

The Research Dialogue

An Online Quarterly Multi-Disciplinary
Peer-Reviewed / Refereed Research Journal

ISSN: 2583-438X

Volume-1, Issue-4, January 2023

www.theresearchdialogue.com



Physical & Thermo dynamical Properties of Mixture of Tertiary alcohol with Secondary alcohol Molecules Using TDR Technique

B. D. Achole

Department of Physics,
Shri Havagiswami Mahavidyalaya,
Udgir-413 517, Maharashtra.

E-mail: b_achole1234@rediffmail.com

ABSTRACT:

The dielectric study of tert-butyl alcohol(TB) with 2-propanol (2P) were determined over the frequency range of 10 MHz to 20 GHz using time domain reflectometry (TDR) at temperature 25⁰C 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. The thermodynamic parameters like molar enthalpy of activation ΔH and molar entropy of activation ΔS are determined from the Eyring rate equation [18] by least square fit method.

Keywords: *Time domain reflectometry, dielectric constant, relaxation time, excess permittivity, Kirkwood correlation factor, Thermo dynamical parameters.*

1. INTRODUCTION

The dielectric relaxation of binary polar liquids provides information regarding their interactions [1]. The objective of the present paper is to report the detailed dielectric relaxation study of tert-butyl alcohol (TB) with 2-propanol (2P) mixtures using TDR at 25 °C temperatures.

2. EXPERIMENTAL

2.1 Materials and Apparatus

TB and 2P (AR grade, Merck Pvt. Ltd., West Mumbai, India) were used without further purification. The solutions were prepared at 11 different volume percentage of 2P 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 i^{th} ($i = 1, 2$) liquids, respectively.

The complex permittivity spectra were studied using the time domain reflectometry [1-4] 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. 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 is used. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were

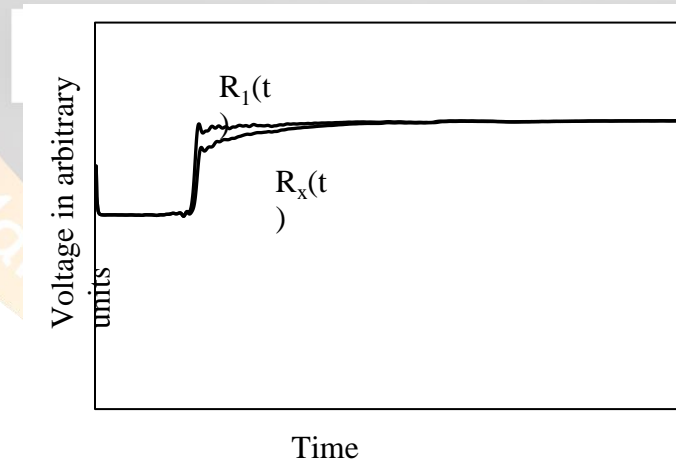


Figure 1: Incident pulse without sample $R_1(t)$, Reflected pulse $R_x(t)$ with sample of tert-butyl alcohol.

