Impact Factor (QJIF): 8.47 E-ISSN: 2583-1615, P-ISSN: 3049-3498

International Journal of Research in Academic World

Received: 03/March/2026 **IJRAW:** 2026; 5(4):150-158 **Accepted:** 14/April/2026

Molecular Behavior of Mixture of Chemical Compounds Using TDR Techniques at Microwave Region

[*1]Balaji D Achole

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

Abstract

The complex permittivity spectra for 2-Propanol (2P) with n-Propanol (nP) and Ethylene Glycol (EG) were determined over the frequency range of 10 MHz to 20 GHz using the time domain reflectometry (TDR) in the temperature range of 25 °C to 35 °C for 11 different concentrations of the system. The static dielectric constant (ε_0) and relaxation time (τ) have been obtained by the least square fit method. The dielectric relaxation spectra in all systems studied fits well with Debye equation. Thermodynamic properties 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 & can be interpreted in terms of its activation energy like molar enthalpy & entropy of activation.

Keywords: Time domain reflectometry, excess permittivity, excess inverse relaxation time, Enthalpy & Entropy.

1. Introduction

The dielectric relaxation of binary polar liquids provides information regarding their interactions. In this work, we report the dielectric study of 2-Propanol (2P) with n-Propanol (nP) and Ethylene Glycol (EG) mixtures separately; all are –OH group molecules. It is interesting to see the effect of mixtures of –OH group molecule. The objective of the present paper is to report the detailed comparative study molecular behavior of 2-propanol (2P) with n-Propanol (nP) and Ethylene Glycol (EG) mixtures separately using TDR at two different temperatures.

2. Experimental

2.1 Chemicals

2P and nP & EG liquids (AR grade, Merck Pvt. Ltd., West Mumbai, India) were used without further purification. The solutions were prepared at 11 different volume percentage of nP & EG separately in 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.

2.2 Apparatus

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.

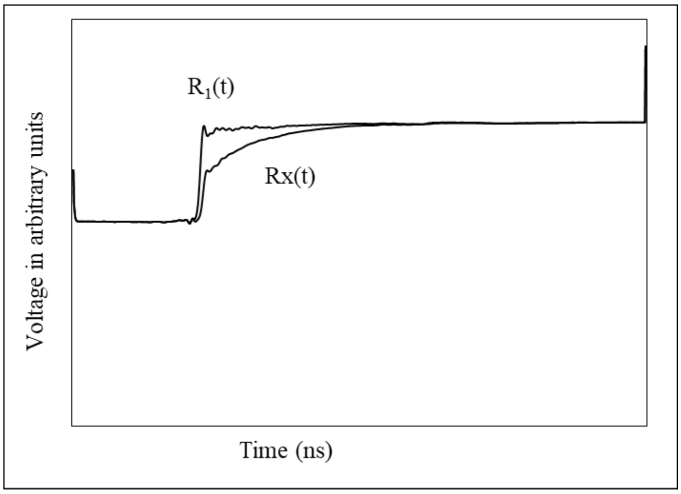

Fig 1: Incident pulse without sample $R_1(t)$ and Reflected pulse Rx(t) from 2-Propanol.

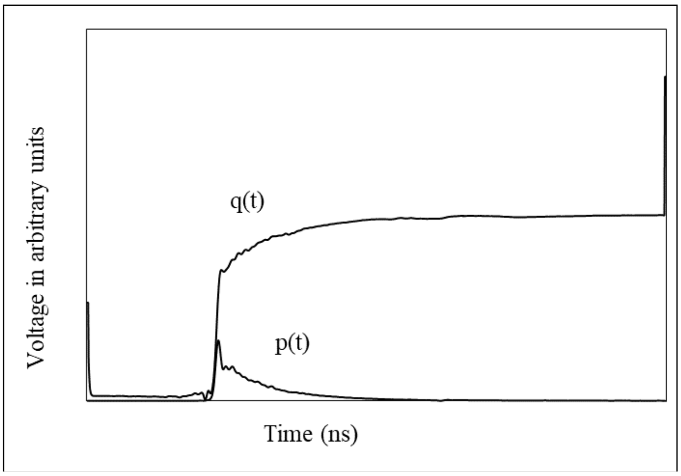

Fig 2: Subtracted pulse p(t) and added pulse q(t) for 2-Propanol.

