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Dielectric Relaxation Study of Binary Mixture Using Kirkwood Correlation Factor - Time Domain Reflectometry Technique

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Abstract

We have reported, the results of dielectric parameters for Diethylene glycol Monomethyl ether (DGME) - chlorobenzene (CB) binary mixture over the entire range of concentrations in the frequency range from 10MHz-20GHz at different temperatures by time domain reflectometry (TDR) technique. Dielectric parameters viz. dielectric constant (ε_0), relaxation time (τ in ps) were obtained from complex permittivity spectra using nonlinear least squares fit method. Using these parameters excess permittivity (${\varepsilon_0}^E$), excess inverse relaxation time$\left({1/\tau}^E\right)$, Kirkwood correlation factor (g^{eff}) were determined. On the basis of these parameters, intermolecular interaction and dynamics of molecules at molecular level are predicated. The Kirkwood correlation factor is used to understand the molecular orientation in the mixture. In this paper, the given data provide information regarding solute-solvent interaction.

Keywords: Time domain reflectometry, dielectric parameters, Kirkwood correlation factor.

Introduction

The objective of this paper is to apply our experimental data of Diethylene glycol Monomethyl ether (DGME) - chlorobenzene (CB) system to verify the Kirkwood correlation factor and investigation of hydrogen bonding dynamics among Diethylene glycol Monomethyl ether (DGME) - chlorobenzene (CB), molecules in the mixture at different temperatures using time domain reflectometry (TDR) technique. In this study, diethylene glycol monomethyl ether has been used in binary mixtures with chlorobenzene. It is interesting to see the effect of aromatic group in glycol ether. The dielectric study of binary polar liquids is important for understanding the hydrogen bonding.

Dielectric relaxation Study of binary mixture in microwave frequencies has become very important tool to get information regarding intermolecular and intramolecular interaction between mixing components. Structural information about the liquids by dielectric relaxation parameter can be obtained by Kirkwood correlation parameter: [1,2]. The Kirkwood correlation factor values of binary mixtures were determined from the measured values of the static dielectric constant and high-frequency limit dielectric constant.

In the study of dielectric relaxation parameters, the Kirkwood correlation factor of polar-polar mixtures

has a considerable significance in providing valuable information about solute solvent interaction. Dielectric relaxation study of solute solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multimers:[3].

The effect of high frequency microwaves causes variations in basic properties of binary mixtures such that their dielectric properties change accordingly. The dielectric parameters reveal intermolecular interactions with extraordinary significance to study effect of high frequency on polarization and structural variations in the solutions at different places such as in scientific research laboratories, medical field and at many other places: [4]. A dielectric study yields the Kirkwood correlation factor, which is strongly correlated with the solute solvent interaction:[5]. Chlorobenzene has a benzene ring with one chlorine atom. It is colourless, flammable liquid and used as a solvent and intermediate in the preparation of other chemicals as well: [6,7].

Dielectric dispersion studies in mono alkyl ethers of ethylene glycol and of diethylene glycol have been carried out in microwave frequency region in pure liquid state: [8]. Dielectric relaxation parameters were reported for chloro group-alcohol systems:[9]. Time domain reflectrometry: [10,11] in reflection mode has been used to obtain the dielectric parameters. Liquid mixtures give very effective information about molecular interactions. Therefore, the study of liquid mixtures having great importance in the field of molecular physics: [12]. The dielectric relaxation parameters of binary mixture give considerable information about solute-solvent interaction. Time Domain Reflectometry (TDR) was used to obtain the dielectric parameters of the system: [13,15]. It also provides the information about the charge distribution in a molecular system. The investigation shows that the effective dipoles of the system decrease and produces opposing field, so that dipole rotates slowly: [16].

The bilinear calibration method has been used to obtain the dielectric parameters, namely static dielectric constant (ε_0), relaxation time (τ). Using these parameters the excess permittivity ($\varepsilon_0{}^{E}$), excess inverse relaxation time $(1/\tau)^{E}$, Kirkwood correlation factor(g^{eff})are calculated. It provides information related to molecular interaction.

The Kirkwood correlation factor (g^{eff}) is also a parameter for obtaining information regarding orientation of electric dipoles in polar liquids: [14,17]. The value of this parameter changes Kirkwood correlation factor from one pure liquid to that of second liquid:[1]. The concept of orientation with increasing and decreasing value of dipoles is revealed using Kirkwood correlation factor:[18]. To understand the significance of association effect due to the hydrogen bonding, it is very useful to compute the values of Kirkwood correlation factor for the binary mixtures. The Kirkwood correlation factor (g^{eff}) explains the short-range interaction between electric dipoles and gives information regarding orientation of electric dipoles in polar liquids [12]. The effective dipoles in the mixture will be more than the corresponding average value in pure liquids: [19].