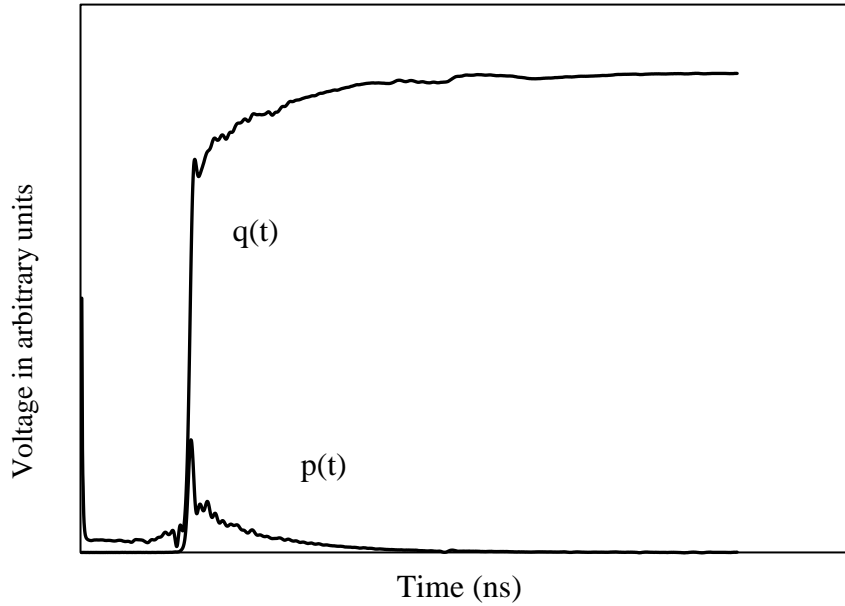


Figure 2: Subtracted pulse $p(t)$ and added pulse $q(t)$.

Figure 1 shows recorded incident pulse $R_i(t)$ and reflected $R_x(t)$ pulse from the sample cell for pure tert-butyl alcohol at 25°C. After getting time referenced the reflected pulses $R_i(t)$ and $R_x(t)$ are subtracted and added in the oscilloscope memory. This time dependent subtracted and added pulses are shown in **Figure 2**.

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 $\pm 1^\circ\text{C}$. 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 [5,6] as

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

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $[R_i(t) - R_x(t)]$ and $[R_i(t) + R_x(t)]$ 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 [1].

The experimental values of ε^* are fitted with the Debye equation [7]

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

with ε_0 , ε_∞ , and τ as fitting parameters. A nonlinear least-squares fit method [8] was used to determine the values of dielectric parameters.

Table 1. The data for the liquids used with literature values at 25°C.

Liquid	ε_0		M	$\rho/(\text{g.cm}^{-3})$
	<i>This work</i>	Literature	Literature	Literature
TB	11.89	11.50 ^c	74.121 ^a	0.8063 ^b
2P	18.46	18.49 ^a	60.095 ^a	0.7809 ^a

where a, b and c data are taken from the refs [4], [11] and [12] 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.

Table 2, 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 25°C.

The information related to liquids 1 and 2 interaction may be obtained by excess properties [9] related to the permittivity and relaxation times 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) respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture as follows:

- (i) $\epsilon^E = 0$ indicates the liquid 1 and 2 do not interact at all.
- (ii) $\epsilon^E < 0$ 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) $\epsilon^E > 0$ 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

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

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 broadening (which is inverse of the relaxation time) in the resonant spectroscopy [10].

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

x_2	25 °C		
	ϵ_0	ϵ_∞	τ (ps)
0.0000	11.89(0)	3.26(3)	289.16(1)
0.1172	14.67(7)	3.19(6)	284.61(17)
0.2300	16.05(9)	3.14(4)	280.92(14)
0.3386	16.54(5)	3.15(7)	276.48(23)
0.4433	16.95(10)	3.13(6)	271.96(19)
0.5443	17.43(4)	3.12(4)	264.31(14)
0.6418	17.69(8)	3.118(9)	259.71(8)
0.7360	17.97(11)	3.11(11)	255.24(5)
0.8269	18.27(12)	3.10(7)	253.874(3)
0.9149	18.36(7)	3.081(5)	252.226(7)
1.0000	18.46(0)	3.15(2)	251.227(0)

* x_2 is the mole fraction of 2P in TB. Number in bracket represent error in the corresponding value, e.g. means 17.43(4) means 17.43 ± 0.4 .

The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [13, 14] 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 Figure 2. Values of Redlich-Kister coefficients are given in **Table 3**.