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 $R_I(t)$ 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. Figure 1 shows sample recorded incident $R_I(t)$ and reflected $Rx(t)$ pulse from the sample cell for pure 2-Propanol at 25°C. After getting time referenced the reflected pulses $R_I(t)$ 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 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.

2.2. 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 [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. Intermolecular hydrogen bonding in the liquid state plays an important role in both viscous flow and relaxation phenomena. A sample $\rho^*(\omega)$ and $\varepsilon^*(\omega)$ spectrum for 50% TB are shown in Figures 3 and Figure 4 for 2P+nP and 2P+EG systems at 25°C respectively.

3. Results and Discussion

i). Complex Permittivity and Relaxation Time

The density and ε_0 values of pure liquids for 2P, nP & EG 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. Figure 5 and Figure 6. Shows the behavior of static dielectric constant of 2P+nP & 2P+EG system, as a function of mole fraction of nP & EG in 2P at different temperatures.

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

Liquid	ε_0		M	$\rho/(g.cm^{-3})$
	This work	Literature	Literature	Literature
2P	18.46	18.49[b]	60.095[a]	0.7809[b]
nP	21.94	21.50[a]	60.11 [b]	0.7997[a]
EG	40.72	41.20[c]	109.18	92.40[c]

Where a, b and c data are taken from the refs [4], [11] and [14] respectively.

ii). The Excess Parameter Model

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

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

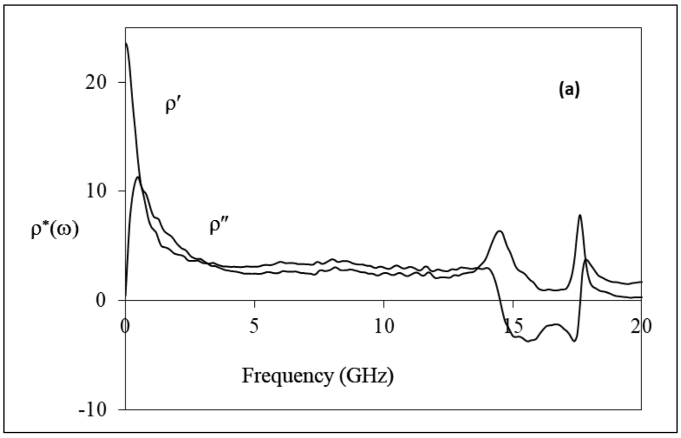

Fig 3(a): $\rho^*(\omega)$ spectra of 2P- nP for 50% of 2P at 25⁰C.

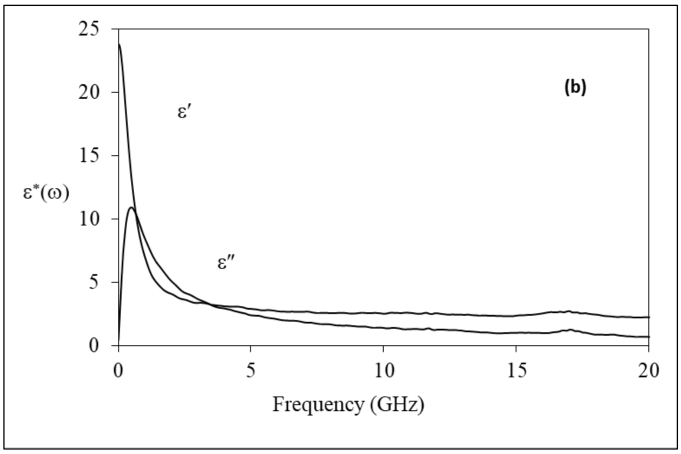

Fig 3(b): $\varepsilon^*(\omega)$ spectra of 2P- nP for 50% of 2P at 25⁰C.

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

The information related to interaction between 2P+nP and 2P+EG systems may be attempted through excess properties related to the permittivity and relaxation times in the mixture. The excess permittivity may provide qualitative information about multimers formation in the mixture. The mixtures is expected to contain three types of clusters (monomer or dimer) in the 2P+nP and 2P+EG systems respectively as-

