Molecular Interaction Study of tert-butyl Alcohol with 2-Propanol using TDR Techniques at Microwave

Balaji D. Achole[1]

[1]Department of Physics, Shri. Havagiswami Mahavidyalaya, Udgir, Maharashtra, India

Email: b_achole1234@rediffmail.com

Abstract— The values of the complex permittivity have been determined over the frequency range of 10 MHz to 20 GHz, at 35°C using the time-domain reflectometry (TDR) method for 11 different concentrations of each tert-Butyl alcohol [TB] with 2-Propanol [2P] systems. The relaxation in these systems can be described by a single relaxation time using the Debye model [1]. The static dielectric constants for the mixtures is fitted with the modified Bruggeman model by assuming an additional parameter. Different physical parameters are described for the mixture.

Keywords: Complex permittivity, Bruggeman model, Entropy, Kirkwood correlation factor, Relaxation time. .

I. INTRODUCTION

The study of dielectric relaxation provides useful information about their molecular interactions [2-3] in liquids. Here, the dielectric study of tert-butyl alcohol [$(CH_3)_3COH$] with 2-propanol [$(CH_3)_2CHOH$] mixtures is reported at 35^0C; all these are having –OH group, at different position resulting different hydrogen bonded interaction. The molecules of .these compounds have severa1 hydrogen bonding sites and enter into intra. or inter molecular hydrogen bonding giving rise to different conformations. Due to great industrial applications , it is necessary to investigate the molecular dynamics of these short-chain molecules in dilute solutions to understand the role of hydrogen bonds and the number of carbon atoms present in the chain. These short chain molecules have end -OH group. Dielectric relaxation times give the conformation about the intra molecular rotation and static hindrance offered by the environment. Alcohols have probably been studied more extensively and their dielectric properties are well established. The effect of hydrogen bonded interaction in TB is expected to be more than in 2P. Earlier to this work, no work was reported on effect of tert-butyl alcohol [TB] and 2-propanol [2P] mixtures in the alcoholic system. The alcohol systems are associative due to hydrogen bonding.

II. EXPERIMENTAL

Chemicals

Without further purification, the TB and 2P (AR grade, Merck Pvt. Ltd., West Mumbai, India) chemicals were used and 11 different concentrations were prepared by adding in steps of 10 % volume percentage of 2P in TB alcohol starting from 0 % to 100 %. The mole fraction x_1 of 2P in the respective mixtures were 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- molecular weight, , v_i- volume percent, and ρ_i - represent density of the i^{th} (i=1 for TB and 2 for 2P respectively) in the mixtures.

Apparatus

The time domain reflectometry [4-9] technique is used for the study of complex permittivity spectra. HP 54750 sampling oscilloscope (Hewlett Packard) with TDR plug in module HP 54754A has been used. A fast rising step voltage pulse of 200 mV about 39 ps rise time generated by a pulse generator was propagated through a coaxial line system of impedance 50 Ω. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA). The change in the pulse after reflection from the sample placed in the cell was monitored by the sampling oscilloscope. The reflected pulse were digitized in 1024 points without sample $R_l(t)$ and with sample $R_x(t)$ in the memory of the oscilloscope and transferred to a PC through 1.44 MB floppy diskette drive. **Figure 1** shows recorded incident pulse $R_l(t)$ and reflected Rx(t) pulse from the sample cell for pure tert-butyl alcohol at 35°C. After getting time referenced the reflected pulses $R_l(t)$ and Rx (t) are subtracted and added in the oscilloscope memory. This time dependent subtracted and added pulses are shown in **Figure 2.** The temperature controller system with water bath and a thermostat is used to maintain the constant temperature within the accuracy limit of ± 0.5 °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.

