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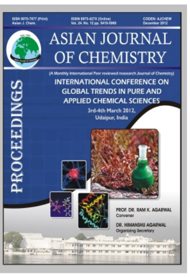

Dielectric Relaxation Study of Polar Liquids Using Time Domain Reflectometry Technique†

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Complex permittivity of binary mixture of 2-methoxyethanol-propanol mixture for various temperatures was obtained in the frequency range of 10 MHz to 10 GHz using the time domain reflectometry technique. The static dielectric constant (ε_s) and relaxation time (τ) have been obtained from complex permittivity spectra using non-linear list square fit method. This values are used for the calculation of access permittivity ε_s, excess inverse relaxation time $(1/\tau)^E$, Kirkwood correlation factor (g^{eff}) Bruggeman factor (f_B) and thermodynamic parameters. On the basis of above parameters, information on the molecular structure and dynamics of the mixture have been discussed.

Key Words: Dielectric constant, Time domain reflectometry, Kirkwood correlation factor, Bruggeman factor, Thermodynamic factor.

INTRODUCTION

The study of dielectric relaxation of liquids gives the important information about molecular structure, molecular interaction between components of solutions, dynamics and kinetics of the solution. Since, the molecular response is in microwave region, most of the measurements are carried out in microwave region to know the liquid properties. The dynamic and kinetic properties of liquid are generally carried out in dilute solution with non-polar solvent, using frequency domain technique. To study the dielectric properties of the solution of polar liquids in polar solvent, the most reliable technique is time domain technique. The time domain reflectometry technique developed by Cole *et al.* gives the dielectric relaxation properties of the solution over wide range of microwave frequencies. This time domain reflectometry technique has been used in present study to find the dielectric relaxation properties of binary mixture of polar liquids[1-5].

EXPERIMENTAL

Time domain reflectometry set up and data acquisition: The complex permittivity spectra of the samples were studied using time domain reflectrometry method[6,7]. 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 Ω. The transmission line system under test was placed at the end of the coaxial line in the standard military application coaxial cell connecter with 3.5 mm outer diameter and 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 5 ns was used. The reflected pulses without sample R_1 (t) and with sample R_x (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 has been used to maintain the constant temperature within the accuracy limit of 273 ± 1 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 transformation[8,9] as:

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

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, w is angular frequency and d is the effective pin length and j = root (-1).

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra, $\rho^*(\omega)$ by applying a

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bilinear calibration method[6]. The experimental values of $\varepsilon^*(\omega)$ are fitted the Debye equation[10].

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

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[11] used to determine the values of dielectric parameters.

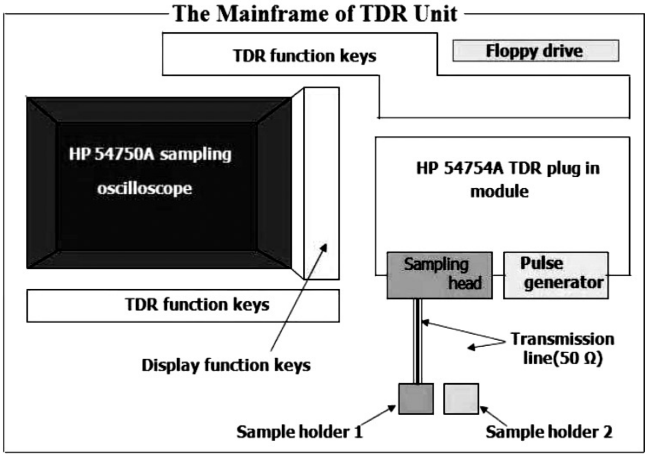

Fig. 1. Block diagram of dual channel time domain reflectometry unit

Information related to solute- solvent interaction may be obtained by excess properties[12-14].

The excess permittivity is defined as:

$$\varepsilon_0^E = (\varepsilon_0)_m - [(\varepsilon_0)_A X_A + (\varepsilon_0)_B X_B] \tag{3}$$

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

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_A X_A + (1/\tau)_B X_B] \tag{4}$$

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.

Bruggeman factor (f_B) helps to depict intermolecular interaction among the liquids. The Bruggeman Modified equation for mixture is given by expression:

$$f_B = \left(\frac{\varepsilon_{0m} - \varepsilon_{0B}}{\varepsilon_{0A} - \varepsilon_{0B}}\right)\left(\frac{\varepsilon_{0A}}{\varepsilon_{0m}}\right)^{1/3} = 1 - \Phi_B \tag{5}$$

Any deviation from this linear relation indicates molecular interaction.

Kirkwood correlation factor 'g' is also a parameter 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.

$$\frac{4\pi N}{9KT}\left[\frac{\mu^2{}_A\rho_A\varphi_A}{M_A} + \frac{\mu^2{}_B\rho_B\varphi_B}{M_B}\right]g^{eff} = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} - \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2} \tag{6}$$

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.

$g^{eff} = 1$, indicates, there is no more correlation between the molecular orientations in the liquid mixture; $g^{eff} < 1$: indicates that the intermolecular interactions are such that total effective value of dipoles reduces. It suggests antiparallel alignment of dipoles; $g^{eff} > 1$: indicates parallel alignment of dipoles.