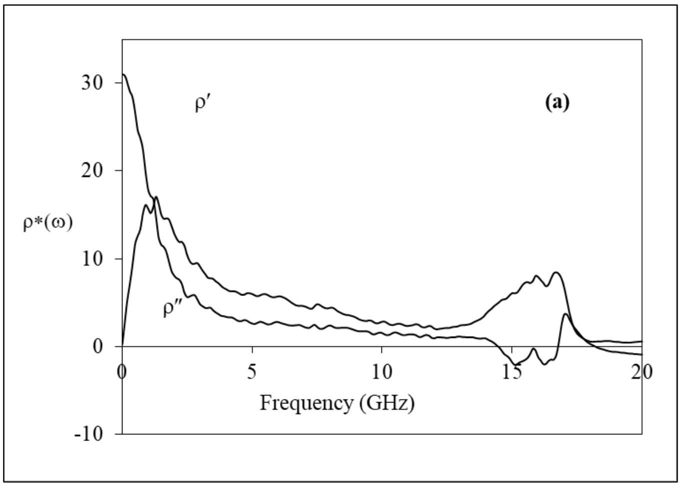

Fig 4(a): $\rho^*(\omega)$ spectra of EG-2P for 50% of 2P at 25^0C.

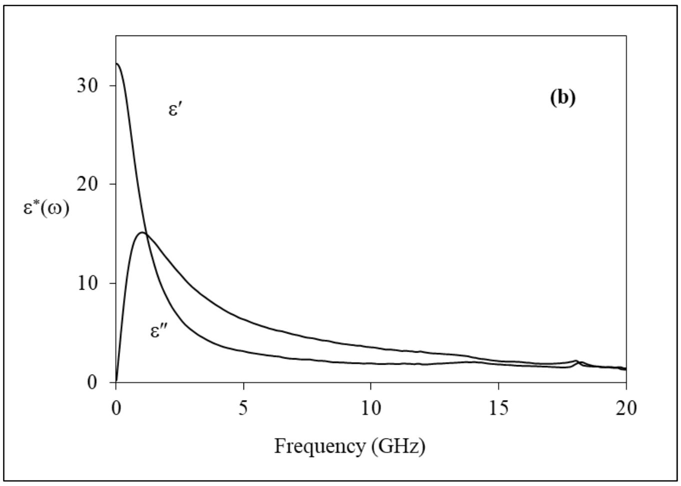

Fig 4(b): $\varepsilon^*(\omega)$ spectra of EG-2P for 50% of 2P at 25^0C.

For 2P-nP system: The pairs corresponding to dimers are 2P-2P, nP-nP and 2P-nP. When nP is added to 2P and some of nP will form dimer with 2P.

For EG-2P system: The pairs corresponding to dimers are 2P-2P, EG-EG and EG-2P. When 2P is added to EG, some of 2P will form dimer with EG. The variation of ε^E and $(1/\tau)^E$ with mole fraction of nP in 2P and 2P in EG respectively at temperatures 25°C and 35°C is shown in Figures 7 and Figure 8.

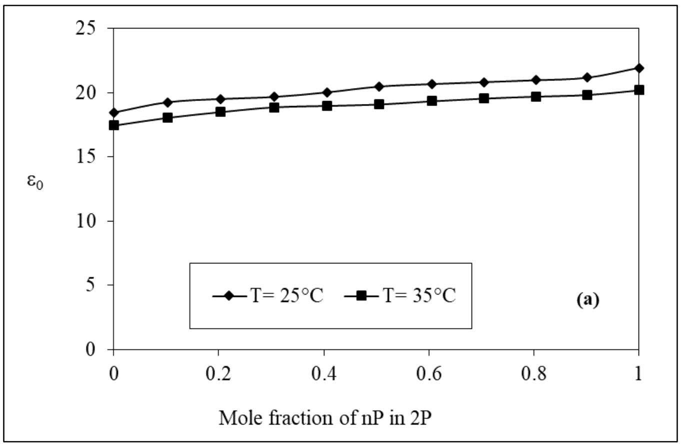

Fig 5(a): Variation of ε_0 versus Mole fraction of nP in 2P at various temperatures.