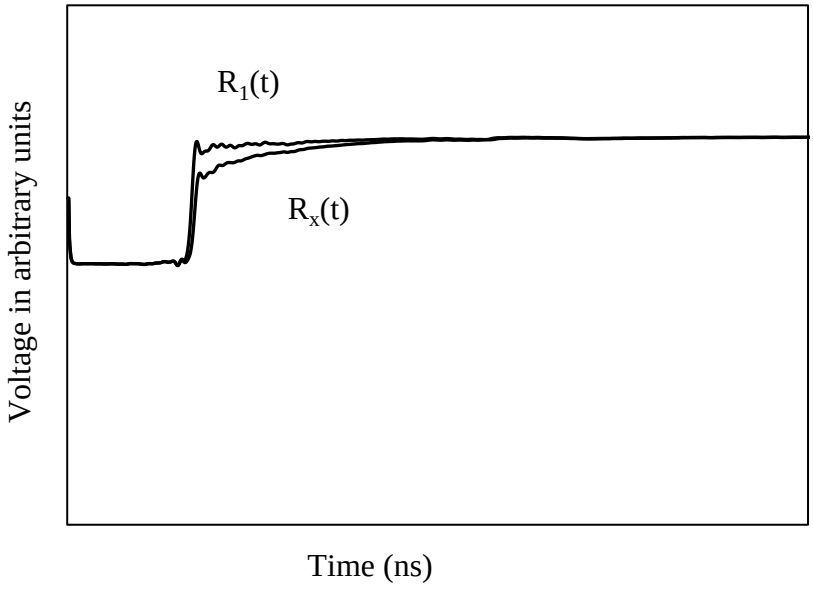

Figure 1: Incident pulse without sample $R_1(t)$, Reflected pulse Rx(t) with sample of tert-butyl alcohol.

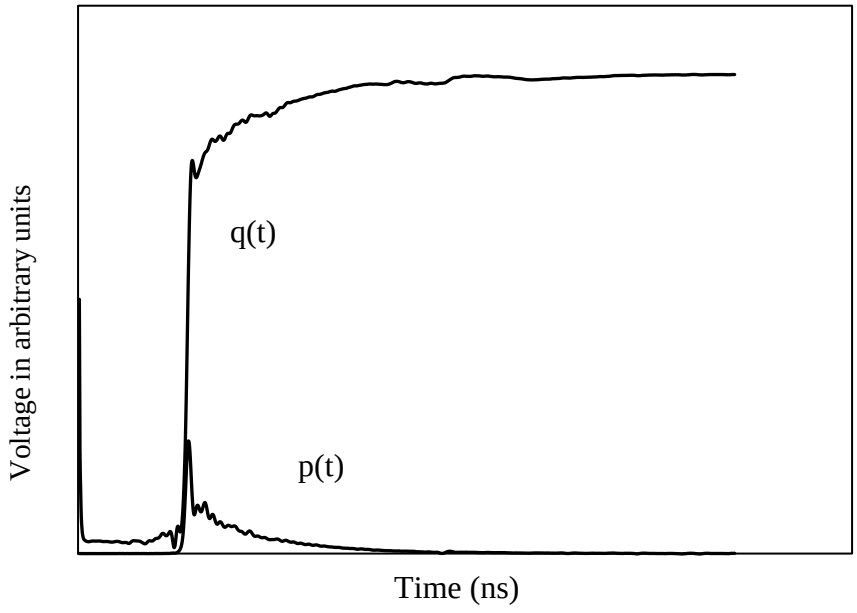

Figure 2: Subtracted pulse p(t) and added pulse q(t).

III. DATA ANALYSIS

By using standard Fourier transform method, the time dependent data were transformed into frequency domain in the frequency range of 10 MHz to 20 GHz and the complex reflection coefficient spectra $\rho^*(\omega)$ were obtained as [10- 12]

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

where $p(\omega) = [R_1(t) - R_x(t)]$ and $q(\omega) = [R_1(t) + R_x(t)]$ are Fourier transforms . Here c, ω, d is the velocity of light, angular frequency and the effective pin length respectively and $j=\sqrt{-1}$. Here $R_1(t)$ is reflected pulse without sample and $R_x(t)$ reflected pulse with sample pulse . By applying bilinear calibration method [2], the complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$.

The values of ε^* obtained experimentally are fitted with the Debye equation [1, 13]

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

where $\varepsilon_0, \varepsilon_\infty$, and τ as fitting parameters. To determine the values of dielectric parameters, nonlinear least-squares fit method [14] was used. A sample $\rho^*(\omega)$ and $\varepsilon^*(\omega)$ spectrum for 20 % TB are shown in **Figures 3** for TB-2P systems at 35°C.

IV. RESULTS AND DISCUSSION

Complex Permittivity Spectra and Relaxation Time

Intermolecular hydrogen bonding in the liquid state plays an important role in both viscous flow and relaxation phenomena. This interaction opposes the molecular reorientation, since breaking and reforming of hydrogen bonds is required for molecular rotation in an alternating electric field. In binary liquid mixtures, a wide range of possible interactions between their constituents like hydrogen bonding, molecular associations, dipole–dipole, and dipole-induced dipole interactions. The density and ε_0 values for pure liquids used are given in **Table 1.** The experimentally obtained values of static permittivity (ε_0), dielectric constant at high frequency (ε_∞) and relaxation time (τ) as obtained by fitting method are listed in **Table 2** for TB-2P system . The values of α and β are taken to be 0 and 1, for the systems. For this system, the behaviour of (ε_0) and relaxation time (τ) in mixtures given as a function of mole fraction of 2-Propanol for different temperatures is as shown in **Figure 4**. The static dielectric permittivity values increases with increase in volume percentage of 2P in TB, which also increases with temperature. The value of relaxation time decreases with increase in volume parentage of 2P in TB. The relaxation time of each compound decreases with the rise in temperature. It is also observed that, the dielectric parameters of these mixtures are intermediate between the pure liquids.

