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Interaction Study of Molecular Behavior of Mixture of Polar liquids at Microwave Frequency

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Abstract

The dielectric study of tert-butyl alcohol (TB) with ethylene glycol (EG) were determined over the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) at temperature 55°C for 11 different concentrations of the system. The static dielectric constant (ε_0) and relaxation time (τ) have been obtained by the least squares fit method. Excess properties and Kirkwood correlation factor of the mixtures have been determined. The static dielectric constants for the mixtures have been fitted with the modified Bruggeman model.

Keywords

Time domain reflectometry, dielectric constant, relaxation time, excess permittivity and Kirkwood correlation factor.

1. Introduction

The dielectric relaxation of binary polar liquids provides information regarding their interactions [1-3]. The objective of the present paper is to report the detailed dielectric relaxation study of tert-butyl alcohol (TB) with ethylene glycol (EG) mixtures using TDR at 55^{0}C temperatures.

2. Experimental

Materials and Apparatus

TB and EG (AR grade, Merck Pvt. Ltd., West Mumbai, India) were used without further purification. The solutions were prepared at 11 different volume percentage of EG from 0 % to 100 % in steps of 10 %. Using these volume percents the mole fraction is calculated as

$$x_1 = (v_1\rho_1/m_1) / [(v_1\rho_1/m_1) + (v_2\rho_2/m_2)]$$

where m_i, v_i, and ρ_i represent the molecular weight, volume percent, and density of the ith

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(i =1, 2) liquids, respectively.

The complex permittivity spectra were studied using the time domain reflectometry [4-6] method. The Hewlett Packard HP 54750 sampling oscilloscope with HP 54754A TDR plug in module has been 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 50 Ohm. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out 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 the experiment, time window of 5 ns was used. The reflected pulse without sample $R_l(t)$ 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.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ±1°C. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system is circulated. The temperature at the cell is checked using the electronic thermometer.

3. 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 [7, 8] as

$$\rho^*(\omega) = (c/j\omega d)[p(\omega)/q(\omega)] \quad (1)$$

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, ω is angular frequency, d is the effective pin length and $j=\sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying bilinear calibration method [6].

The experimental values of ρ^* are fitted with the Debye equation [9]

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

with ε_0, ε_∞, and τ as fitting parameters. A nonlinear least-squares fit method [10] was used to determine the values of dielectric parameters.

Table 1. The data for the liquids used with literature values at normal temprature.

Liquid	ε_0	M	$\rho/(g.cm^{-3})$
	Literature	Literature	Literature

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TB	11.50[a]	74.121[a]	0.8063[b]
EG	40.89[a]	62.068[a]	1.1135[c]

where a, b and c data are taken from the refs [1], [2] and [13] respectively.

4. Results and Discussion

The density and ε_0 values of pure liquid used are given in Table 1. The static dielectric constant (ε_0), dielectric constant at high frequency (ε_∞) and relaxation time (τ) obtained by fitting experimental data with the Debye equation are listed in Table 2.

Figure 1, shows the behavior of static dielectric constant (ε_0) and relaxation time (τ) of TB+2P system, as a function of mole fraction of 2P in TB at 45°C.

The information related to liquids 1 and 2 interaction may be obtained by excess properties [11] related to the permittivity and relaxation times in the mixture. The excess permittivity ε^E is defined as

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_\infty)_\mu - [(\varepsilon_0 - \varepsilon_\infty)_1 \ \xi_1 + (\varepsilon_0 - \varepsilon_\infty)_2 \ \xi_2] \quad (3)$$

where x- mole fraction and suffices m, 1, 2 represents mixture, liquid 1 (TB) and liquid 2 (2P) respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture as follows:

(i) $\varepsilon^E = 0$ indicates the liquid 1 and 2 do not interact at all.

(ii) $\varepsilon^E < 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipoles get reduced. The liquid 1 and 2 may form multimers leading to the less effective dipoles.

(iii) $\varepsilon^E > 0$ indicates the liquid 1 and 2 interaction in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^E = (1/\tau)_\mu - [(1/\tau)_1 \ \xi_1 + (1/\tau)_2 \ \xi_2] \quad (4)$$

where $(1/\tau)^E$ is excess inverse relaxation time which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadenin

(which is inverse of the relaxation time) in the resonant spectroscopy [12].

