



Dielectric Relaxation Study of Diethylene Glycol Monomethyl Ether with Aromatic Compounds Using Time Domain Reflectometry Technique†

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AJC-11737

Complex permittivity spectra $\epsilon^* = \epsilon' - j\epsilon''$ of binary mixtures of diethylene glycol monomethyl ether with aromatic compounds were obtained in the frequency range of 10 MHz to 20 GHz at different temperatures 288, 298, 308 and 318 K using the time domain reflectometry technique. Dielectric parameters viz. dielectric constant (ϵ_0), relaxation time (t) were obtained from complex permittivity spectra using nonlinear least squares fit method using these parameters excess permittivity (ϵ_0^E), excess inverse relaxation time ($1/\tau$)^E, Bruggeman factor (f_B), Kirkwood correlation factor (g^{eff}) were determined. On the basis of above parameters, intermolecular interaction and dynamics of molecules at molecular level are predicated.

Key Words: Time domain reflectometry, Excess properties, Bruggeman factor, Kirkwood correlation factor.

INTRODUCTION

The dielectric study of binary polar liquids is important for understanding the hydrogen bonding and intermolecular dynamics of molecules at molecular levels. In this study, diethylene glycol monomethyl ether has been used in binary mixtures with nitrobenzene, chlorobenzene, one with glycol ether group and other with aromatic group. It is interesting to see the effect of aromatic group in glycol ether. Dielectric dispersion studies in monoalkyl ethers of ethylene glycol and of diethylene glycol have been carried out by Purohit and Sengwa¹ in microwave frequency region in pure liquid state. Dielectric relaxation parameters were reported by Pawar and Mehrotra for chloro group-alcohol systems².

Time domain reflectometry^{3,4} in reflection mode has been used to obtain the dielectric parameters. With these parameters, the excess permittivity, the excess inverse relaxation time, the Bruggeman factor, the Kirkwood correlation factor, has also been determined.

EXPERIMENTAL

The chemicals used in the present work were diethylene glycol monomethyl ether (LR grade), nitrobenzene, chlorobenzene were of spectroscopic grade and were obtained commercially with 99 % purity and used without further purification.

The solutions were prepared at eleven different compositions in steps of 10 % by volume. These volume fractions are converted to mole fractions for further calculations. Using this volume percentage the weight fraction is calculated as:

$$X_A = V_A \rho_A / (V_A \rho_A + V_B \rho_B) \quad (1)$$

where, V_A and V_B are the volume and ρ_A and ρ_B is the density of liquid A and B respectively.

Time domain reflectometry set up and data acquisition: The complex permittivity spectra of the samples were studied using time domain reflectometry method⁵. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A time domain reflectometry plug-in module was 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 ohm. The transmission line system under test was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell connector with 3.5 mm outer diameter and 1.35 mm effective pin length. 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 5 ns was used. The reflected pulses without sample $R_1(t)$ and with sample $R_2(t)$ were digitized in 1024 points in the memory of the oscilloscope and transferred to a pc through 1.44 MB floppy diskette drive. A temperature controller system with a water bath and thermostat

†Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

has been used to maintain the constant temperature within the accuracy limit of ± 273 K.

Data analysis: The time dependent data were processed to obtain complex reflection coefficient spectra, $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz using Fourier transformation⁶ as:

$$\rho^*(\omega) = \left[\frac{c}{j\omega d} \right] \left[\frac{p(\omega)}{q(\omega)} \right] \quad (2)$$

where, $p(\omega)$ and $q(\omega)$ 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 $\epsilon^*(\omega)$ were obtained from reflection coefficient spectra, $\rho^*(\omega)$ by applying a bilinear calibration method. The experimental values of $\epsilon^*(\omega)$ are fitted the Debye equation⁷.

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \quad (3)$$

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 method⁸ used to determine the values of dielectric parameters.