Methods And Materials

Materials

The chemicals used in this work are diethylene glycol monomethyl ether (LR grade) and chlorobenzene. Diethylene glycol Monomethyl ether (DGME) and chlorobenzene (CB) are polar liquids, one belongs to Glycol ether group and other with aromatic group. The chemicals are of spectroscopic grade and are used without further purification. The solutions are prepared at eleven different volume fractions of chlorobenzene from 0 to 1 in step of 0.1. These volume fractions are converted to mole fractions for further calculations.

Apparatus and Data Analysis

The complex permittivity spectra of the mixtures of Diethylene glycol Monomethyl ether (DGME) with chlorobenzene (CB) at different temperatures have been measured in the frequency range between 10 MHz to 20 G Hz using time domain reflectometry method: [20- 22].

The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug -in module is used. A fast-rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of characteristic impedance of 50 Ω. The transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell connecter with 3.5mm outer diameter & 1.35 mm effective pin length. All measurements were done under open load conditions.

The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. In this experiment, a time window of 5ns was used. The reflected pulses without sample R_1 (t) & with sample R_x (t) were digitized in 1024 points in the memory of the oscilloscope & transferred to a pc through 1.44 MB floppy diskette drive.

A temperature controller system with a water bath & thermostat has been used to maintain the constant temperature within the accuracy limit of + or - 273 k. "Figure 1". Shows Block Diagram of Experimental setup.

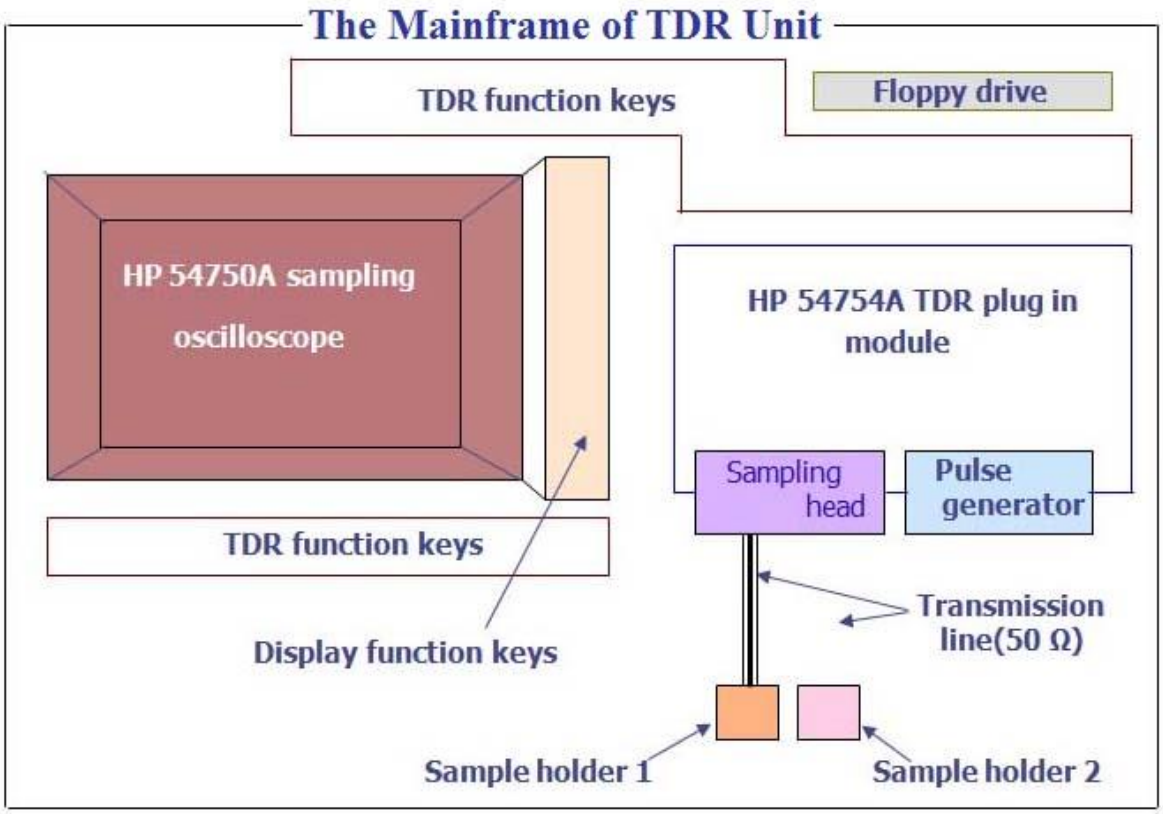

Fig .1. Block Diagram of Dual Channel TDR Unit.