The variation of ε^E and $(1/\tau)^E$ with mole fraction of alcohols at temperature 25°C is shown in Figure 2.

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [14, 15] as

Table 2. Temperature dependent dielectric relaxation parameters for TB+EG mixtures*

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x_2	55 °C		
	ε_0	ε_∞	τ (ps)
0.0000	9.34(0)	2.61(1)	139.83(0)
0.1549	15.06(4)	3.39(5)	119.85(8)
0.2919	18.89(4)	3.44(6)	107.37(4)
0.4141	20.79(6)	3.62(3)	91.00(7)
0.5237	24.21(8)	3.74(1)	86.20(3)
0.6225	24.88(7)	3.91(9)	75.01(4)
0.7121	26.87(4)	4.08(6)	65.31(8)
0.7937	28.40(8)	4.21(5)	59.51(7)
0.8684	27.41(3)	4.38(3)	58.65(4)
0.9369	30.49(6)	4.46(1)	55.95(6)
1.0000	36.12(0)	4.62(0)	51.33(1)

*x_2 is the mole fraction of EG in TB. Number in bracket represent error in the corresponding value, e.g. means 18.89(4) means 18.89 ± 0.4.

$$A^E = (x_1 x_2) \sum_n B_n (x_1 - x_2)^n \quad (5)$$

where A is either ε^E or $(1/\tau)^E$. By using these B_n values, A^E values were calculated and used as guideline to draw the smooth curves in Figure 2. Values of Redlich-Kister coefficients are given in Table 3.

From Figure 2, the excess permittivity values are positive in the TB rich region and negative in the EG rich region. The positive value of excess permittivity indicates the parallel alignment of the dipoles of the system. Negative excess inverse relaxation time values indicate slower rotation of the dipoles of the system. The coefficient B_n for n= 0 to 3 are listed in Table 3. It is observed that values of B_0 to B_1, B_2 and B_3 get positive to negative values with decrease in molecular size of EG. This provides information regarding formation of multimers in the mixture.

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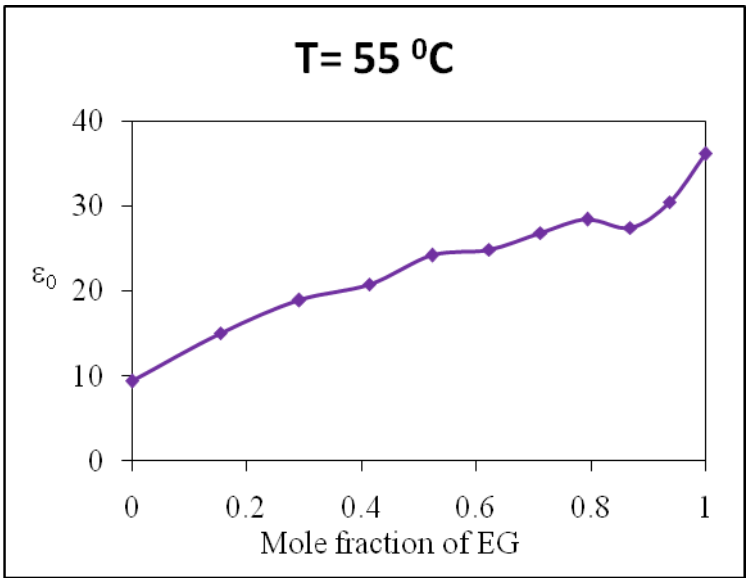