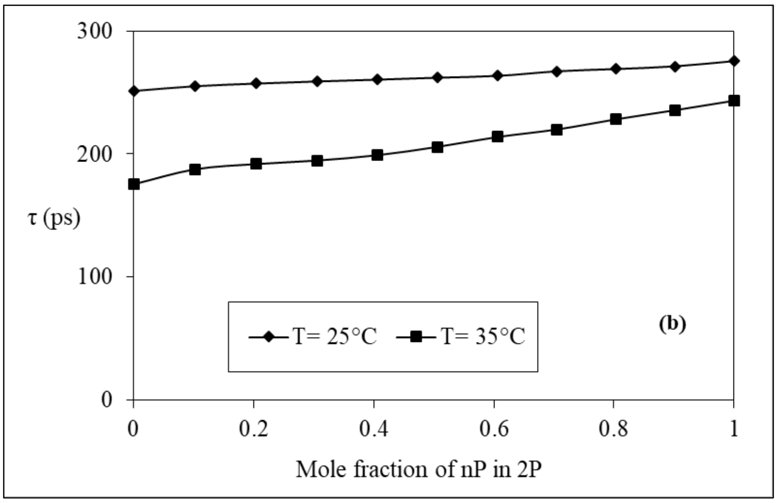

Fig 5(b): Variation of τ (ps) versus Mole fraction of nP in 2P at various temperatures.

Figure 7 a, b: the values of ε^E are positive near 2P rich region and they become negative near nP region. It indicates that dimer structure in surrounding of 2P rich region is different from nP rich region.

Figure 8 a, b: The values of ε^E and $(1/\tau)^E$ are positive near 2P rich region and they become negative near EG region. It indicates that dimer structure in surrounding of 2P rich region is different from EG rich region. It is expected as 2P has stronger hydrogen bonded interaction as compared to EG. The positive peak value of excess permittivity in 2P rich region is observed at 0.8670 mole fraction at 25^0C and negative peak in the EG rich region is at 0.7450 mole fraction of 2P in EG at 35^0C.

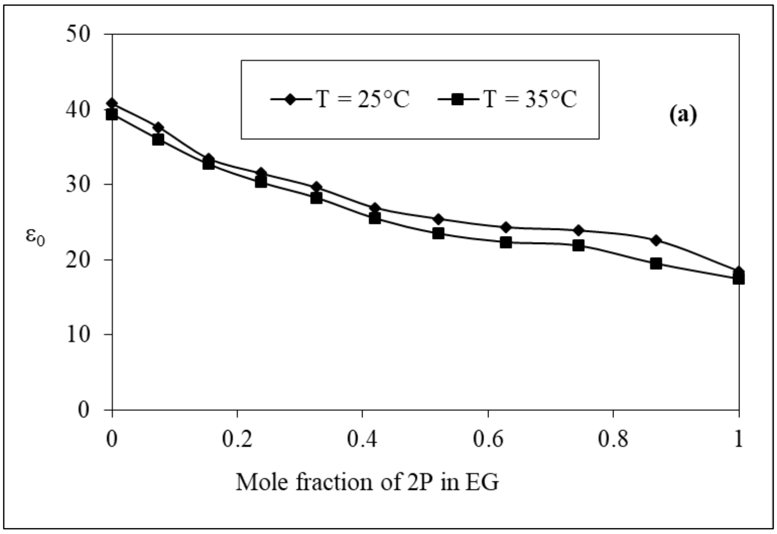

Fig 6(a): Variation of ε_0 versus Mole fraction of 2P in EG at various temperatures.

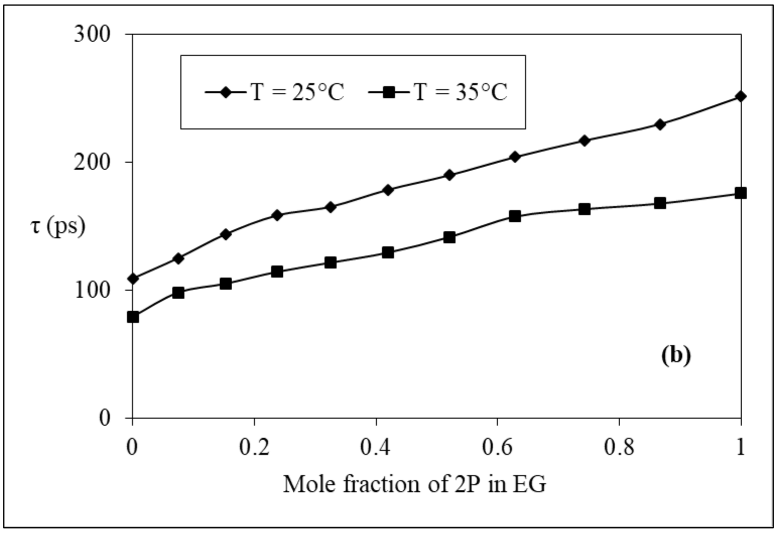

Fig 6(b) Variation of τ (ps) versus Mole fraction of 2P in EG at various temperatures.