Information related to solute- solvent interaction may be obtained by excess properties⁹ *i.e.* static dielectric constant and relaxation time in the mixtures. The excess permittivity is defined as:

$$\epsilon_0^E = (\epsilon_0)_m - [(\epsilon_0)_A X_A + (\epsilon_0)_B X_B] \quad (4)$$

where, X is the mole fraction and the subscripts m , A and B represent mixture, solute and solvent respectively. The excess permittivity provides qualitative information about multimer formation in the mixture as follows:

- (a) $\epsilon^E = 0$ Indicates that liquid A liquid B do not interact;
- (b) $\epsilon^E < 0$ Indicates that liquid A and liquid B interact in such a way that the effective dipole moment gets reduced. The solute and solvent may form multimers leading to less effective dipoles;
- (c) $\epsilon^E > 0$ Indicates liquid A and liquid B interact in such a way that the effective dipole moment increases.

Similarly, the excess inverse relaxation time is defined as:

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \quad (5)$$

where, $(1/\tau)^E$ is the excess inverse relaxation time, which represent the average broadening of dielectric spectra. Information regarding the dynamics of solute solvent interaction obtainable from this excess property is as follows:

- (a) $(1/\tau)^E = 0$: There is no change in the dynamics of liquid A and liquid B interaction;
- (b) $(1/\tau)^E < 0$: Liquid A and liquid B interaction produces a field such that the effective dipoles rotate slowly;
- (c) $(1/\tau)^E > 0$: Liquid A and B interaction produces a field such that the effective dipoles rotate quickly that is the field co operates in rotation of dipoles.

The experimental values of both the excess parameters were fitted to the Redlich-Kister¹⁰ equation.

$$Y^E = X(1-X) \sum_{j=0}^a B_j (2X-1)^j \quad (6)$$

where, Y^E is either ϵ_0^E or $(1/\tau)^E$. By using B_j values, Y^E values were calculated and used as guidelines to draw the smooth curves.

Bruggeman mixtures formulae¹¹ can be used as evidence of molecular interactions in binary mixture. The Bruggeman modified equation for mixture is given by expression.

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0B}}{\epsilon_{0A} - \epsilon_{0B}} \right) \left(\frac{\epsilon_{0A}}{\epsilon_{0m}} \right)^{1/3} = 1 - \Phi_B \quad (7)$$

According to above equation linear relationship is expected which will give a straight line when f_B plotted against Φ_B . Any deviation from this linear relation indicates molecular interaction.

Kirkwood correlation factor ' g '¹² is also a parameter containing information regarding orientation of electric dipoles in polar liquids provides information about parallel or anti-parallel alignment of dipoles. The effective angular correlation (g^{eff}) between molecules is calculated using modified form of equation.

$$\frac{4\pi N}{9KT} \left[\frac{\mu_A^2 \rho_A \Phi_A}{M_A} + \frac{\mu_B^2 \rho_B \Phi_B}{M_B} \right] g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} - \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (8)$$

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.

RESULTS AND DISCUSSION

The static permittivity (ϵ_0) and relaxation time (τ) for the mixture obtained by fitting experimental data with the Debye equations (3) at four different temperatures are shown in Figs. 1 and 2 respectively.