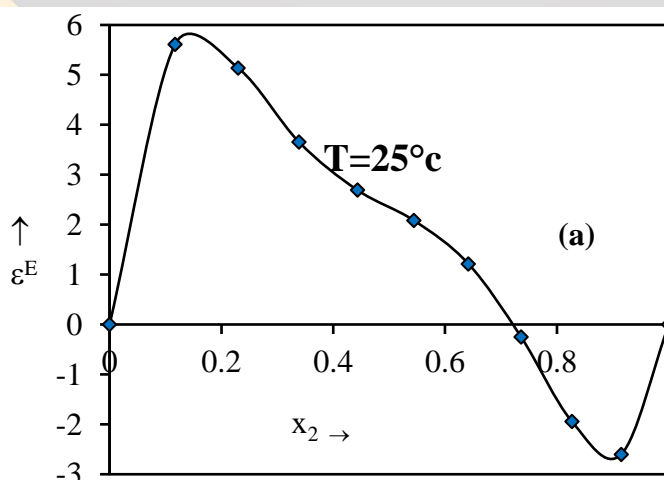
From **Figure 3**, the excess permittivity values are positive in the TB rich region and negative in the 2P rich region. The positive value of excess permittivity indicates the parallel alignment of the dipoles of the system. Negative excess inverse relaxation time values indicate slower rotation of 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 and B_1 get positive to negative values with decrease in molecular size of 2P. This provides information regarding formation of multimers in the mixture. As the physical meanings of B_0 , B_1 , B_2 and B_3 are correlated to rates for forming multimers as dimer TB-2P, trimer 2TB-2P, quartermers 2TB-22P and pentamer 3TB-2 2P respectively.

The Kirkwood correlation factor g_f [15] 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

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

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 1.68 D respectively [4, 11]. Temperature dependent values of g_f are shown in **Table 4**.



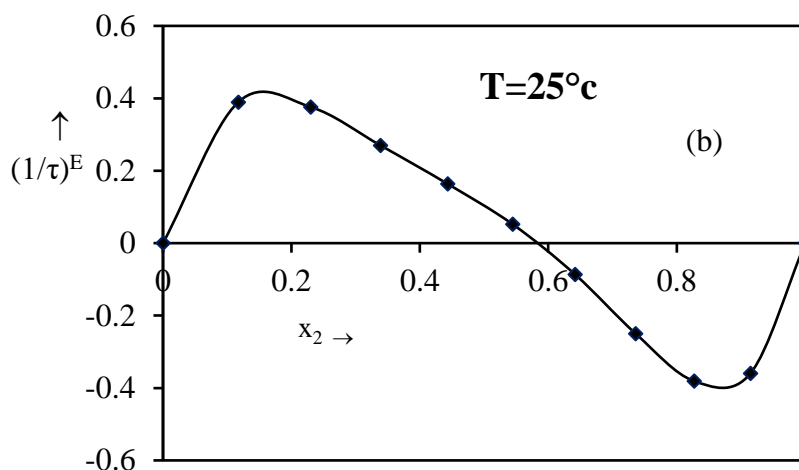


Figure 3. (a) Excess permittivity (ϵ^E) (b) Excess relaxation time $(1/\tau)^E$, versus mole fraction (x_2) of 2P in TB at temperature 25°C.

Table 3. B_n coefficients of the Redlich-Kister equation

°C	B_0	B_1	B_2	B_3
	Excess permittivity			
25	9.39(6)	-11.46(24)	8.81(29)	-68.89(64)
	Excess inverse relaxation time			
25	0.42(0)	-2.20(0)	-0.76(0)	-4.69(0)

The value of 'a' greater than one indicates that the dipoles of TB and 2P will be orientated in such a way that the effective dipole will be greater than corresponding values of pure liquids. The modified Bruggeman equation [16] is another parameter which may be used as an indicator of liquid 1 and 2 interaction. The Bruggeman factor f_B is given by,

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{02}}{\epsilon_{01} - \epsilon_{02}} \right) \left(\frac{\epsilon_{01}}{\epsilon_{0m}} \right)^{1/3} = (1 - \phi_2) \quad (7)$$

Table 4. Temperature dependent values of g_f for TB+2P mixture at $T=25^\circ\text{C}$.

