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Dielectric Relaxation Studies on Binary Polar Mixtures of Diethylene Glycol with Ethyl Benzoate Using Time Domain Reflectometry*

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Abstract: It is interesting to study the nature of intermolecular interactions between associative and non-associative polar liquids. Dielectric relaxation measurements on polar-polar binary mixtures of ethyl benzoate with mono diethylene glycol were carried out for eleven different concentrations at temperatures (298K, 303K, 308K and 313K) using Time Domain Reflectometry (TDR) over the frequency range from 10MHz to 10 GHz. The Kirkwood correlation factor and excess dielectric properties were determined and discussed to yield information about the intermolecular interactions in binary system. The non-linear variation has been observed in relaxation time with increasing of alcohol mole concentration. The Bruggeman plot shows a deviation from linearity. This deviation was attributed to some sort of molecular interaction, which may take place between the ester and alcohol molecules. The excess static permittivity and excess inverse relaxation time values are negative for the studied binary systems, indicating the solute-solvent interaction to exist between ester and alcohol, producing a field in such a way that the effective dipole rotation is hindered.

Keywords: Dielectric relaxation, Time domain reflectometry, Bruggeman factor, Kirkwood correlation factor.

Introduction

Dielectric relaxation study of solute-solvent mixture at microwave frequency gives information about molecular interactions in the system, formation of monomers and multimers. The characterization of dielectric materials includes the measurement of complex permittivity as a function of frequency at a given temperature or as a function of temperature at a given frequency. The measurement of dielectric properties at wide frequency range gives information regarding the conduction mechanism, interfacial polarization, molecular dynamics and relaxation behavior phenomena [1]. The confirmations of the homogeneous and heterogeneous molecular interactions in polar binary mixtures are the central topics in liquid state physics and chemistry [1-18]. Dielectric relaxation spectroscopy was proved to be a powerful tool for the investigation of H-bond rearrangement dynamics and has been widely applied to study the pure solvents, solvent-solvent mixtures [19, 20]. The presence of hydrogen bonding brings a considerable change in the relaxation time and dipole moment of the binary system, with respect to the corresponding values in the pure components [21]. Dielectric investigation of binary polar liquid mixtures consisting of one associative and other non-associative liquids, provides valuable

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information regarding molecular complex formation in solution. Esters are non-associated polar liquids with C = 0 group. Alcohols are industrially and scientifically important organic compounds and their physical and chemical properties are largely determined by the OH-group. Alcohols are strongly associated in solution because of dipole-dipole interaction and hydrogen bonding.

The strength of the molecular association depends on several factors, including the molecular structure, temperature, solvent and other factors [22]. Therefore, the solution chemistry of these compounds can be strongly influenced by the aggregation phenomena, which can play a significant role in the physical properties of these polar molecules [23]. Dielectric relaxation studies of aromatic esters in the microwave region for different temperatures are reported by Saxena *et al*. [24] using the Higasi method. There are many studies of the dielectric behavior of alcohol mixtures with structure breaking and structure making [25-30]. The studies of Kirkwood correlation factor provide valuable information regarding the solute-solvent interactions in binary mixtures, especially when one of the components has antiparallel orientation of dipoles [31].

In course of the present study, the dielectric parameters for aromatic ester ethyl benzoate, with diethylene glycol were investigated experimentally for different concentrations in the microwave region (10MHz to 10 GHz) at 298K, 303K, 308K and 313K using time domain reflectometry (TDR). The relaxation behavior of these mixtures was explained by the Debye model. The excess dielectric properties are reported. The Kirkwood correlation factor is used to understand the molecular orientation in the mixture.

Materials and Methods

Materials and Sample Preparation

AR grade alcohol (≥99.5% of diethylene glycol) was purchased from Sd Fine Chemicals. AR grade esters (≥99.5% of ethyl benzoate) were supplied by Sigma Aldrich India. The chemical compounds were used without further purification. In each system, nine different solute concentration binary mixtures were prepared gravimetrically.