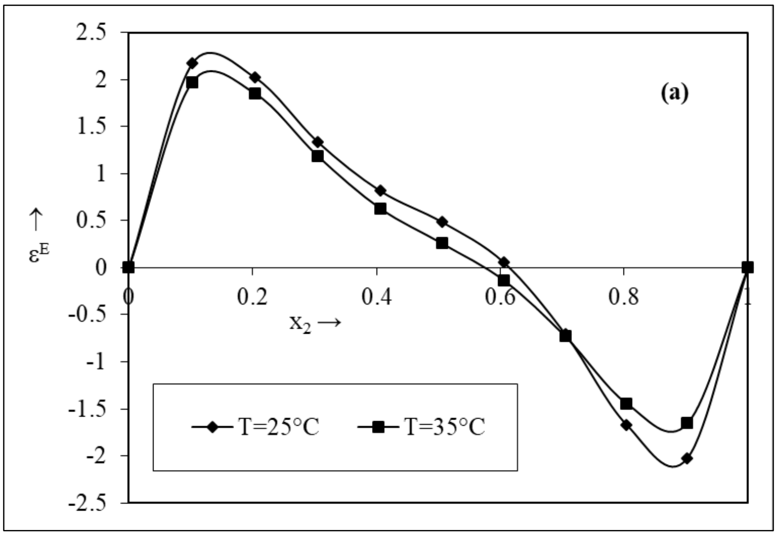

Fig 7(a): Variation of ε^E versus Mole fraction of nP in 2P at various temperatures.

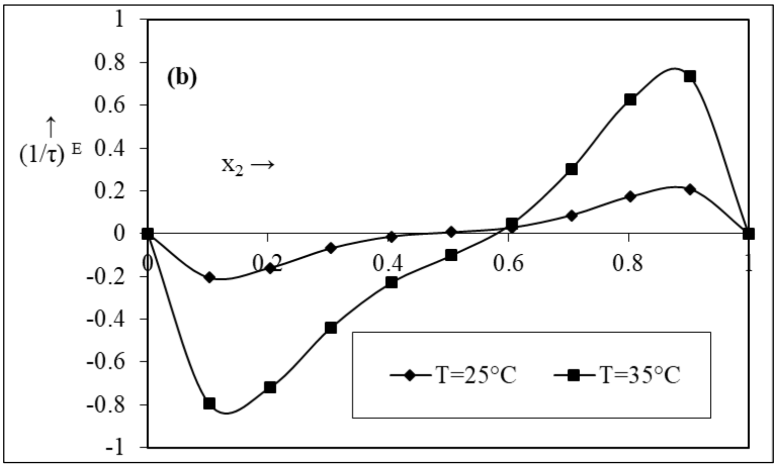

Fig 7(b): Variation of $(1/\tau)^E$ versus Mole fraction of nP in 2P at various temperatures.

In the 2P rich region peak of excess permittivity and relaxation times are different. Also the values of excess inverse relaxation times increases as temperature of the system increases The experimental values of ε^E and $(1/\tau)^E$ with mole fraction of nP in 2P and 2P in EG in respective systems for both temperatures. The experimental values of both the excess parameters were fitted to the Redlich-Kister equation. By using these B_n values, A^E values were calculated and used as guideline to draw the smooth curves in Figures 7 to Figure 8, gives information as –

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.

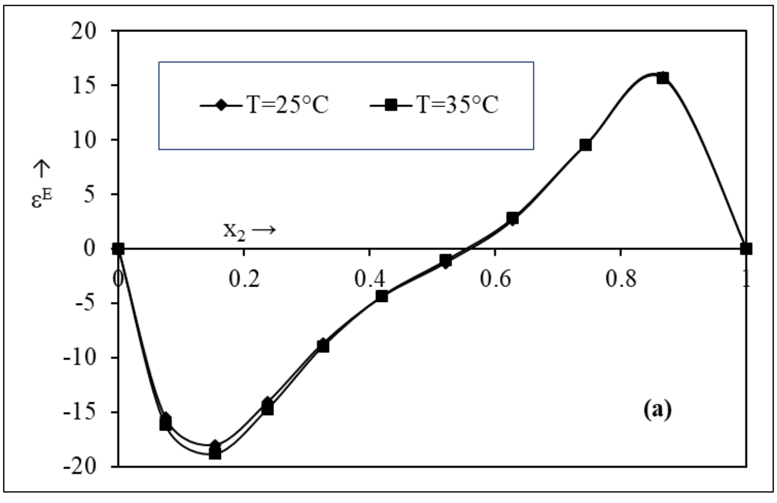

Fig 8(a): Variation of ε^E versus Mole fraction of 2P in EG at various temperatures.