Table 1: Comparison of data for the liquids used with literature values at 22°C.

Name of liquid	Dielectric Constant ε_0		Dielectric Relaxation Time τ	
	Observed Value	Literature value	Observed Value	Literature value[c]
tert-Butyl alcohol	11.88	11.51[a]	289.10	276.89[a]
2-Propanol	18.47	18.48[b]	251.25	245.87[b]

where a and b data are taken from references [4,9] respectively.

IV. I The Excess Permittivity Model

The information related to interactions between TB-2P system may be attempted through excess properties [15] related to the permittivity factor and relaxation time in the mixture. The excess permittivity ε^E is defined as

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_\infty)_m - [(\varepsilon_0 - \varepsilon_\infty)_1 \ x_1 + (\varepsilon_0 - \varepsilon_\infty)_2 \ x_2] \quad (3)$$

where x- mole fraction and suffices m, 1, 2 represents mixture, liquid 1 (TB) and liquid 2 (2P) of mixtures .

The qualitative information provided by excess permittivity about dimmers in the mixture is as :

(i) $\varepsilon^E = 0$ indicates that no multimer has been formed.

(ii) $\varepsilon^E < 0$ indicates that the total effective dipoles get reduced resulting less effective dipole polarization.

(iii) $\varepsilon^E > 0$ indicates that the structure of dimer is such that the total effective dipole moment increases resulting more effective dipole polarization.

The mixtures is expected to contain three types of clusters (monomer or dimer) in for TB-2P system: The pairs corresponding to dimers are TB-TB, 2P-2P and TB-2P.When 2P is added to TB, some of 2P will form dimer with TB.