According to Eyring rate equation[15] the relation between activation enthalpy and entropy and relaxation time is given by:

$$\tau = h/kTe^{(\Delta H - T\Delta S)/RT} \tag{7}$$

where, ΔH is the enthalpy (heat) of activation and ΔS is the entropy of activation for dipole relaxation process.

All positive value of molar enthalpy of activation (ΔH) suggests endothermic interaction *i.e.* less energy is required to achieve group dipole orientation[2]. All negative value of molar entropy of activation (ΔS) indicates relatively higher ordered arrangement of molecules in the activated state exists[16].

RESULTS AND DISCUSSION

Static permittivity and relaxation time: The dielectric parameters for different temperatures and concentrations are given in Table-1 (Figs. 2 and 3). From these values it is observed that static dielectric constant (ε_s) and relaxation (τ) increases with increase in the mole fraction of ML in the mixture but decreases with increase in temperatures. The increase in dielectric constant may be due to the transition of spherical molecular aggregates into elongated aggregates to give rise to parallel orientation of the dipoles. This indicates the hetero-interaction, which may arise due to formation of hydrogen bonding between -OH group of 1-PL and 2-ME molecules.

Excess parameters: The values of ε^E are negative for all concentration of 1-PL in the mixture for all temperature studied as shown in Fig. 2. This indicates that the molecules of mixture may form multimers structures in such a way that the effective dipoles get reduced. The values of $(1/\tau)^E$ is also negative shown in Fig. 3 for all concentration of 1-PL in the mixture for all temperature studied. This indicates a slower rotation of the dipoles due to the solute-solvent interaction form the hydrogen bonded structures, which produces a field such that the effective dipole rotation is hindered.

Bruggeman factor: The Bruggeman plot shows non-linear behaviour. The non-linearity of the curves indicates hetero-interaction which may be due to hydrogen bonding of the -OH group of 1-PL and 2-ME in the mixture. Bruggeman plot shows temperature dependent nature of molecular interactions.

TABLE-1
TEMPERATURE DEPENDENT DIELECTRIC PARAMETERS FOR BINARY MIXTURE OF 1-PL + 2-ME

Mole fraction of 1-propanol	288 K		298 K		308 K		318 K	
	ε_s	τ(ps)	ε_s	τ(ps)	ε_s	τ(ps)	ε_s	τ(ps)
0.000	17.50	29.60	15.70	27.90	15.50	24.50	15.30	24.20
0.105	17.97	38.90	16.01	36.20	15.70	32.10	15.15	29.50
0.209	18.41	59.20	16.28	54.30	15.90	51.30	15.17	43.20
0.311	18.72	73.50	16.52	71.20	16.02	69.20	15.19	56.10
0.413	19.16	95.20	16.81	92.10	16.15	88.40	15.51	72.30
0.513	19.59	137.50	17.13	129.93	16.39	124.40	15.83	95.20
0.613	20.15	168.20	17.61	161.20	16.83	155.60	16.16	120.20
0.711	20.63	189.30	18.08	189.10	17.27	172.10	16.51	135.70
0.808	21.25	224.40	18.45	220.20	17.65	184.30	16.95	149.80
0.905	21.87	266.20	19.09	261.40	18.26	192.60	17.51	156.30
1.000	22.50	293.40	19.80	285.20	19.10	231.30	18.50	190.50

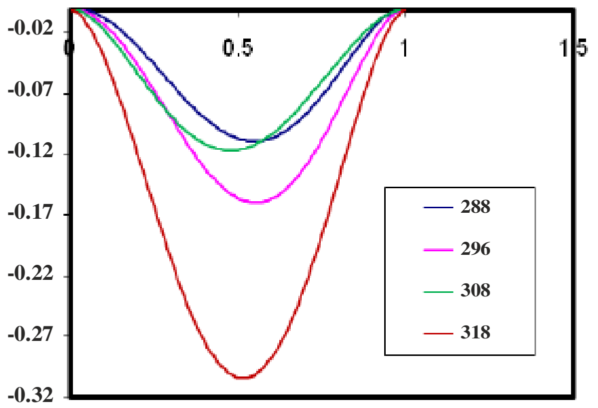

Fig. 2. Variation of excess permittivity (ε^E) as a function of mole fraction of 1-Propanol at 288, 298, 308 and 318 K

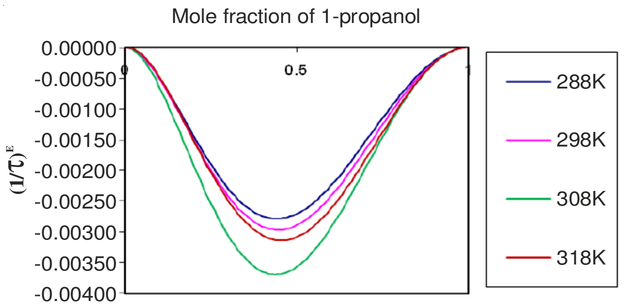

Fig. 3. Variation of excess inverse relaxation time (1/t) E, as a function of mole fraction of 1-Propanol at 288, 298, 308 and 318 K

