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Dielectric Study of TB + EG At Microwave Frequency Using Time Domain Reflectometry Technique

B. D. Achole[a*] and V. P. Pawar[b]

[a]*Department of Physics, Shri. Havagiswami Mahavidyalaya, Udgir, Maharashtra (INDIA)*
[b]*Department of Physics and Electronics, Maharashtra Udayagiri Mahavidyalaya, Udgir, Maharashtra (INDIA)*

Abstract

The dielectric relaxation study of tert-Butyl alcohol[TB] with ethylene glycol[EG] were determined in the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) in the temperature range 25°C and 35°C for 11 different concentrations of the system. The dielectric parameters viz. static dielectric constant(ε_0), dielectric constant at infinite frequency(ε_∞) and relaxation time (τ) have been obtained by the least squares fit method. The Kirkwood correlation factor of the mixtures have also been determined. For temperature range, considered here, the permittivity increases and relaxation time decreases with the percentage of ethylene glycol [EG]. The static dielectric constants for the mixtures have been fitted with the modified Bruggeman model.

Keywords: Time domain reflectometry, excess parameter, Kirkwood correlation factor, Bruggeman factor.

INTRODUCTION

The dielectric relaxation of binary polar liquids provides information regarding solute- solvent interactions[1-3]. In this work, we report the dielectric study of tert-butyl alcohol (TB) with ethylene glycol[EG] mixture; both are –OH group molecule. It is interesting to see the effect of mixtures of –OH group molecule. 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 different temperatures.

MATERIALS AND METHODS

TB and EG (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-

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

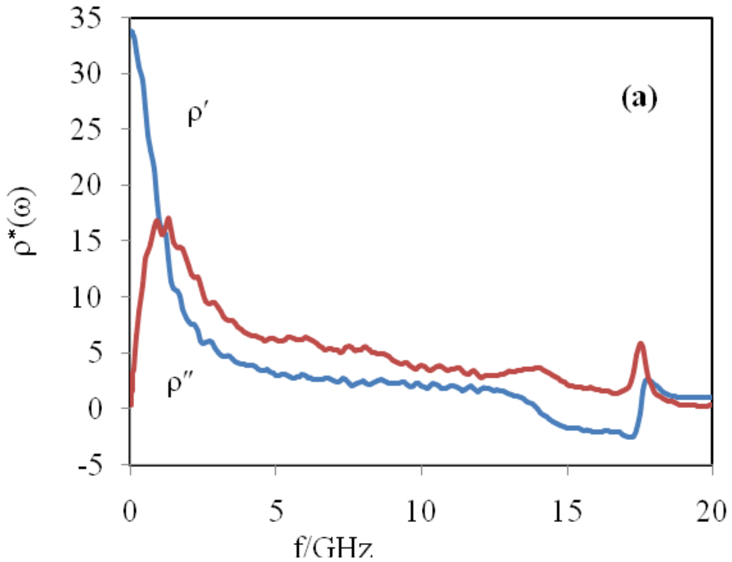
where m_i, v_i, and ρ_i represent the molecular weight, volume percent, and density of the ith (i=1, 2) liquids, respectively. The density and molecular weight of the liquids[2,5] at 25^{0}C are as follows:

Tert-Butyl alcohol[TB] -Density - 0.8063 gm.cm^{-3} ; Mol. Wt.- 74.121.
Ethylene glycol[EG] -Density - 1.1135 gm.cm.$^{-3}$; Mol. Wt.- 62.068.

Apparatus

The complex permittivity spectra were studied using the time domain reflectometry **[**4-5] 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^{o}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.