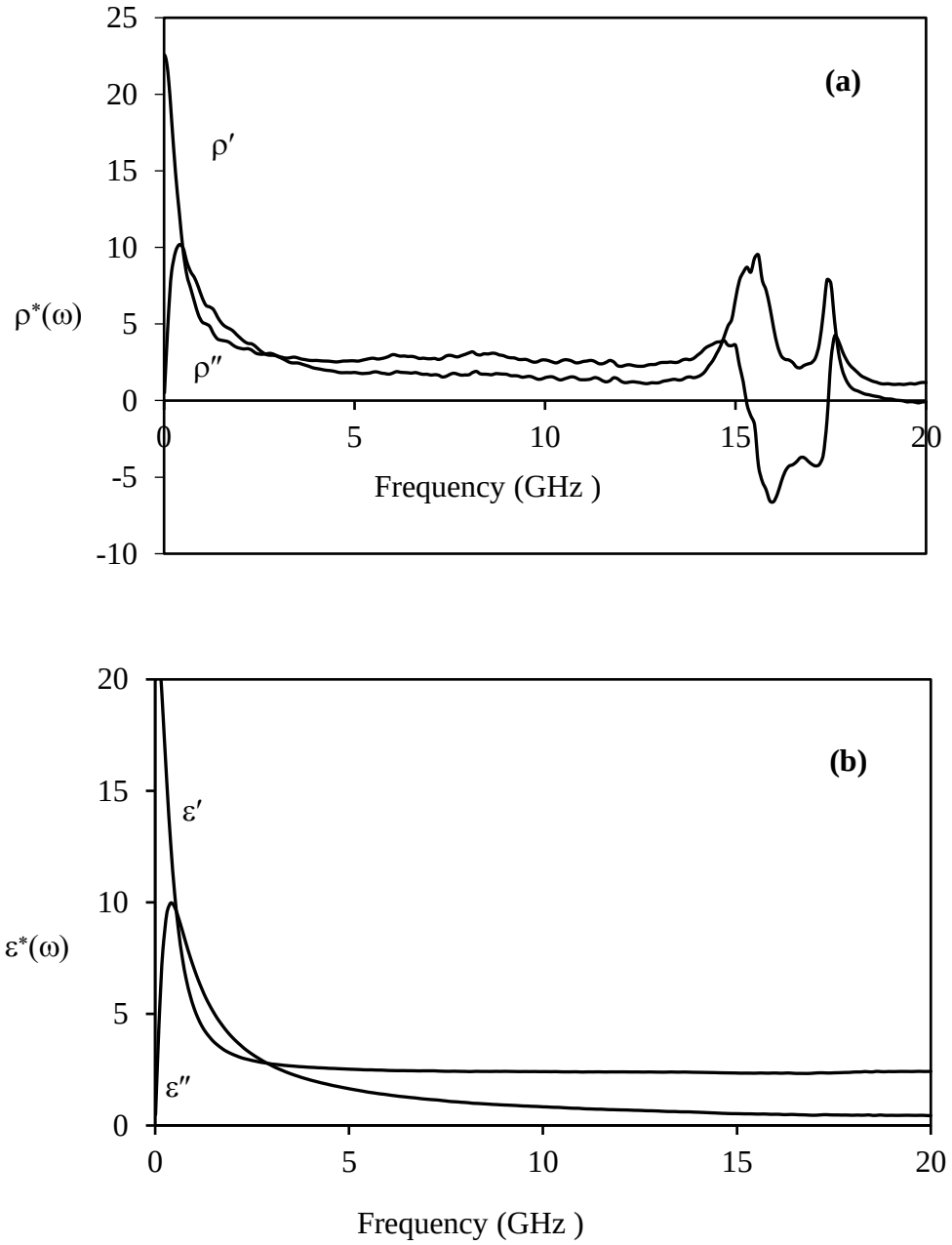

Figure 3 a) $\rho^*(\omega)$ spectra of TB-2Propanol for 20 % of TB at 35^0C.

b) $\varepsilon^*(\omega)$ spectra of TB-2Propanol for 20 % of TB at 35^0C.

Table 2: Dielectric relaxation of Temperature dependent parameters for TB+2P mixtures[a]

x_2	T= 35 °C		
	ε_0	ε_∞	τ (ps)
0.0000	11.29(0)	3.08(0)	251.39(0)
0.1172	13.34(8)	3.12(7)	238.90(3)
0.2300	13.91(2)	3.13(1)	232.60(4)
0.3386	14.29(1)	3.14(3)	224.13(8)
0.4433	14.80(5)	3.15(6)	219.42(1)
0.5443	15.18(8)	3.18(7)	213.89(5)
0.6418	15.66(6)	3.21(4)	208.25(3)
0.7360	15.93(1)	3.25(6)	200.97(7)
0.8269	16.60(7)	3.28(3)	187.15(2)
0.9149	16.98(1)	3.29(5)	180.90(1)
1.0000	17.42(0)	3.35(0)	175.60(0)

[a] x_2 be the mole fraction of 2-Propanol in TB mixture. The number in parentheses indicates error in values e.g. 17.24(9) means 17.24 ± 0.9.

IV. II Excess Relaxation Time Model

The excess inverse relaxation time given as

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 x_1 + (1/\tau)_2 x_2] \quad (4)$$

where $(1/\tau)^E$ gives excess inverse relaxation time represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening, (which is inverse of the relaxation time) in the resonant spectroscopy [16]. The values of ε^E and $(1/\tau)^E$ variation with mole fraction of 2-Propanol in TB at various temperatures are shown in **Figures 6.** The information regarding the dynamics from this excess property is as follows:

(i) $(1/\tau)^E = 0$:There is no change in the dynamics of liquid 1 and 2 interaction indicating no formation of multimer.

(ii) $(1/\tau)^E < 0$: Interaction of the liquids 1 and 2 produces a field where the effective dipoles rotate slowly.

(iii) $(1/\tau)^E > 0$: Interaction of the liquids 1 and 2 produces a field where the effective dipoles rotate quickly i.e. the field will co-operate in rotation of dipoles.

Figure 6. a, b: shows that the values of ε^E and $(1/\tau)^E$ are positive near TB rich region and they become negative near 2P region. It indicates that dimer structure in surrounding of TB rich region is different from 2P rich region. It is expected as TB has stronger hydrogen bonded interaction as compared to 2P, as indicated by values of TB-2P system, the values of ε^E and $(1/\tau)^E$ decreases with increase in temperature of the system. But in TB-nP system, ε^E decreases as temperature increases and $(1/\tau)^E$ increases at 35^0C.

Both the excess parameters experimentally obtained were fitted to the Redlich-Kister equation [17, 18] as

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

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 **Figures 5.**

For TB-2P system: It is observed that values of B_0 and B_1 get positive to negative with decrease in molecular size of 2P. The values of B_2 becomes positive for 35°C of TB-2P as liquid 1 changes from TB to 2P, where as the values of B_3 becomes smaller. For TB-2P system represents: B_0 as rate for forming dimer TB-2P, B_1 as rate for forming trimer 2TB-2P, B2 as rate for forming quartermers 2TB-2 2P, B_3 as rate for forming pentamer 3TB-2 2P respectively. There is no report of theoretical molecular simulation study for the systems to support the finding and very interesting to perform the theoretical simulation on clusters to get detail structural information. The Values of numerical fitting parameter 'a' for mixtures is -0.173 at 35^0C temperatures.