Measurements

The densities of pure compounds were measured by relative density method using 10 ml specific gravity bottle. The mass measurements were performed using digital electronic balance (Adventurer OhausAR2140) with an accuracy of ±0.0001g. Abbe's refractometer (SIPCON model) with sodium D line was used to measure the refractive indices of mixture solutions at different temperatures. Constant temperature was maintained by water circulating (ESCY IC 201 model) temperature controller system with an accuracy of 0.1 K. The square of refractive index value was taken as optical frequency dielectric constant ($n^2 = \varepsilon_\infty$). The uncertainties of measured density and refractive index were ± 0.2 $kg \cdot m^{-3}$ and 0.00005, respectively. Frequency dependent complex dielectric spectra of pure compounds and their binary mixtures were determined by (AgilentnfiniiumDCA-J86100 A with sample oscilloscope HP 54754 A model) TDR. A 39 ps rise time step voltage pulse was generated by a tunnel diode and fed through50 Ω impedance semi rigid coaxial cable having pin length of 0.135 mm. Coaxial probe was dipped in the sample cell which was shielded by water circulating temperature control system with an accuracy of 0.5 K. All measurements were carried out in an open load condition. The variation in step pulse was monitored after it is reflected from air and sample by sample oscilloscope and recorded in time window of 2 ns. The reflected pulses were digitized into 1200 points and used for further data analysis. The frequency dependent complex spectra were obtained from reflection coefficient spectra. The procedures for data analysis were discussed in previous reports [32, 33]. The measured refractive index and density values were reported in Table 1(a) &1(b), respectively.

TABLE 1(a). Refractive index values of DEG + EB binary mixture at different temperatures.

X_2	298k	303k	308k	313k
0	1.38723	1.38300	1.37895	1.37484
0.1	1.38698	1.38273	1.37861	1.37452
0.2	1.38675	1.38247	1.37831	1.37422
0.3	1.38650	1.38219	1.37797	1.37389
0.4	1.38623	1.38189	1.37760	1.37353
0.5	1.38594	1.38157	1.37722	1.37315
0.6	1.38565	1.38126	1.37683	1.37278
0.7	1.38532	1.38089	1.37638	1.37235
0.8	1.38496	1.38048	1.37590	1.37187
0.9	1.38458	1.38005	1.37538	1.37136
1	1.38418	1.37961	1.37484	1.37084

TABLE 1(b). Density values of DEG and EB at different temperatures.

Temp	Diethyleneglycol	Ethyl benzoate
298k	1.12894	1.04152
303k	1.10963	1.03801
308k	1.10372	1.03486
313k	1.09830	1.03099

Results and Discussion

An example of frequency spectrum of complex dielectric constant (ε', ε") of diethylene glycol at 298K is shown in Fig. 2. The values of maximum dielectric loss (ε''_{max}) decrease with the increase in degree of polymerization (Fig. 1). It is because of the increase in molecular size of the DEG molecules.

The complex dielectric permittivity $\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$ was fitted with the Havriliak- Negami epression [34]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1 + (j\omega\tau)^{1-\alpha}\right]^\beta} \quad (1)$$

with ε_0, ε_∞, τ, α and β as fitting parameters. ε_0 is the static permittivity at limiting low frequency, ε_∞ is the limiting high frequency permittivity and is not fitted and assumed to be 3.5 for all concentrations studied here, τ is the average relaxation time, α and β are the distribution parameters and ω is the angular frequency.

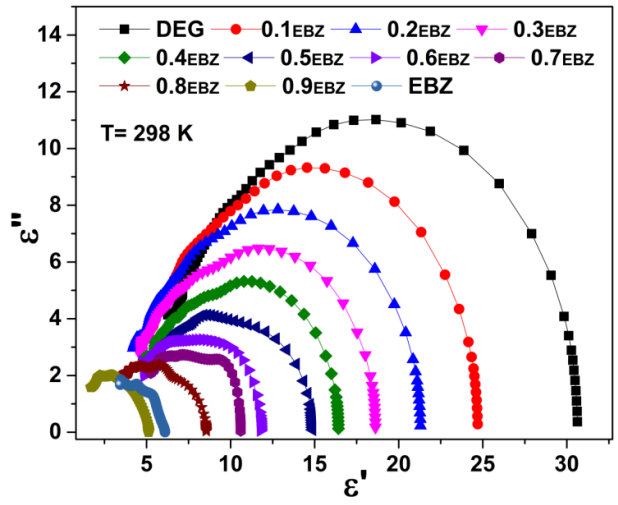

FIG. 1. Cole-cole plot at 298K for 11 different molefractions.