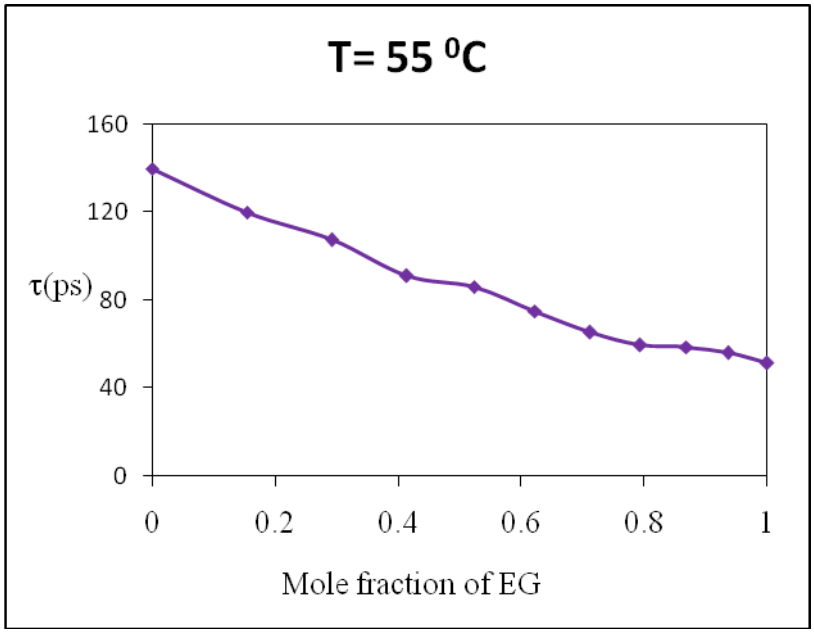

Figure 1. (a) Static dielectric constant (ε_0), (b) relaxation time (τ), versus mole fraction (x_2) of EG in TB at temperature 55⁰C.

As the physical meanings of B_0, B_1, B_2 and B_3 are correlated to rates for forming multimers as dimer TB-EG, trimer 2TB-EG , quartermers 2TB-2EG and pentamer 3TB-2 EG respectively.

The Kirkwood correlation factor g_f [16] is also a parameter for getting information regarding orientation of electric dipoles in polar liquids.

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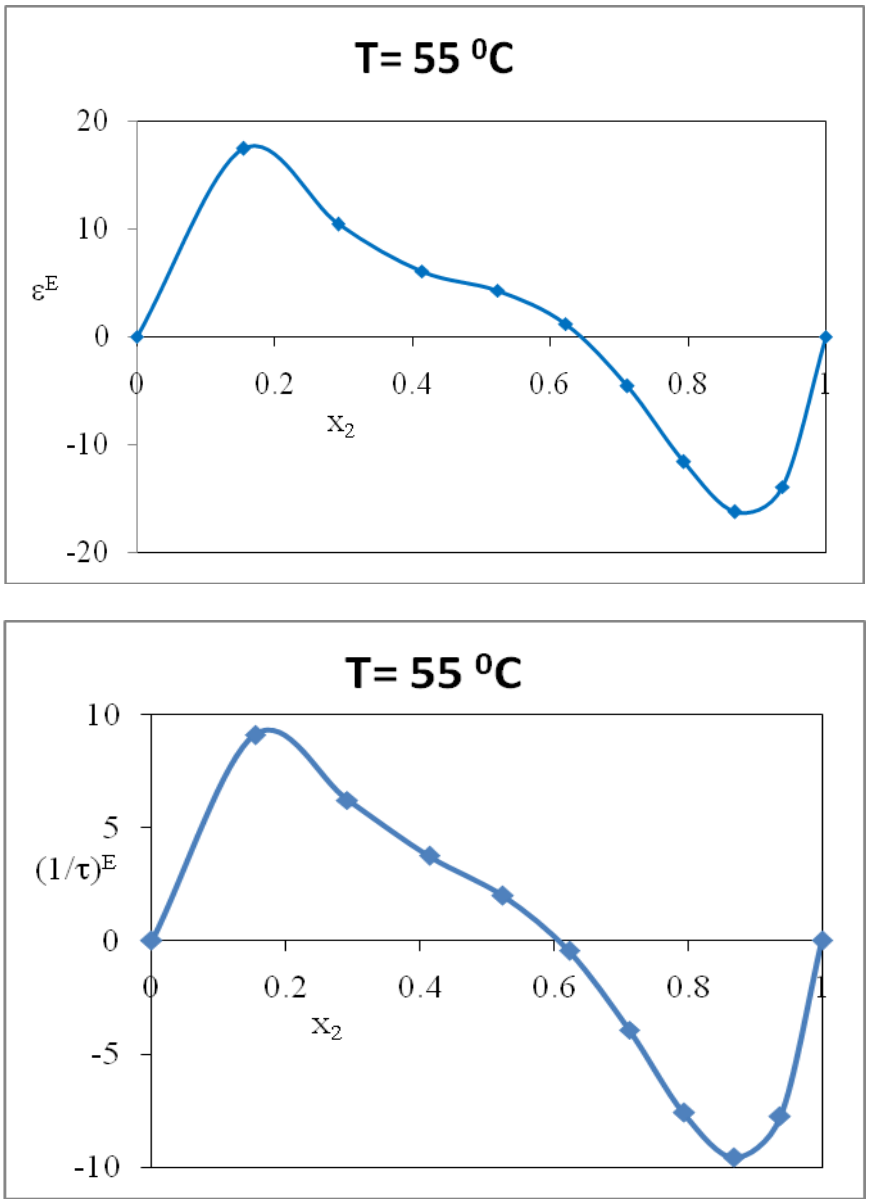