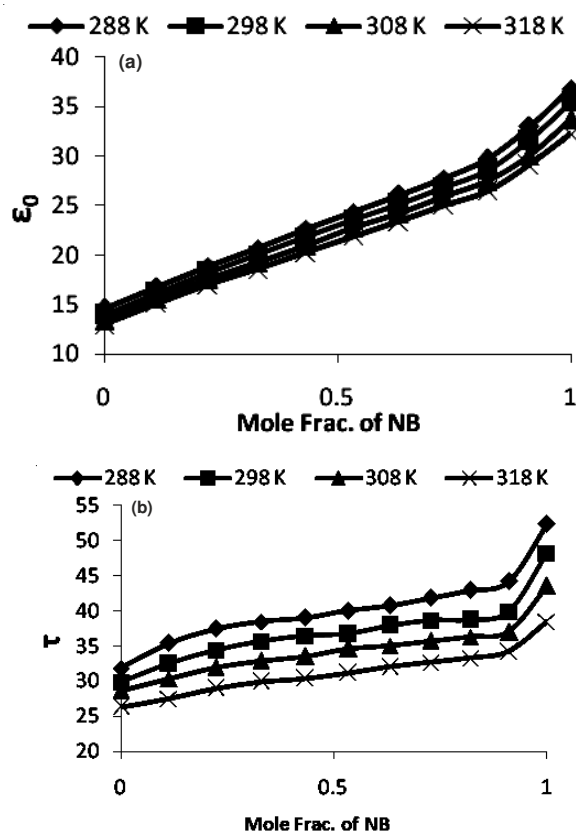


Fig. 1. Diethylene glycol monomethyl ether-nitrobenzene system (a) static permittivity (ϵ_0) at 288 K, 298 K, 308 K and 318 K. (b) Relaxation time (τ) at 288, 298, 308 and 318 K

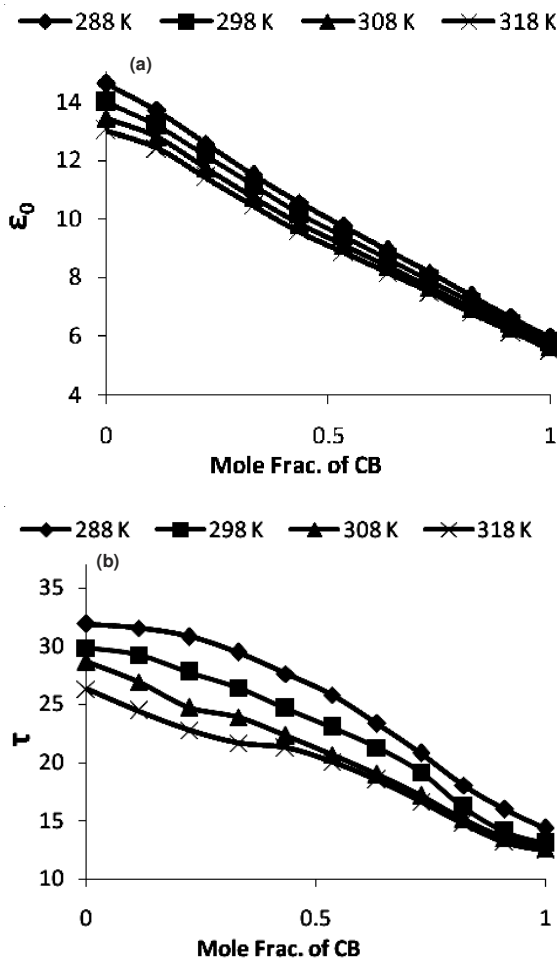


Fig. 2. Diethylene glycol monomethyl ether- chlorobenzene system (a) Static permittivity (ϵ_0) at 288, 298, 308 and 318 K. (b) Relaxation time (τ), at 288, 298, 308 and 318 K

In this study, the variation in the static permittivity and relaxation time with mole fraction of nitrobenzene, chlorobenzene in diethylene glycol monomethyl ether in diethylene glycol monomethyl ether-nitrobenzene system and diethylene glycol monomethyl ether-chlorobenzene system at different temperatures are shown in Figs. 1 and 2. In an ideal mixture of polar liquids, if the molecules are non interacting linear variation in the values of static dielectric constant and relaxation time with concentration is expected. But Figs. 1 and 2 shows nonlinear variation in dielectric constant and relaxation time with change in mole fraction of nitrobenzene and chlorobenzene in diethylene glycol monomethyl ether. This suggests that the intermolecular association is taking place in all these systems¹³.

The variation of (ϵ_0^E) and ($1/\tau$)^E with the mole fraction of nitrobenzene, chlorobenzene in diethylene glycol monomethyl ether at different temperatures is shown in Figs. 3 and 4, respectively. The experimental values of both parameters were fitted to Redlich-Kister equation.