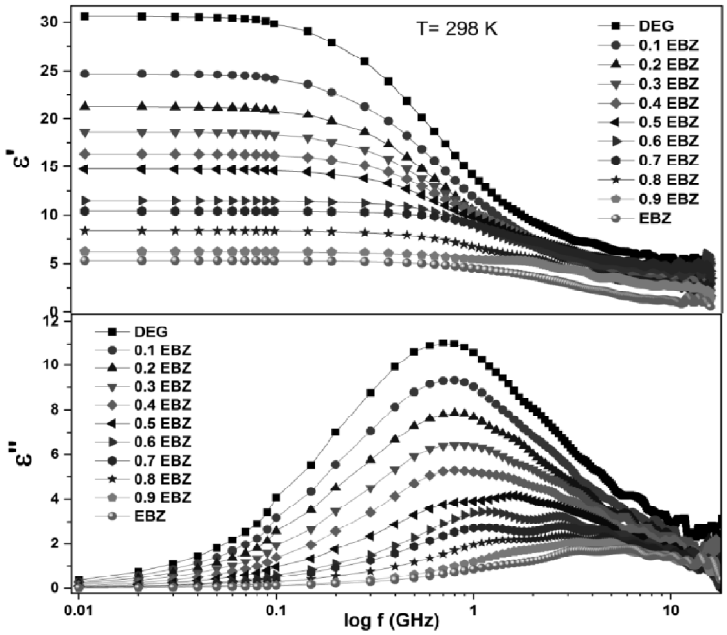

FIG. 2. Complex permittivity spectra of DEG+EB at 298K for 11 different molefractions.

The Havriliak-Negami [34] expression includes the Cole-Cole (β=1), Davidson-Cole (α=0) and Debye (α=0, β=1) relaxation models. A non- linear least squares fitting method was used to determine the values of the dielectric parameters [35]. Complex permittivity spectra for the binary mixture of DEG + EB are plotted in Fig.2.

The values of different dielectric parameters for DEG + EB binary mixture obtained by the Havriliak-Negami equation are presented in Table 2. It is observed that the dielectric relaxation in these mixtures can be represented by the Davidson-Cole relaxation behavior. However, at higher concentrations of EB in DEG, the dielectric dispersion spectra (Fig. 2) can be fitted with the Debye behavior (α=0, β=1). The observed values of dielectric parameter for DEG are in good agreement with those reported earlier [25]. The static dielectric constant decreases with the increase in degree of polymerization (Table 2). This is consistent with the behavior obtained by Sengwa *et al.* [36, 37].

The static dielectric constant decreases with the increase in molefraction of EB. Relaxation time also decreases with the increase in molefraction of EB. The increase in static dielectric constant in DEG + EB combination suggests that a single volume effect arises from the solute particles, thereby reducing their ability to orient in the applied field and so reducing the static dielectric constant. From the dielectric relaxation studies, it has been observed that the relaxation time (τ_0) of DEG in EB solutions increases with increasing DEG concentrations.

TABLE 2. Dielectric parameters of DEG + EB mixtures.

	ε_0				τ_0(ps)			
(X_2)	298K	303K	308K	313K	298K	303K	308K	313K
0.1	30.6	29.6	27.3	26.0	198.1	168.6	143.6	120.0
0.2	24.3	25.1	23.5	23.4	186.0	163.0	135.7	116.5
0.3	20.9	22.1	19.9	19.3	177.8	171.2	126.7	110.2
0.4	18.2	16.8	16.5	16.7	154.5	130.0	110.8	96.3
0.5	16.0	15.2	14.5	14.0	133.3	119.4	98.6	90.5
0.5	14.4	12.6	12.2	12.4	121.2	108.2	86.7	80.5
0.6	11.4	11.0	9.5	10.5	93.0	90.6	60.1	68.5
0.7	10.4	10.2	8.2	8.2	69.4	76.2	62.9	46.0
0.8	8.2	7.2	7.0	6.1	72.5	57.4	44.3	31.6
0.9	6.1	6.3	6.0	5.6	50.7	36.4	35.7	24.3
1.0	5.5	5.5	4.9	5.3	45.6	32.8	25.5	22.1

Kirkwood Correlation Factor

The Kirkwood correlation factor g gives the association effect due to the hydrogen bonding in the system [34]. The value of g in pure liquid can be obtained by the following equation [38]:

$$\frac{4\pi N\rho}{9kTM} g\mu^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2} \quad . \qquad (2)$$