Figure 2. (a) Excess permittivity (ε^E) (b) Excess relaxation time $(1/\tau)^E$, versus mole fraction (x_2) of EG in TB at temperature 55⁰C.

Table3. B_n coefficients of the Redlich-Kister equation

°C	B_0	B_1	B_2	B_3
	Excess permittivity			
55	1.93	-10.84	-1.11	-50.60
	Excess inverse relaxation time			
55	0.80	-1.24	-0.62	-13.72

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The g_f for pure liquid may be obtained by the expression

$$\frac{4\Pi N\mu^2\rho}{9kTM}g_f = \frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \quad (6)$$

where μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, k is Boltzman constant, and N is Avogadro's number. The dipole moments for TB and 2P in gas phase are taken as 1.69 D and 2.2 D respectively [1-2,13].

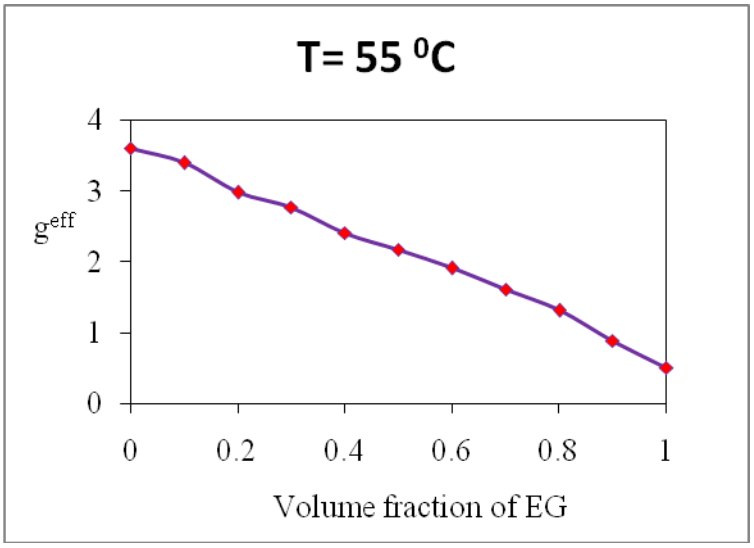
For the mixture of two polar liquids 1, 2 Eq. (3) is modified by [12] with the following assumptions:

Assume that g_f for the binary mixture is expressed by an effective averaged correlation factor g^{eff} such that the Kirkwood equation for the mixture can be expressed by

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1}{M_1}\phi_1+\frac{\mu_2^2\rho_2}{M_2}\phi_2\right)g^{eff} = \frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad (7)$$

with ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

In equation (7), the values of g^{eff} will change from g_1 to g_2 as concentration of molecule 2 will decrease from 100% to 0%. The Kirkwood correlation factor, g_f, which gives angular correlation between the molecules of the system, are less than 1. The values of g^{eff} and g_f are calculated from equation (6) and (7) are given in Figure 3. Shows the temperature dependent values of a) g^{eff} and b) gf verses volume fraction of EG for TB+EG mixture at T=45°C.