Vol.% of TB	g_f	Vol.% of TB	g_f
1.0	1.0000	0.4	0.9447
0.9	0.9626	0.3	0.9545
0.8	0.9512	0.2	0.9710
0.7	0.9410	0.1	0.9830
0.6	0.9366	0.0	1.0000
0.5	0.9409		

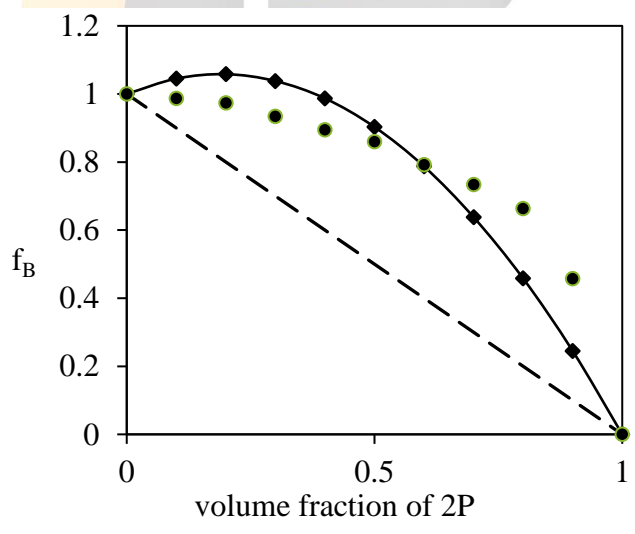


Figure 4. The Bruggeman plot for TB+2P mixture at 25°C . Dashed line denote original model (equation 6). Continuous line is the theoretical curve obtained from equation (8). Experimental points are shown by the symbol \bullet .

Table 5: Molar energy of activation (ΔH) and entropy of activation (ΔS) for Polar liquid systems.

Volume % of TB	ΔH KJ mol ⁻¹	ΔS J mol ⁻¹ K ⁻¹
	TB-2P	
1.0	18.49 ± 0.16	0.229 ± 0.010
0.9	18.94 ± 0.10	0.230 ± 0.009
0.8	19.09 ± 0.40	0.231 ± 0.010
0.7	19.67 ± 0.27	0.233 ± 0.010
0.6	19.29 ± 0.20	0.232 ± 0.010
0.5	18.69 ± 0.35	0.230 ± 0.010
0.4	18.21 ± 0.14	0.229 ± 0.010
0.3	17.81 ± 0.87	0.228 ± 0.009
0.2	16.92 ± 0.36	0.225 ± 0.007
0.1	17.35 ± 0.53	0.227 ± 0.008
0.0	17.21 ± 0.40	0.226 ± 0.007

According to equation (7), 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 has been modified [17]

$$FB=1-[a-(a-1) \phi_2] \phi_2 \quad (8)$$

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 -0.612 at 25°C . The small deviation of ' a ' suggest that weaker interaction between TB and 2P.

Thermodynamic Parameters

Thermodynamic properties may be used to access the dipole under the influence of applied field. When two liquids are mixed together, there is change in energy of the system. This change in energy can be interpreted in terms of its activation energy. The thermodynamic parameters like molar enthalpy of activation ΔH and molar entropy of activation ΔS are determined from the Eyring rate equation [18] by least square fit method as

$$\tau = \frac{h}{KT} \exp (\Delta H-T\Delta S) / RT \quad (9)$$

The values of activation energies ΔH and ΔS are shown in **Table 5**. The values of enthalpy are positive and remain positive for all the concentrations studied. The positive values of enthalpy indicate endothermic interaction and strong hydrogen bonding between liquid 1 and liquid 2. The increase in enthalpy suggests that there is more hydrogen bonding. The thermodynamic parameters evaluated by considering dielectric relaxation and viscosity as rate process are independent of temperature within the experimental errors. The values reported are average values. The viscous flow involves translation and rotational motion of the molecules. Enthalpy refers to the total energy content of the system. It is basically the difference in heat of the product and reactants. Entropy is a term for disorder in a system and that the overall entropy in a system always increases.