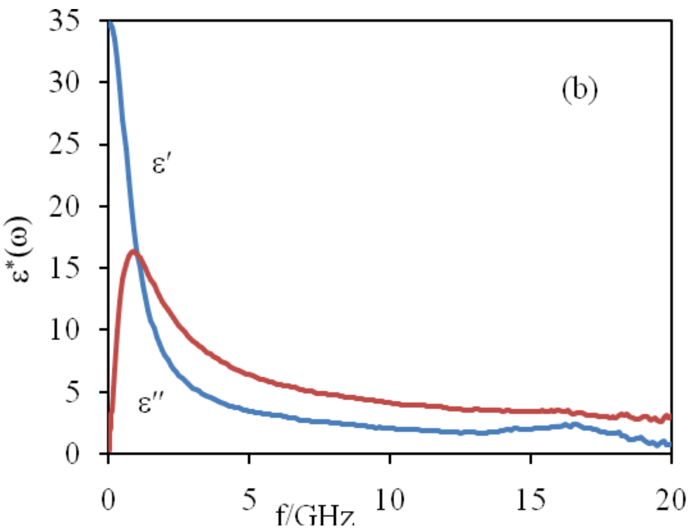


Figure 1. (a) $\rho^*(\omega)$ spectrum for tert-butyl alcohol + ethylene glycol mixture for x_1= 0.5237 (b) $\varepsilon^*(\omega)$ spectrum for tert-butyl alcohol + ethylene glycol mixture for x_1= 0.5237 both at T=25^{0}C

Table 1. Comparison of data for the liquids used with literature values at 25^{0}C

25^0C	TB		EG	
	Ref. values [a]	Reported values	Ref. values [b]	Reported values
ε_0	11.50	11.89	40.89	40.16
ε_∞	3.00	3.26	4.16	4.24
τ	276.9	289.15	104.6	109.181

[a]Ref. is [1] and [b]ref. is [2].

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 [6 ,7] 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 [4].

The experimental values of $\varepsilon^*(\omega)$ are fitted with the Debye equation [8]

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

with ε_0, ε_∞, and τ as fitting parameters. A nonlinear least-squares fit method [9] was used to determine the values of dielectric parameters. A sample of complex reflection coefficient $\rho^*(\omega)$

and complex permittivity spectra $\varepsilon^*(\omega)$ are shown in Figure 1 a,b. This corresponds to 60% of TB and 40% of EG mixture at 25^0C.

RESULTS AND DISCUSSION

The values of ε_0, ε_∞ and τ for the pure liquids used are given in Table 1. The static dielectric constant (ε_0), dielectric constant at infinite frequency (ε_∞) and relaxation time (τ) obtained by fitting experimental data with the Debye equation are listed in Table 2. The values of dielectric constant(ε_0) increases and relaxation time decreases with temperature as expected. Figure 2, shows the behaviour of static dielectric constant and relaxation time for the system as a function of mole fraction of EG in TB at different temperatures.

The Kirkwood correlation factor g_f [10] is also a parameter for getting information regarding orientation of electric dipoles in polar liquids.

The g_f for pure liquid may be obtained by the expression

$$\frac{4\Pi N\mu^2\rho}{9kTM}g_f = \frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \tag{3}$$

where μ is dipole moment in gas phase, ρ is density at temperature T, M is molecular weight, k is Boltzman constant, N is Avogadro's number. The dipole moments for TB and EG in gas phase are taken as 1.69 D and 2.2 D[11] respectively.

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

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

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

In equation (4), 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 (3) and (4) are given in Table 3 for the mixtures of the system. Errors are also estimated by assuming 2 % error in the values of the permittivity. The effective values of the correlation factor for EG is larger than the corresponding value in TB. Initially g_f value increases to its peak value at 100 % of TB then it decreases upto 40 %. Further from 50 % it increases linearly to the EG pure value. The g_f values are less than unity. The correlation factor g provide information about formation of multimers in the liquid as

i) g = 1 indicates, there is no interaction between the molecules in liquid. The system may be considered like nonpolar.
ii) g < 1 indicates that the intermolecular interaction is such that the total effective value of dipoles gets reduced. It suggests antiparellel alignment of dipoles.

iii) g > 1 indicates parellel alignment of dipoles in multimers.