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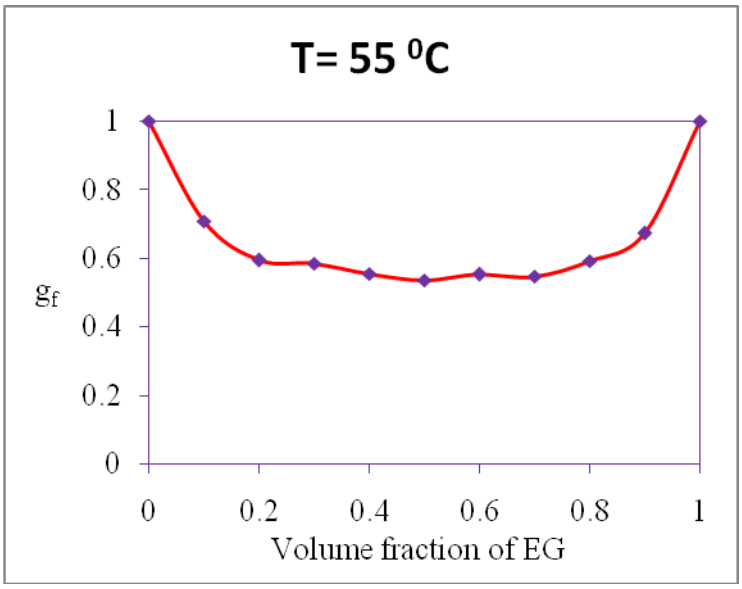

Figure 3. Shows the temperature dependent values of a) g^{eff} and b) g_f verses volume fraction of EG for TB+EG mixture at T=55°C.

The modified Bruggeman equation [17] is another parameter which may be used an

indicator of liquid 1 and 2 interaction. The Bruggeman factor f_B is given by,

$$f_B = \left(\frac{\varepsilon_{0m} - \varepsilon_{02}}{\varepsilon_{01} - \varepsilon_{02}}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3} = (1 - \phi_2) \quad (8)$$

According to equation (8), a linear relationship is expected which will give a straight line when plotted f_B against ϕ_2. However, here the experimental values of f_B were found to deviate from the linear relationship. The Bruggeman dielectric factor f_B versus volume fraction ϕ_2 of 2P at 25°C is given in Figure 4.

To fit the experimental data, the above equation (8) has been modified [18]

$$f_B = 1 - [a - (a-1)\,\phi_2]\,\phi_2 \quad (9)$$

where 'a' is numerical fitting parameter.

The parameters 'a' has been determined by the least squares fit method. The value of 'a' = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to corresponding liquids 1 and 2 interactions. The value of a is 0.272 at 45°C. The small deviation of 'a' suggest that weaker interaction between TB and EG.

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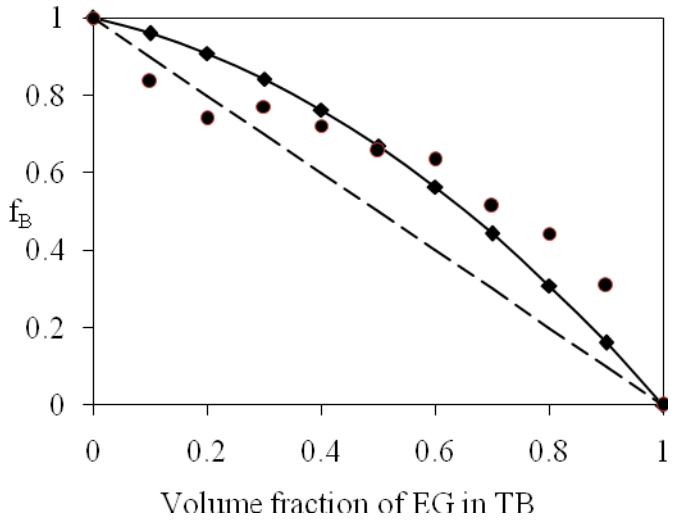

Figure 4. The Bruggeman plot for TB+EG mixture at 45°C. Dashed line denote original model (equation 8). Continuous line is the theoretical curve obtained from equation (9). Experimental points are shown by the symbol •.

5. Conclusion

We have computed the values of effective volume in the mixture of TB+EG by using four different models based on excess permittivity, excess logarithmic of relaxation time, the modified Bruggemen equation & Kirkwood equation respectively. The parameter 'a' which represents significance of change in volume is determined. This provides a unified approach to understand the interaction between two constituents in the liquid mixtures, using different models.

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