In the diethylene glycol monomethyl ether-nitrobenzene system, the excess permittivity, values are negative for all concentrations of nitrobenzene in the mixture for all temperature. On the other hand, for diethylene glycol monomethyl ether-chlorobenzene system, these values are positive in diethylene glycol monomethyl ether rich region and negative in chlorobenzene rich region for all temperature studied. The negative

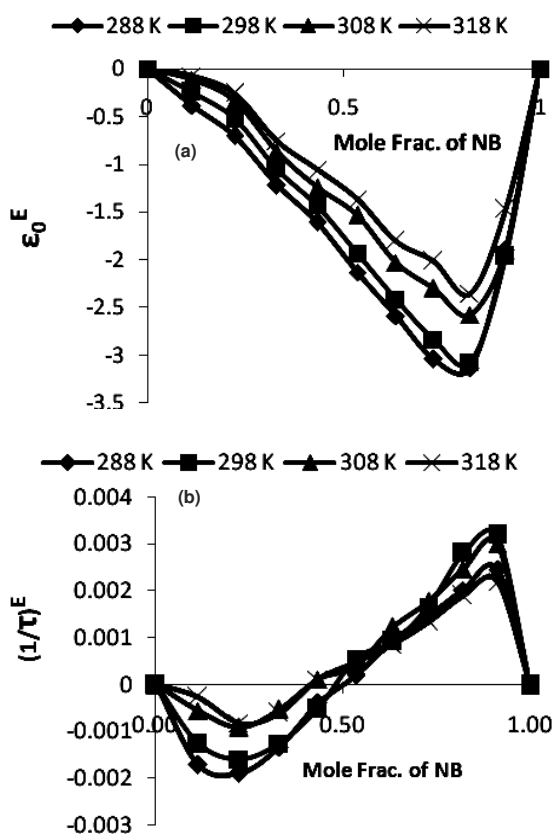


Fig. 3. Diethylene glycol monomethyl ether-nitrobenzene system (a) Excess permittivity at 288, 298, 308 and 318 K. (b) Excess inverse relaxation time at 288, 298, 308 and 318 K

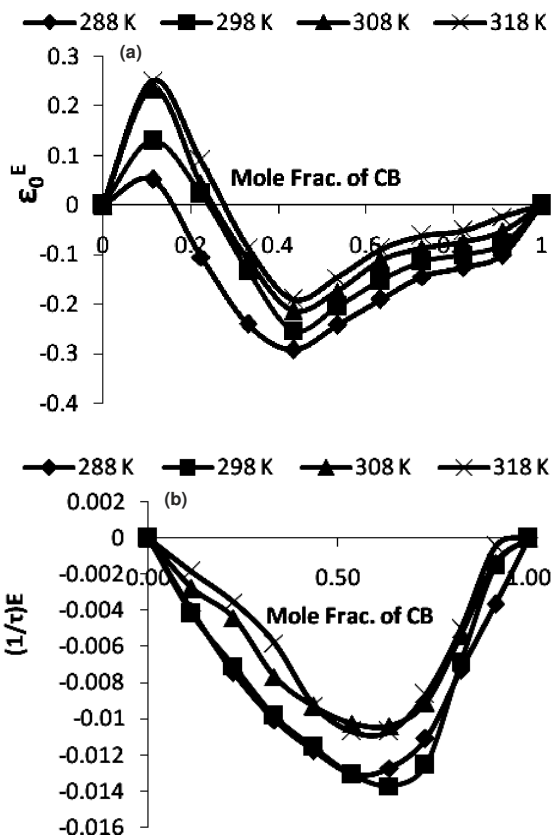


Fig. 4. Diethylene glycol monomethyl ether- chlorobenzene system (a) Excess permittivity at 288, 298, 308 and 318 K. (b) Excess inverse relaxation time at 288, 298 308 and 318 K

excess permittivity values indicate anti parallel alignment of the dipoles and the positive excess permittivity value indicates parallel alignment of dipoles in the system.