The modified Bruggeman equation [13] is another parameter, which may be used an indicator of liquid 1 and 2 interaction. The Bruggeman factor f_B is given by,

$$f_B = \left(\frac{\varepsilon_{0m} - \varepsilon_{02}}{\varepsilon_{01} - \varepsilon_{02}}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3} = (1 - \phi_2) \tag{5}$$

According to equation (5), 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 EG at 25°C is given in Figure 3.

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

x_2	T= 25°C	T= 35°C	x_2	T= 25°C	35°C
ε_0					
0.0000	11.89(1)	11.31(0)	0.7121	31.18(7)	30.66(7)
0.1549	19.01(6)	18.31(4)	0.7937	34.09(8)	32.93(3)
0.2919	22.78(8)	21.66(7)	0.8684	36.59(4)	34.66(4)
0.4141	25.01(7)	24.54(6)	0.9369	38.65(2)	36.83(2)
0.5237	27.95(3)	27.27(5)	1.0000	40.76(0)	39.39(8)
0.6225	29.94(6)	28.52(8)			
ε_∞					
0.0000	3.26(1)	3.09(0)	0.7121	4.04(4)	3.76(5)
0.1549	3.51(3)	3.31(5)	0.7937	4.12(5)	3.89(6)
0.2919	3.68(6)	3.37(3)	0.8684	4.15(3)	4.08(1)
0.4141	3.75(5)	3.41(11)	0.9369	4.17(4)	4.16(3)
0.5237	3.84(11)	3.57(6)	1.0000	4.24(0)	4.31(1)
0.6225	3.92(7)	3.64(9)			
τ(ps)					
0.0000	289.15(0)	251.30(0)	0.7121	187.06(3)	138.64(13)
0.1549	258.19(4)	222.49(7)	0.7937	162.12(7)	119.69(6)
0.2919	241.99(8)	209.95(3)	0.8684	145.23(8)	101.40(3)
0.4141	233.97(7)	181.12(7)	0.9369	119.05(3)	97.96(4)
0.5237	215.90(11)	165.18(13)	1.0000	109.18(0)	79.29(0)
0.6225	205.62(6)	153.50(11)			

** x_2 is the mole fraction of EG in TB. Number in bracket represent error in the corresponding value, e.g. means 19.01(6) means 19.01 ±0.6.*