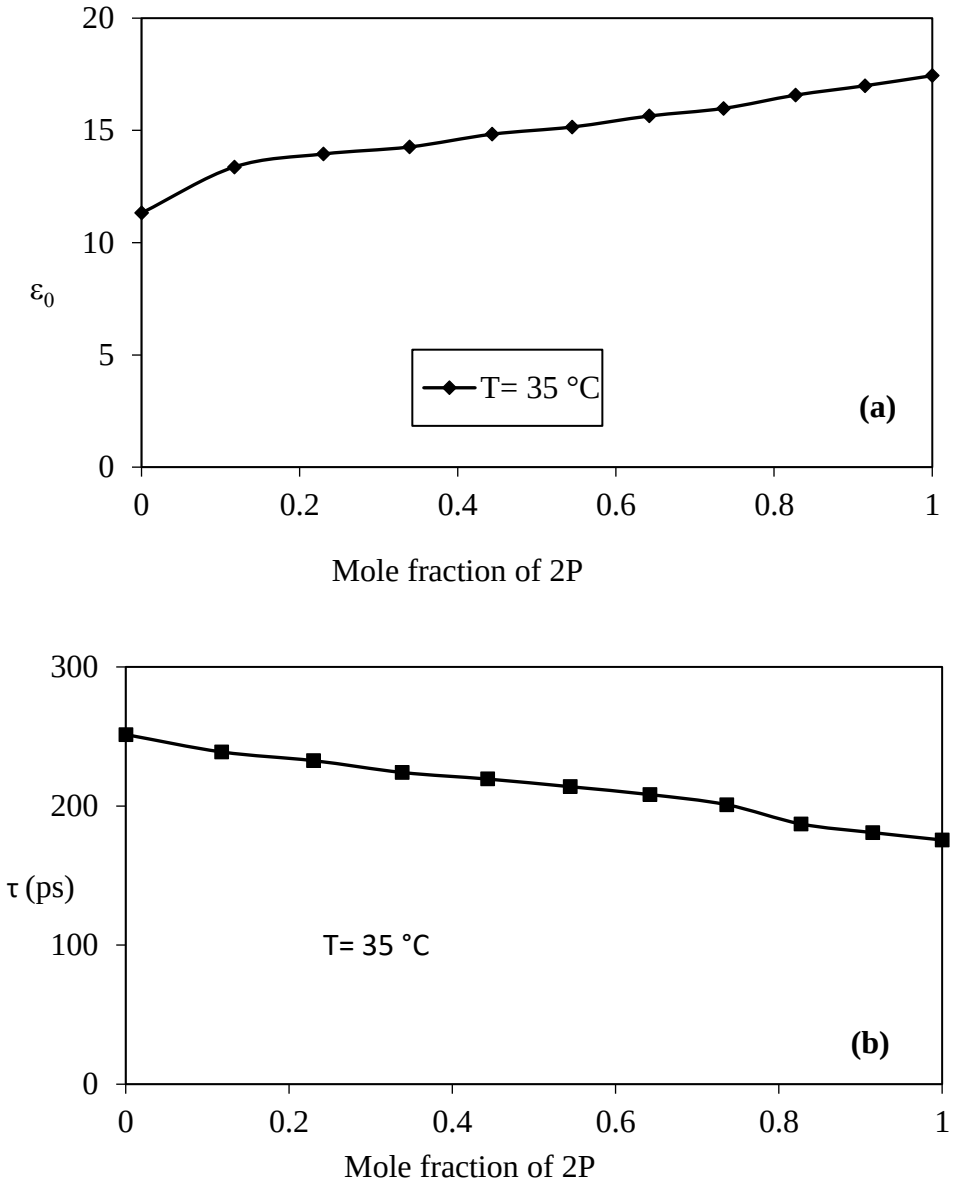

Figure 4: **(a)** Variation of ε_0 verses Mole fraction of 2-Propanol in TB at various temperatures.

(b) Variation of τ (ps) versus Mole fraction of 2-Propanol in TB at various temperatures.