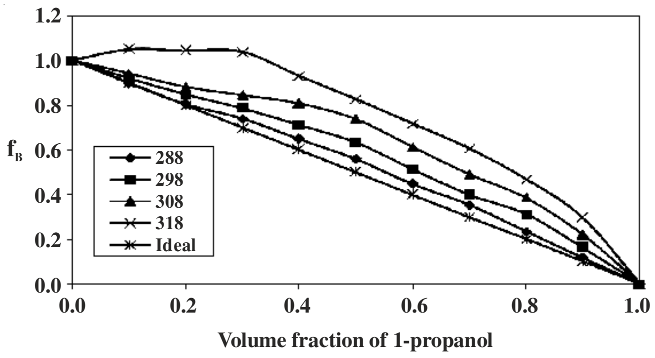

Fig. 4. Bruggeman plot for 1-PL + 2 ME

Kirkwood correlation factor: The g^{eff} values are greater than unity as listed in Table-2 for the mixtures and at all temperatures suggesting parallel orientation of electric dipoles. The values confirm the formation of hydrogen bonding in the mixture.

TABLE-2
KIRKWOOD CORRELATION FACTOR (g^{eff}) FOR 1-PL + 2ME

Volume fraction of 1-propanol	288 K	298 K	308 K	318 K
0.0	1.41	1.30	1.32	1.35
0.1	1.52	1.38	1.40	1.39
0.2	1.63	1.48	1.49	1.46
0.3	1.74	1.57	1.57	1.53
0.4	1.87	1.68	1.66	1.64
0.5	2.02	1.81	1.78	1.77
0.6	2.20	1.97	1.94	1.91
0.7	2.39	2.14	2.11	2.07
0.8	2.61	2.33	2.29	2.27
0.9	2.87	2.57	2.53	2.50
1.0	3.17	2.86	2.85	2.84

From Table-3, the value of g_f is unity for an ideal mixture and deviation from unity may indicate interaction between two components of the mixture. The g_f value less than one indicates that the dipoles of mixture will be oriented in such a way that the effective dipole will be less than the corresponding values of pure liquid. The g_f value greater than one indicates that the dipoles of mixture will be oriented in such a way that the effective dipole will be more than the corresponding values of pure liquid.

TABLE-3
KIRKWOOD CORRELATION FACTOR (g_f) FOR 1-PL + 2ME

Volume fraction of 1-propanol	288 K	298 K	308 K	318 K
0.0	1.00	1.00	1.00	1.00
0.1	1.00	0.99	0.99	0.97
0.2	0.99	0.98	0.98	0.95
0.3	0.98	0.97	0.96	0.93
0.4	0.98	0.97	0.95	0.93
0.5	0.98	0.96	0.94	0.93
0.6	0.98	0.97	0.95	0.93
0.7	0.98	0.97	0.95	0.94
0.8	0.99	0.97	0.96	0.94
0.9	0.99	0.98	0.97	0.96
1.0	1.00	1.00	1.00	1.00

Thermodynamic parameters: The molar enthalpy of a ctivation (ΔH) increases with increase in volume fraction of 1-PL in 2-ME from 3.09 KJ/mol up to 8.85 KJ/mol. This means that more energy is needed for group dipole reorientation with increase in volume fraction of EL in the mixture. All negative value of molar entropy of activation (ΔS) with volume fraction of EL indicates relatively high ordered arrangement of molecules in the activated state. Arrhenius plot for the system is shown in Fig. 5. The linear nature of Arrhenius plot shows that equivalent incremental change in temperature causes equivalent changes in values of activation enthalpy (ΔH) in temperature range under consideration.

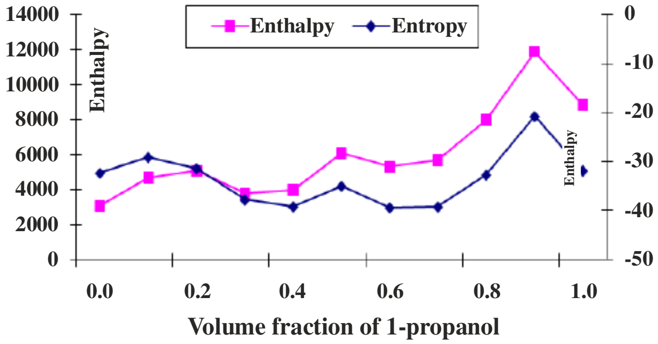

Fig. 5.

Conclusion

The study provides information of intermolecular interaction between the systems with hydrogen bonding and the system with shielded configuration dominated by dipole-dipole interaction. Although the interaction found to be weak, the excess properties show the interesting behaviour. It appears that the dipole-dipole interaction favours antiparallel structures; whereas the hydrogen bonded interaction favours parallel structures. The interaction between these two types seems to give small nonlinear behaviour, indicating they do not interfere much in the mixtures.

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