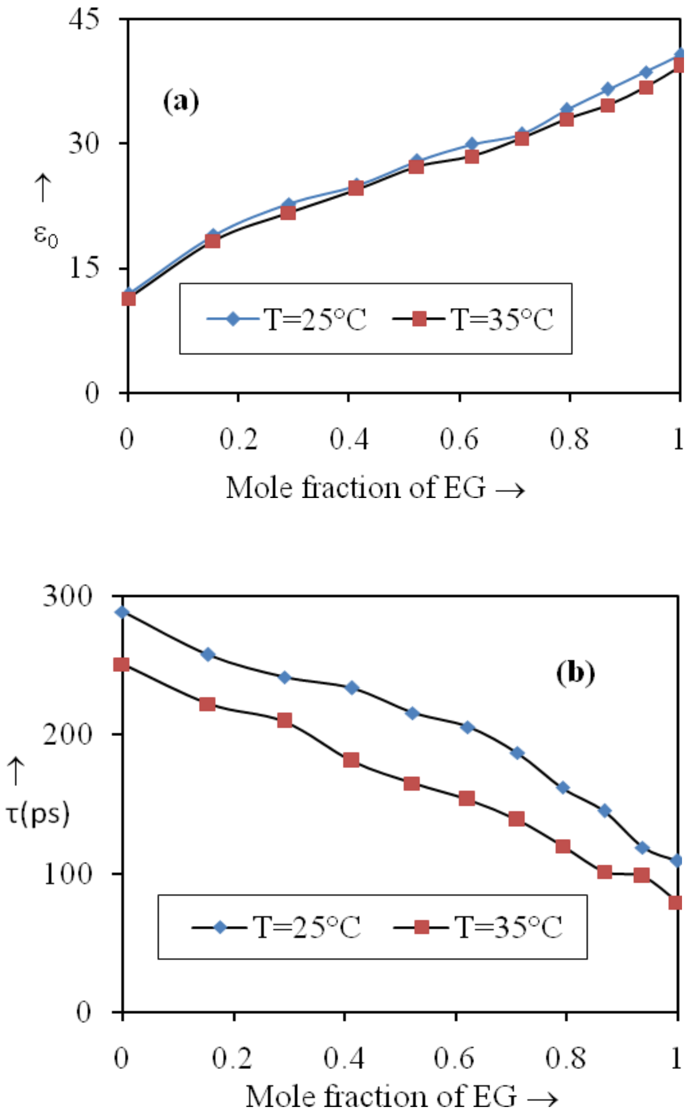


Figure 2. (a) Static dielectric constant (ε_0), (b) relaxation time (τ), versus mole fraction (x_2) of EG in TB at different temperatures

Table 3. Temperature dependent values of g^{eff} and g_f for TB+EG mixture

ϕ_1	25°C	35°C	25°C	35°C
	g^{eff}		g_f	
1.0	0.99	0.87	1.00	1.00
0.9	1.12	0.93	0.76	0.79
0.8	1.22	0.98	0.68	0.69
0.7	1.29	1.24	0.63	0.66
0.6	1.31	1.37	0.62	0.64
0.5	1.44	1.55	0.61	0.63
0.4	1.67	1.88	0.61	0.65
0.3	1.83	2.01	0.64	0.67
0.2	2.10	2.33	0.69	0.70
0.1	2.45	2.49	0.82	0.81
0.0	2.88	2.70	1.00	1.00

To fit the experimental data, Eq. (5) has been modified [14]

$$f_B = 1-[a-(a-1)\phi_2]\phi_2 \tag{6}$$

where 'a' is numerical fitting parameter. The parameters ‘a’ has been determined by the least squares fit method and it is found to be 0.314, and -0.142 for temperature 25^{O}C, 35^{O}C respectively. The value of ‘a’ = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to corresponding liquids 1 and 2 interaction.

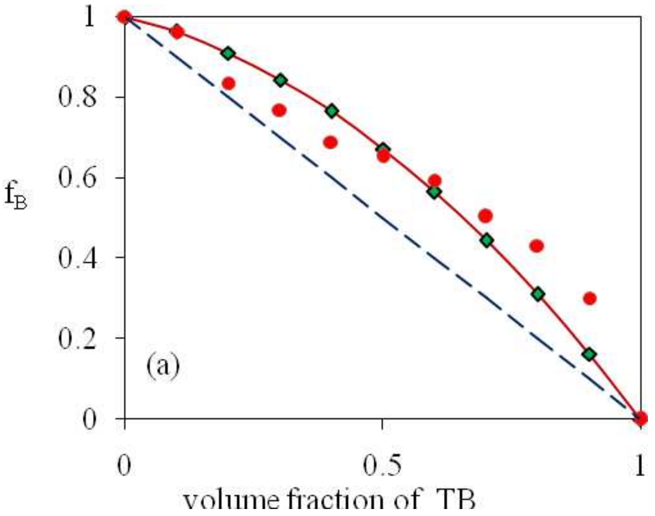


Figure 3. The Bruggeman plot for TB-EG mixture at 25°C. Dashed line denote original model (equation5). Continuous line is the theoretical curve obtained from equation (6). Experimental points are shown by the symbol •

CONCLUSION

Dielectric relaxation parameters and Kirkwood correlation factors are reported in the paper for tert-butyl alcohol with ethylene glycol mixtures of –OH group molecules for various concentrations and temperature. This data provide information regarding solute-solvent interaction in liquids. The dielectric behavior of this binary mixture is found to agree with the modified Bruggeman equation.

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