR) Technique. The literature survey shows that, many group studied the dynamics of glycols, different characterizations were studied using different techniques like light scattering [22-24], optical Kerr-effect [25] as well as photo thermal. [26] The dielectric relaxation response was reported earlier [14-15] using Johari-Goldstein beta relaxation also primary alpha and secondary beta relaxation process has been discussed [13-15,27]. Moreover some physical properties of aqueous mono, di and tri propylene glycol have been reported. [28] The dielectric spectra of propylene glycol and Tripropylene Glycol have been studied using TDR technique; [29-30] the dielectric relaxation study is very useful for the understanding intermolecular interaction and hydrogen bonding interaction in aqueous mixture due to dipole-dipole interaction.

In this study we performed temperature dependent dielectric properties of following binary mixtures

1. Propylene Glycol
2. Propylene Glycol-1, 3
3. Dipropylene Glycol
4. Tripropylene Glycol

The physical properties of glycols are given in Table 1.1 and the structural formula for Propylene Glycol (1,2-propanediol), Propylene Glycol-1,3 (1,3-propanediol), Dipropylene Glycol and Tripropylene Glycol are shown in Figure 1.1(a),(b),(c) and (d), respectively.
**Physical Parameters of systems studied**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mol. Wt. (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Electric Dipole Moment (D)</th>
<th>Static dielectric constant (ε₀)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>18.1</td>
<td>0.997</td>
<td>1.85</td>
<td>79.10</td>
<td>1.33</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>76.10</td>
<td>1.035</td>
<td>2.20</td>
<td>26.85</td>
<td>1.4314</td>
</tr>
<tr>
<td>Propylene Glycol-1,3</td>
<td>76.09</td>
<td>1.051</td>
<td>2.50</td>
<td>35.29</td>
<td>1.4386</td>
</tr>
<tr>
<td>Dipropylene Glycol</td>
<td>134.2</td>
<td>1.022</td>
<td>1.72</td>
<td>20.16</td>
<td>1.4415</td>
</tr>
<tr>
<td>Tripropylene Glycol</td>
<td>192.3</td>
<td>1.019</td>
<td>2.27</td>
<td>13.39</td>
<td>1.444</td>
</tr>
</tbody>
</table>

Table 1.1 Physical properties of water and Glycols
Molecular Structures of system studied

Figure 1.1(a) Molecular Structure of Propylene Glycol

Figure 1.1 (b) Molecular Structure of Propylene Glycol-1, 3
**Figure 1.1 (c)** Molecular structure of Dipropylene Glycol

**Figure 1.1 (d)** Molecular Structure of Tripropylene Glycol
Time Domain Reflectometry (TDR) [31-38] is used to describe a technique of observing time dependence reflection response of sample under study. H Fellner-Feldegg [31] first developed it for measurement of loss and permittivity at very high frequency. Time domain reflectometry is prepared to suitable fast rising pulse is applied to a transmission line, usually a co-axial line with 50 Ω impedance. A co-axial line is connected to sampling device (sample holder).

The complex permittivity spectra of aqueous solution are determined by the Havrlik-Negami (HN) equation [29, 30]. The data were analyzed using Havrliki-Negami model. The non linear least square fit method is used to calculate the dielectric relaxation parameters by the following equation [29].
\[ \varepsilon^* (\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega \tau)^{1-\alpha}}^\beta \]

Where \( \varepsilon_0 \) is the static dielectric constant, \( \varepsilon_\infty \) is the permittivity at high frequency, \( \tau \) the relaxation time, \( \alpha \) and \( \beta \) are the distribution parameters.

The main purpose of this study is to determine microwave dielectric relaxation study and complex permittivity spectra of water and aqueous systems in the frequency range of 10MHz-30GHz at different concentration using Time Domain Reflectometry technique (TDR). The dielectric parameters like static Dielectric constant, Relaxation time, Kirkwood correlation factor, Bruggeman factor and Thermodynamic parameters have also been investigated for Glycol-Water mixture.

The present thesis comprises of seven chapters.

The first chapter presents an introduction to Glycol, Water and aqueous systems and significance of the dielectric studies. A brief review of literature regarding the dielectric study of Glycols selected for the present investigation is outlines.

The second chapter related to the theory of dielectric permittivity, the Debye relaxation theory, Cole relaxation theory, Cole-Davidson relaxation theory, the Havriliak-Nagami relaxation theory and Kirkwood dielectric theory, Bruggeman dielectric theory, Excess dielectric theory and Thermo dynamical properties are included in this chapter.

Third chapter deals with the methodology adopted for the study of water and Glycols–Water mixtures, which includes principles of Time Domain Reflectometry, measurement procedure of dielectric permittivity and data analysis.
Chapter four deals with systematic dielectric relaxation studies of binary mixture of Propylene Glycol-water. The values of dielectric permittivity measured at different temperature and at different concentrations in the frequency range of 10 MHz to 30 GHz. Dielectric parameters such as static dielectric constant, Relaxation time, Kirkwood correlation factor, Excess dielectric properties and thermo dynamical properties are also determined.

Chapter five deals with dielectric study of binary mixture of Dipropylene Glycol-Water. The values of dielectric permittivity measured at different concentrations and temperature in the frequency range of 10 MHz to 30 GHz with temperature variation. The dielectric parameters such as static dielectric constant, Relaxation time, Kirkwood correlation factor, Excess dielectric constant, Bruggeman factor are also determined.

Chapter six deals with systematic dielectric study of binary mixture of Tripropylene Glycol-Water. The values of dielectric permittivity measured at different concentrations and temperatures in the frequency range of 10 MHz to 30 GHz and dielectric parameters such as static dielectric constant, Relaxation time, Kirkwood correlation factor and Excess dielectric constant are also determined.

The summary and conclusion of the present study are given in Chapter seven.
References:


[27] M. Köhler, P. Lunkenheimer, Y. Goncharov, R. Wehn, A. Loidl. PACS: 64.70.pm, 77.22.Gm


[34] Tektronix DSA8200 Samplig Oscilloscope and 80E08 TDR Plug-in Modules user guide.