To study the dielectric properties of the mixture of polar liquids, the most reliable technique is time domain technique developed by Cole et.al. :[11, 23-25]. The time dependent data were processed to obtain complex reflection coefficient spectra ρ*(ω) over the frequency range from 10 MHz to 20 GHz using Fourier transformation: [26, 27], as

$$\rho^{*}(\omega) = \left[\frac{c}{j\omega d}\right]\left[\frac{p(\omega)}{q(\omega)}\right] \quad (1)$$

Where p (ω) and q(ω) are Fourier transforms of [R_1 (t) - R_x (t)] and [R_1 (t) +R_x (t)], respectively. C is the velocity of light, ω is angular frequency and d is the effective pin length and j $= \sqrt{-1}$.

The complex permittivity spectra ε*(ω) were obtained from reflection coefficient spectra ρ*(w) by applying a bilinear calibration method: [28]. The experimental values of ε*(ω) are fitted the Debye equation:[29].

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + j\omega\tau} \quad (2)$$

where, ε_0, ε_∞ and τ as fitting parameters. The value of ε_∞ was kept to be constant as the fitting parameters are not sensitive to ε_∞.A non-linear least squares fit method:[30] used to determine the values of dielectric parameters.

Information related to solute- solvent interaction may be obtained by excess properties: [31,32] i.e. static dielectric constant and relaxation time in the mixtures. Using these parameters the excess dielectric properties, Kirkwood correlation factor was determined. Kirkwood correlation factor (g^{eff}) : [33] is also a parameter containing information regarding orientation of electric dipoles in polar liquids provides information about parallel or antiparallel alignment of dipoles. The effective angular correlation (g^{eff}) between molecules is calculated using modified form of equation,

$$\frac{4\pi N}{9kT}\left(\frac{\mu_A{}^2\rho_A}{M_A}\varphi_A + \frac{\mu_B{}^2\rho_B}{M_B}\varphi_B\right) g^{\text{eff}} = \frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad (3)$$

where, μ is the dipole moment in Debye, ρ is density at temperature T. M is molecular weight. K is Boltzmann constant, N is Avogadro's number, φ_A is volume fraction of liquid A, φ_B is volume fraction of liquid B.

RESULT AND DISCUSSION

The g^{eff} values calculated from equation (3) are given in Table 1.for the Binary Mixture.

Table 1: Kirkwood correlation factor for DGME-Chlorobenzene system

Volume fraction of CB	288 K	298 K	308 K	318 K
0	3.22	3.17	3.14	3.12
0.1	2.93	2.91	2.90	2.90
0.2	2.61	2.60	2.58	2.58
0.3	2.31	2.30	2.27	2.27
0.4	2.04	2.02	2.00	2.00
0.5	1.81	1.79	1.78	1.78
0.6	1.59	1.58	1.57	1.57
0.7	1.39	1.37	1.37	1.36
0.8	1.18	1.17	1.17	1.17
0.9	0.99	0.99	0.98	0.98
1	0.83	0.82	0.81	0.80

The value of g^{eff} is 3.22 for Diethylene glycol Monomethyl ether at 288 K which decreases to 3.12 at 318 K. The values confirm the formation of hydrogen bonding in pure Diethylene glycol Monomethyl ether system. These values greater than unity at all temperatures suggesting parallel orientation of electric dipoles. The corresponding values for CB are 0.83 and 0.80 respectively, indicating weak dipole interaction resulting formation of anti-parallel arrangement of dipoles in the pure system of CB: [34-38].
It can be seen from the table that for diethylene glycol monomethyl ether (DGME), g^{eff} values are greater than unity for the system at all temperatures, suggesting parallel orientation of electric dipoles. The g^{eff} values for pure chlorobenzene are less than unity indicating antiparallel orientation of electric dipoles. The g^{eff} values for pure chlorobenzene are close to unity for all temperatures studied indicating no dipole correlation: [38,39].
The observed g^{eff} values are greater than unity in the mixtures leads to the conclusion that the molecules associate to form multimers. The g^{eff} values of these mixed solvents show some deviation from ideality, which confirms the net change in dipolar ordering of the mixture constituents due to H-bond complexion. The Kirkwood correlation factor is greater than unity and forms multimers with a parallel ordering of their dipole moment in the mixtures. The values of Kirkwood correlation factor g^{eff} are greater than unity which shows that there are large multimers form with parallel dipole moment:[12]. The concept of orientation with increasing and decreasing value of dipoles is revealed using Kirkwood correlation factor.g^{eff} value show that the dipole dipole interactions are increased showing parallel orientation with strong interactions:[40].

CONCLUSION

The concentration and temperature dependent dielectric parameters values are taken as evidence to interpret the nature of intermolecular interaction and dynamic structure in binary mixture molecules. The Kirkwood correlation factor is used to understand the molecular orientation in the mixture. This data provides information regarding solute solvent interaction in liquids. It appears that the dipole -dipole interaction favours antiparallel structures; whereas the hydrogen bonded interaction favours parallel structures. The technique has been proved to be an efficient tool for the study of molecular dynamics in mixtures under the sufficiently wide frequency range.

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