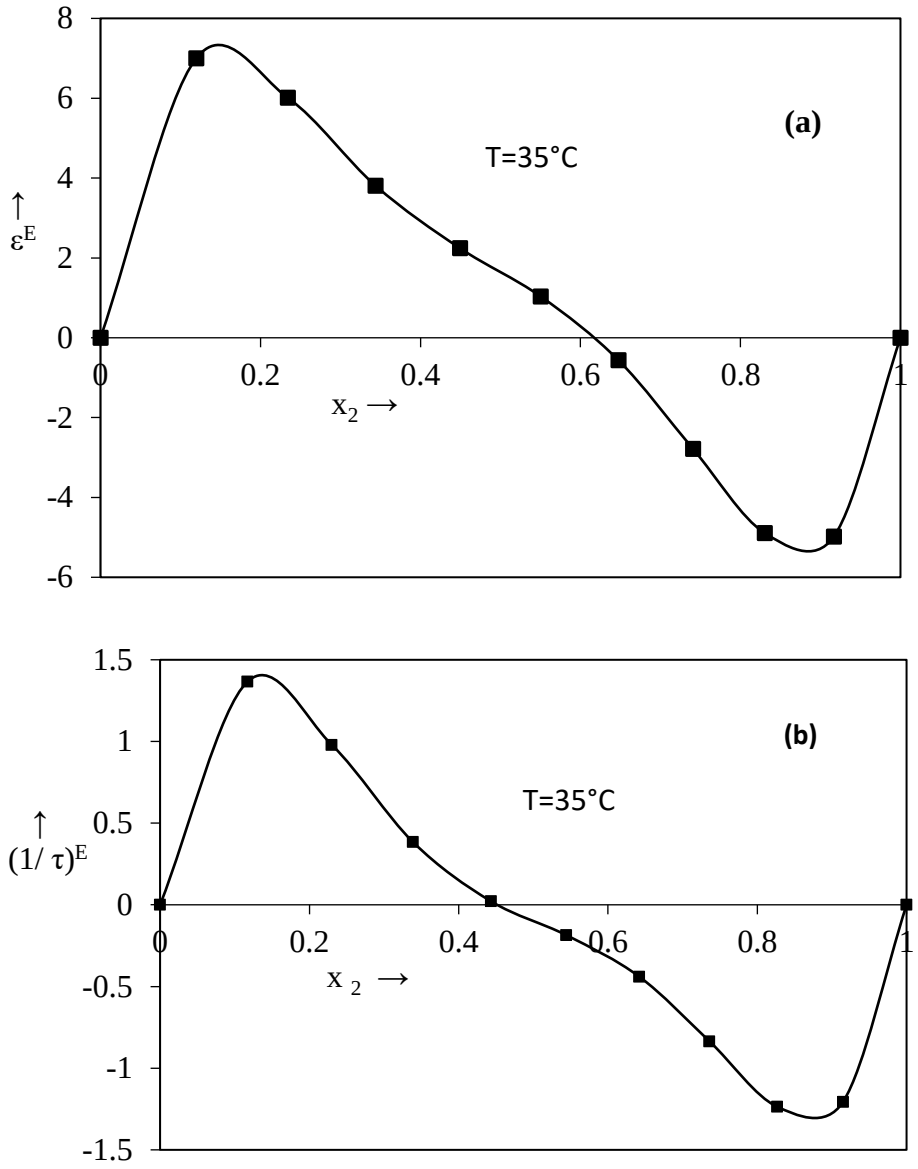

Figure 5: **(a)** Variation of ε^E versus Mole fraction of 2-Propanol in TB at 35°C temperatures.

(b) Variation of $(1/\tau)^E$ versus Mole fraction of 2-Propanol in TB at 35°C temperatures.

IV. iii Kirkwood Parameter Model

The Kirkwood correlation parameter g [19] is also a parameter for getting information regarding correlation between two molecules in mixture. The g for pure liquid may be obtained by the expression

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

where μ is dipole moment in gas phase, ρ is density, M is molecular weight, k is Boltzman's constant, N is Avogadro's number. The dipole moments for TB, 2P, nP and EG in gas phase are taken as 1.69 D , 1.68 D, 1.68 D and 2.2 D respectively, where the dipole moment D is 10^{-18} e. s. u. For the mixtures of two polar liquids 1, 2, equation (4.6) is modified [09] with the following assumptions:

1. Kirkwood correlation parameter g for the binary mixture is expressed interms of an effective averaged correlation factor g^{eff}. Hence, the Kirkwood equation for the mixture can be expressed as

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

where ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively. The g^{eff} will provide overall average information about TB-2P, TB-nP and TB-EG dimmers.