For a binary mixture of dipolar liquids, the static dielectric permittivity needs to be considered as the dipole orientation correlation factor [38]. The modified form of Eq. (2) is used to study the orientation of electric dipoles in the binary mixtures as follows:

$$\left.\begin{aligned} &\frac{4\pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}X_1 + \frac{\mu_2^2\rho_2}{M_2}X_2\right) \\ &\times g^{eff} = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} + \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2} \end{aligned}\right\} \qquad (3)$$

where μ_1, ρ_1, M_1 and X_1 represent the Diethylene glycol dipole moment in gaseous state, density, molecular weight and molefraction, respectively. μ_2, ρ_2, M_2 and X_2 represent the ethyl benzoate dipole moment in gaseous state, density, molecular weight and molefraction, respectively. The ε_{0m} and $\varepsilon_{\infty m}$ are mixture dielectric constant and mixture dielectric constant at optical frequency ($n^2 = \varepsilon_{\infty m}$), respectively. g^{eff} is the effective Kirkwood correlation factor, that changes from Kirkwood correlation factor of one pure liquid to that of another liquid. If $g^{eff} = 1$, it

indicates that no association exists between unlike molecules in the mixture. If $g^{eff} > 1$, it indicates the existence of association between unlike molecules through parallel dipole interaction. Similarly, if $g^{eff} < 1$, it indicates the existence of association between unlike molecules through anti-parallel dipoles. The Kirkwood correlation factors for DEG in EB at different temperatures are given in Table 3. The observed (g^{eff}) values are greater than unity in all these DEG molecules, which leads to the conclusion that the molecules associate to form a multimer with parallel dipole moment. The Kirkwood correlation factor values for DEG are smaller than the corresponding values in EB.

TABLE 3. Kirkwood correlation factor for DEG + EB binary mixtures.

	g^{eff}			
(X_2)	298K	303K	308K	313K
0.0	3.340	3.298	3.101	3.013
0.1	2.767	2.932	2.800	2.849
0.2	2.495	2.705	2.483	2.457
0.3	2.286	2.149	2.154	2.224
0.4	2.121	2.045	1.991	1.968
0.5	2.016	1.783	1.759	1.838
0.6	1.681	1.644	1.427	1.631
0.7	1.624	1.627	1.290	1.322
0.8	1.335	1.170	1.158	0.996
0.9	1.004	1.075	1.042	0.980
1.0	0.972	0.983	0.856	0.988

The excess permittivity ε_0^E and the excess inverse of the relaxation time $(1/\tau)^E$ for diethylene glycol in ethyl benzoate mixtures are determined using the following equations [10, 38]:

$$\varepsilon_0^{\ E} = (\varepsilon_0)_M - \left[(\varepsilon_0)_W X_2 + (\varepsilon_0)_S (1 - X_2)\right] \quad (4)$$

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_1 X_1 + \left(\frac{1}{\tau}\right)_2 X_2\right] \quad (5)$$

Here, the subscripts M, W and S correspond to the mixture, Diethylene glycol and Ethyl benzoate, respectively and X_2 is the molefraction of EB in DEG. The variations of $(\varepsilon_0)^E$ and $(1/\tau)^E$ with molefraction of EB (X_2) in DEG are shown in Fig. 3(a, b).

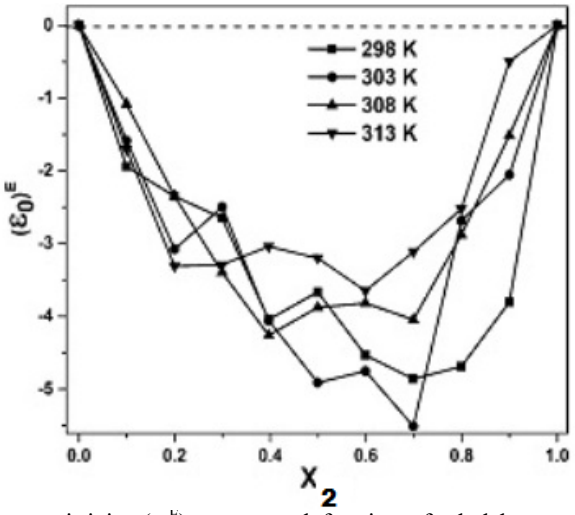

FIG. 3(a). Excess dielectric permittivity (ε_0^E) *versus* molefraction of ethyl benzoate (X_2) in DEG at different temperatures.

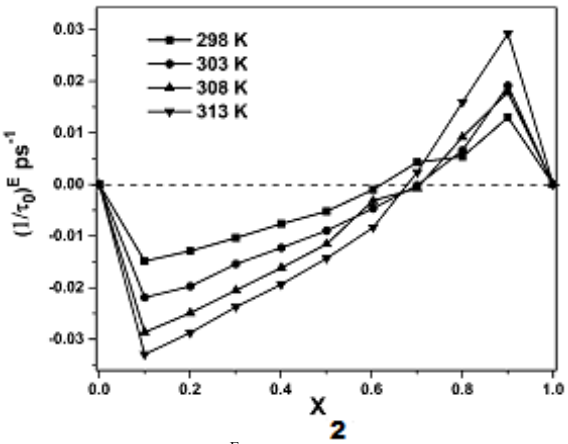

FIG. 3(b). The excess inverse relaxation time $(1/\tau)^E$) in GHz *versus* molefraction (X_2) of ethyl benzoate in DEG at different temperatures.