In the diethylene glycol monomethyl ether-nitrobenzene system, the excess inverse relaxation time, $(1/\tau)^E$ values, are negative in diethylene glycol monomethyl ether rich region and further it becomes positive in nitrobenzene rich region at all temperatures. On the other hand, in diethylene glycol monomethyl ether-chlorobenzene system these values are negative for all the concentrations of chlorobenzene in diethylene glycol monomethyl ether at all temperatures. The positive values of excess inverse relaxation time indicate the faster rotation of dipoles whereas negative excess inverse relaxation time values indicate slower rotation of dipoles in the system¹⁴.

The information about the interaction can also be obtained by Bruggeman factor as in Fig. 5a, b.

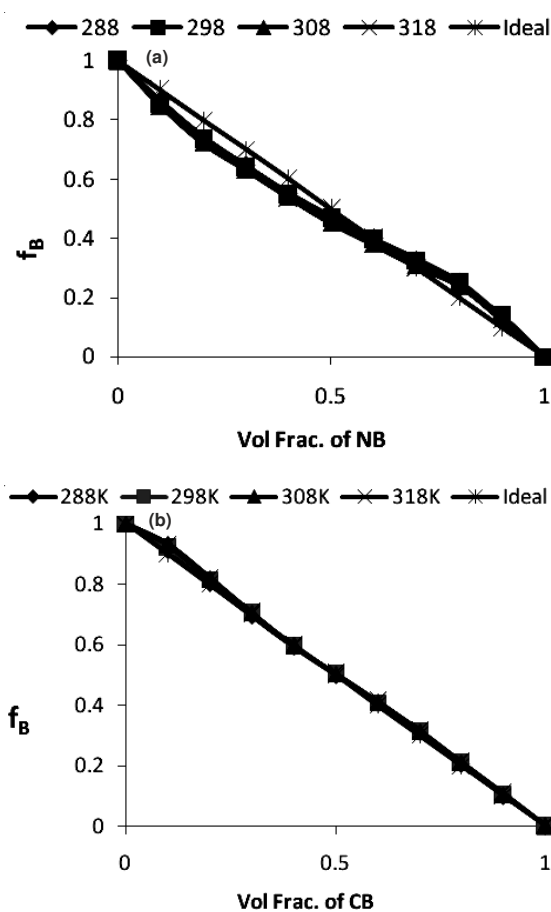


Fig. 5. Bruggeman factor for (a) diethylene glycol monomethyl ether-nitrobenzene system b) diethylene glycol monomethyl ether-chlorobenzene system

It can be seen from these plots that f_B shows a deviation from the ideal Bruggeman behaviour. This confirms the intermolecular interaction in the mixture. Several similar observations have been reported in the literature⁴.

The g^{eff} values calculated from equation (8) are given in Table-1. It can be seen from the table that for diethylene glycol

monomethyl ether, g^{eff} values are greater than unity for both the systems at all temperatures suggesting parallel orientation of electric dipoles and the g^{eff} values for pure nitrobenzene and chlorobenzene are less than unity indicating antiparallel orientation of electric dipoles¹³.

TABLE-1
KIRKWOOD CORRELATION FACTOR FOR (A)
DGME- NITROBENZENE SYSTEM (B) DGME-
CHLOROBENZENE SYSTEM

Volume	288 K	298 K	308 K	318 K
Nitrobenzene				
0	3.22	3.17	3.14	3.12
0.1	2.26	2.25	2.24	2.23
0.2	1.82	1.82	1.81	1.80
0.3	1.54	1.54	1.53	1.52
0.4	1.37	1.36	1.35	1.34
0.5	1.23	1.23	1.22	1.21
0.6	1.12	1.12	1.11	1.11
0.7	1.04	1.04	1.04	1.03
0.8	0.98	0.97	0.97	0.96
0.9	0.97	0.96	0.95	0.94
1	0.98	0.98	0.96	0.94
Chlorobenzene				
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

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