2. Assume that the correlation factors, g_f for molecules 1 and 2 in the mixture contribute to the effective g proportionality to their pure-liquid values g_1, g_2. With this assumption, the above equation for the mixture can be written as

$$\frac{4\Pi N}{9kT}\left(\frac{\mu_1^2\rho_1 g_1}{M_1}\phi_1+\frac{\mu_2^2\rho_2 g_2}{M_2}\phi_2\right)g_f=\frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \quad (8)$$

where g_f - the Kirkwood correlation factor for a mixture and ϕ_1 and ϕ_2 as volume fractions of liquids 1 and 2 respectively.

The correlation factor provide information about formation of multimers in liquid as

i) g = 1 indicates, there is no interaction between the molecules in liquid. The system may be considered like non-polar.

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 value of the Kirkwood factor, g_f, will be one for pure liquid. It will deviate from one for the mixture indicating presence of interaction between two molecules. For TB-2P system: The values of the correlation factor for 2P are more effective than the corresponding value in TB region. The g^{eff} values increases with increase in volume % of 2-Propanol in TB. The values of Kirkwood factor g_f are less than or equal to unity for all measured temperature, indicating that the intermolecular interaction is such that the total effective value of dipoles gets reduced. It suggests anti-parallel alignment of dipoles.

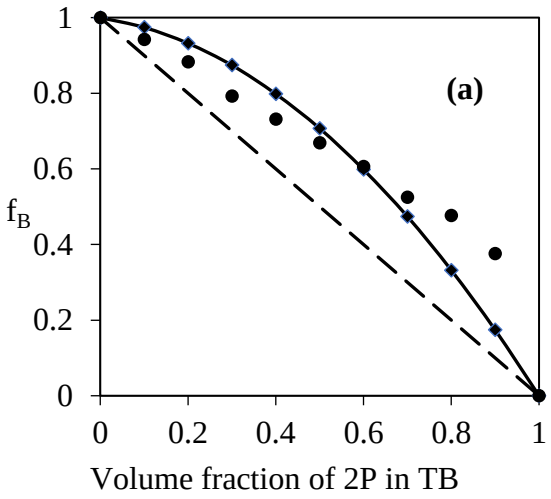

Figure 6: Bruggeman factor f_B verses Volume fraction of 2 Propanol in TB at 35^0C. Dashed line represents original Bruggeman model. Solid point's line represents theoretical Bruggeman model obtained from equation (9). Experimental points are shown by the Marker •.

IV. iv Bruggeman Parameter Model

The modified Bruggeman equation [20] is used as indicator for liquid 1 and 2 interactions. The Bruggeman factor f_B is given by,

$$f_B=\left(\frac{\varepsilon_{0m}-\varepsilon_{02}}{\varepsilon_{01}-\varepsilon_{02}}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{1/3}=(1-\phi_2) \quad (9)$$

According to equation (9), when plotted f_B against ϕ_2 , a linear relationship is expected giving a straight line . However, the experimental values of f_B were found to be deviated from the linear relationship. The Bruggeman dielectric factor f_B versus volume fraction ϕ_2 of 2P as in **Figure 6**. The above equation has been modified to fit the experimental data is as [21-23]

$$f_B = 1-[a-(a-1)\,\phi_2]\,\phi_2 \quad (10)$$

where a is numerical fitting parameter and has been determined by using the least squares fit method .The value of a = 1 corresponds to the ideal Bruggeman mixture formula. The deviation from one relates to corresponding liquids 1 and 2 interactions.

Conclusion

The study provides the permittivity parameters for the mixture of binary polar liquids. The main features are: The molecules of these compounds have several hydrogen bonding sites and enter into intra or inter molecular hydrogen bonding giving rise to different conformations. Alcohols are used as industrial solvents, surfactants, detergents, wetting agents and many more. Due to great industrial applications of these molecules, investigation of their molecular dynamics in dilute solutions to understand the role of hydrogen bonds and the number of carbon atoms present in the chain. These molecules have end -OH group and they can enter into intra- and intermolecular hydrogen bonding In pure liquid state, the major contribution to the relaxation process is due to overall rotation whereas in case of dilute solutions the group rotations are more significant. The dielectric permittivity of a liquid depends on the temperature, density, viscosity and permanent dipole moment. Relaxation Time: due to reorientation of the molecules as a whole generally increases (1) increases due to increases in the molar volume of the molecule and (2) also due to increase in the viscosity of the solute.The ε^E values of the mixtures in 2P rich region is negative over the concentration range in the respective system .This behavior may be interpreted at the molecular level, because negative ε^E values can arise either from dipolar association between the components in the mixture or from dipolar self-association of the polar component to form species of lower dipole moment. The other high resolution spectroscopy is needed to get detail structure of the dimers. The interaction of the -OH group of polar molecules is discussed.