5. CONCLUSION

We have computed the values of effective volume in the mixture of TB+2P 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. The positive values of enthalpy indicate endothermic interaction and strong hydrogen bonding between liquid 1 and liquid 2. The increase in enthalpy suggests that there is more hydrogen bonding.

REFERENCES

- [1] R. H. Cole, J. G. Barbarian, S. Mashimo, G. Chryssikos, A. Burns and E. Tombari, *J. Appl. Phys.*, 66 (1989) 793.
- [2] S. M. Puranik, A. C. Kumbharkhane and S. C. Mehrotra, *J. Chem. Soc. Faraday Trans.*, 87 (1991) 1569.
- [3] V. P. Pawar and S. C. Mehrotra, *J. Mol. Liq.*, 95 (2002) 63-74.
- [4] S. M. Puranik, A. C. Kumbharkhane and S. C. Mehrotra, *J. Microwave Power and EM. Energy*, 26 (1991) 196.
- [5] C. E. Shannon, *Proc. IRE*, 37 (1949) 10.
- [6] H. A. Samulan, *Proc. IRE*, 39 (1951) 175.
- [7] P. Debye, *Polar molecules*, Chemical Catalog, New York (1929).
- [8] P. R. Bevington, *Data reduction and error analysis for the physical sciences*, Mc-Graw Hill, New York, (1969).
- [9] M. Tabellout, P. Lancelleur, J. R. Emery, D. Hayward and R. A. Pethrick, *J. Chem. Soc. Faraday Trans.*, 86 (1990) 1453.
- [10] S. C. Mehrotra and J. E. Boggs, *J. Chem. Phys.*, 66 (1977) 5306.
- [11] R. C. Weast, *Handbook of Chemistry and Physics*, 64th ed., CRC Press: Boca Ratan, Florida, (1983-84).
- [12] *Catalog Handbook of fine chemicals*, Aldrich chemical Co., Inc., USA, (1990-91)
- [13] M.I. Aralaguppi, T.M. Aminabhavi, R.H. Balungi, S.S. Joshi, *J. Phys. Chem*, 95 (1991) 5299.
- [14] S.F. Al-Azzawl, A.M. Awwad, A.M. Al-Dujaili, M.K. Al-Noori, *J. Chem. Eng. Data*, 35 (1990) 463.
- [15] H. Frohlich, *Theory of dielectrics*, Oxford University Press, London, (1949).
- [16] D. A. G. Bruggeman, *Ann. Phys. (Leipzig)*, 5 (1935) 636.
- [17] S. M. Puranik, A. C. Kumbharkhane and S. C. Mehrotra, *J. Mol. Liq.*, 59 (1994) 173.
- [18] Eyring H., *J. Chem. Phys.*, 4, 283 (1936)

THE RESEARCH DIALOGUE

An Online Quarterly Multi-Disciplinary
Peer-Reviewed / Refereed Research Journal

ISSN: 2583-438X

Volume-1, Issue-4, January 2023

www.theresearchdialogue.com

Certificate Number-January-2023/19



Certificate Of Publication

This Certificate is proudly presented to


B. D. Achole

For publication of research paper title

**Physical & Thermo dynamical Properties of Mixture of
Tertiary alcohol with Secondary alcohol Molecules Using
TDR Technique**

Published in 'The Research Dialogue' Peer-Reviewed / Refereed Research Journal and

E-ISSN: 2583-438X, Volume-01, Issue-04, Month January, Year-2023.


Dr. Neeraj Yadav
Executive Chief Editor


Dr. Lohans Kumar Kalyani
Editor-in-chief

Note: This E-Certificate is valid with published paper and the paper
must be available online at www.theresearchdialogue.com