The excess dielectric constants for DEG + EB binary mixtures show negative behavior. The maxima are found to be in the EB-rich region (X_2 = 0.7). The negative values of excess parameters suggest that the addition of DEG to EB may create multimeric structure leading to a decrease in total permittivity as indicated by Fig. 3(a). The excess inverse relaxation times of these systems are positive in the EB-rich region. This indicates fast rotation of the dipoles. This may be due to the formation of monomeric structures in this region. In the DEG-rich region, these values are negative. This indicates the formation of structures;probably dimeric, which rotate slowly as in Fig. 3(b).

Bruggeman Dielectric Factor

The static permittivity of a mixture of two liquids lies in between two extremes of the static permittivity of the components.

Bruggeman [39] equation for binary mixture is given by:

$$f_B = \left[\frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})}\right]\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3} = 1 - X_2 \qquad (6)$$

where f_B is the Bruggeman dielectric factor. ε_{0m}, ε_{01} and ε_{02} are the static dielectric constants corresponding to mixture DEG.

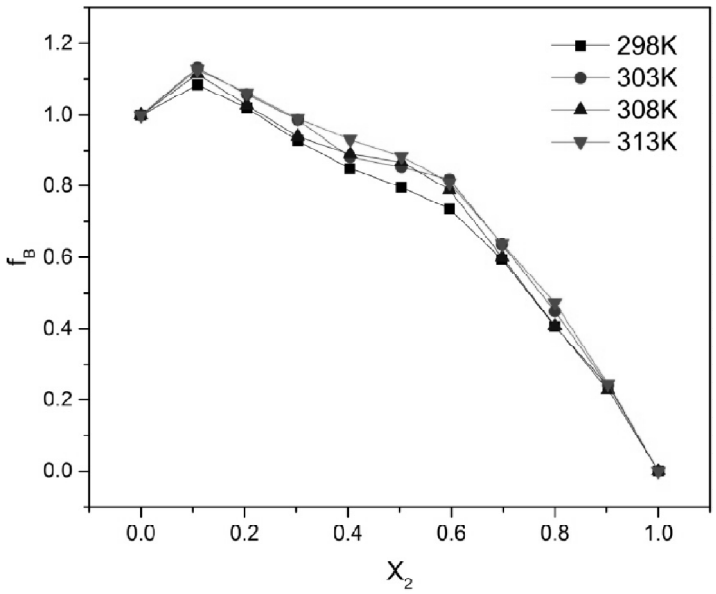

FIG. 4. Bruggeman dielectric factor (f_B) *versus* molefraction of EB in DEG at different temperatures.

X_2 is the molefraction of EB. The non-linear variation of Bruggeman factor with molefraction shows hetero-interaction, which may be due to hydrogen bonding of the-OH group of DEG with C=O of EB. The Bruggeman equation may be modified as:

$$f_B = \left[\frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})}\right]\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3} = 1 - \left[a - (a-1)X_2\right]X_2 \quad (7)$$

The molefraction (X_2) is modified by a factor of $1 - \left[a - (a-1)X_2\right]X_2$. The value of a contains the information regarding the change in the orientation of EB molecules in the mixture. The value of a has been determined by the least squares fit method and found to be 1.85 in DEG-EB mixtures. The value of a suggests that the effective volume fraction of diethylene glycol in ethyl benzoate solution is reduced considerably, indicating significant interaction between diethylene glycol and ethyl benzoate in the mixtures.

Conclusion

In this study, the concentration- and temperature-dependent dielectric complex spectra of ethyl benzoate with diethylene glycol have been investigated in the frequency range from 10 MHz to 10 GHz using Time Domain Reflectometry (TDR) method. The following conclusions could be drawn from the detailed analysis. The value of dielectric parameters shows the systematic change with increase in EB concentration, temperature and alcohol chain length. The formation of intermolecular interaction between solute and solvent molecules in the mixture has been confirmed from non-linear behavior of dielectric parameters with EB molefraction. The excess dielectric constant results show that the heterogeneous interaction strength increases with the increase in alcohol molecular size and stable aggregates formed at 1:2 ratio in DEG + EB binary systems. The excess inverse relaxation time values confirm that the intermolecular interaction produces the electric field which leads effective dipoles to rotate faster.

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