References

[1] Debye P., Polar molecules, Chemical Catalog, New York **(1929)**.

[2] Cole R. H., Berbarian J. G., Mashimo S., Cryssikos G., Burns A. and Tombari E., Time domain reflection methods for dielectric measurements to 10 GHz, *J. Appl. Phys*., 66, 793-802 **(1989)**

[3] Davidson D. W. and Cole R. H., Dielectric relaxation study of glycerine, *J. of Chem. Phys*., 18, 1417 **(1950)**

[4] Puranik S. M., Kumbharkhane A. C. and Mehrotra S. C., Dielectric relaxation of tert-butyl alcohol-water mixtures using a time domain technique, *J. of Chem. Soc., Faraday Trans*., 87, 1569-1773 **(1991a)**

[5] Hosamani M. T., Fattepur R. H., Deshpande D. K. and Mehrotra S. C, Temperature and frequency-dependent dielectric studies of p-fluorophenyl acetonitrile-methanol mixtures using time domain reflectometry, *J. of Chem. Soc., Faraday Trans*., 91(4), 623-626 **(1995)**

[6] Patil S. P., and Mehrotra S. C., Dielecric measurements of aniline and alcohol mixtures at 283, 293, 303 and 313 K using the TDR technique, *J. of Chem. Eng. Data*, 44, 875-878 **(1999).**

[7] Pawar V. P. and Mehrotra S. C., Dielectric relaxation study of chloro benzene-dimethylformamide using TDR technique, *J. Mol. Liq.*, 95,63-74 (**2002**).

[8] Khirade P. W. and Mehrotra S. C., Temperature-dependent dielectric relaxation of 2-ethoxyethanol, ethanol, and 1-propanol in dimethylformamide solution using the time domain technique, *J. Sol. Chem*., 28(8), 1031 **(1999).**

[9] Kumbharkhane A. C. , Puranik S. M. and Mehrotra S. C., Dielectric properties of 2 Propanol-water mixtures using a time domain reflectometry. J. of pure and Applied physics,vol-4 no-2 ,196 **(1992)**.

[10] Shannon C. E., Communication in the presence of noise, *Proc. IRE*. **(1949).**

[11] Samulon H. A., Spectrum analysis of transient response curves, *Proc. IRE*., 39, 175-186 **(1951).**

[12] Cole K. S. and Cole R. H., Dispersion and absorption in dielectrics, *J. Chem. Phys*., 9, 341-345 **(1941)**

[13] Frolhich H., Theory of dielectrics, *Oxford University press, London* **(1949)**

[14] Bevington P. R., Data reduction and error analysis for the physical sciences, *McGraw Hill, New York* **(1969)**

[15] Tabellout M., Lanceleur P., Emery J. R., Hayward D. and Pethrick R. A., Dielectric, ultrasonic and carbon-13 nuclear magnetic resonance relaxation measurements of t-butyl alcohol-water mixtures, *J. of Chem. Soci. Faraday Trans*., 86(9), 1453-1501 **(1990)**

[16] Mehrotra S. C. and Boggs J. E. , Effect of collison-induced phase shifts on the line widths and line shifts of rotational spectral lines, *J. Chem. Phys*., 66, 5306-5312 **(1977)**

[17] Aralaguppi M. I., Aminabhavi T. M., Balundgi R. H. and Joshi S. S., Thermodynamic interactions in mixtures of bromoform with hydrocarbons, *J. Phys. Chem*., 95, 5299 **(1991)**

[18] Al-Azzawl S. F., Awwad A. M., Al-Dujaili A. M. and Al-Noori M. K., Dielectric constant and excess volume of pyrrolidone+water at several temperature, *J. Che. Engg. Data*., 35, 463 **(1990).**

[19] Frolhich H., Theory of dielectrics, Oxford University Press, London, (1949).

[20] Bruggeman D. A. G., Ann. Phys. (Leipzig), 5, 636 **(1935)**.

[21] Puranik S. M., Kumbharkhane A. C. and Mehrotra S. C., The static permittivity of binary mixtures using improved Bruggeman model, J. Mol. Liq., 59, 173 **(1994)**.

[22] B D Achole and V P Pawar , Molecular Interaction Study of Multi functional group of Alcohols through Dielectrics using TDR , *Journal of Physics, Conference series* 490 (2014) 012036.

[23] B D Achole and V P Pawar , Molecular Interaction Study between some Multi functional groups [-OH and –CH3] of Alcohols through Dielectrics using TDR , *International journal of Engineering and Technology , management and Applied Sciences* **(2016)** *volume 4, Issue 3.*