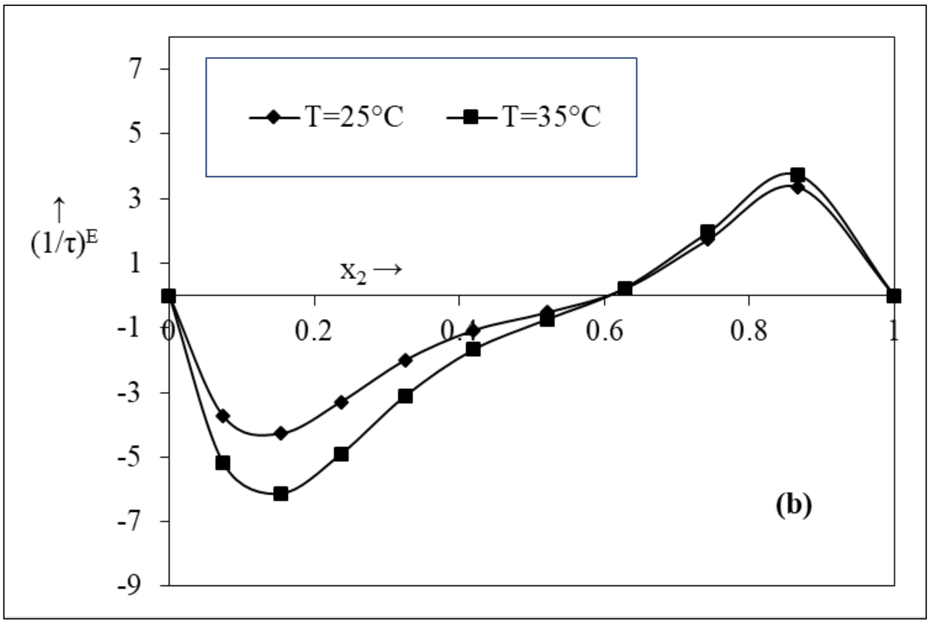

Fig 8(b): Variation of $(1/\tau)^E$ versus Mole fraction of 2P in EG at various temperatures.

Similarly, the excess inverse relaxation time is defined as

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

*x_2 is the mole fraction of nP in 2P. 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]. The information regarding the dynamic of liquid 1 and 2 interaction 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.
- **ii). $(1/\tau)^E < 0$:** The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate slowly.
- **iii). $(1/\tau)^E > 0$:** The liquid 1 and 2 interaction produces a field such that the effective dipoles rotate fastly i.e. the field will co-operate in rotation of dipoles.

The variation of ε^E and $(1/\tau)^E$ with mole fraction of alcohols at temperature 25°C, and 35°C are shown in Figure 7 & Figure 8. The experimental values of both the excess parameters were fitted to the Redlich-Kister equation [12, 13] as

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

Where A is either ε^E or $(1/\tau)^E$. By using these B_n values, A^E values were calculated. The values for the Redlich-Kister coefficients B_n for 2P-nP and EG-2P systems are given in Table 2.

For 2P-nP system: the coefficient B_n for n= 0 to 3 are listed in Table 2. It is observed that values of B_0 and B_1 get positive to negative values with decrease in molecular size of 2P. The values of B_2 becomes positive for 35°C, whereas the values of B3 becomes still smaller. As the physical meanings of B_0, B_1, B_2 and B_3 are correlated to rates for forming multimers as follows:

B_0 represents rate for forming dimer 2P-nP, B_1 represents rate for forming trimer 2 2P-nP, B_2 represents rate for forming quartermers 2 2P-2 nP, B_3 represents rate for forming pentamer 3 2P-2 nP respectively.

Table 2: B_n coefficients of the Redlich-Kister equation

°C	B_0	B_1	B_2	B_3
	Excess permittivity			
25	2.01	-6.42	-2.06	-35.40
35	1.11	-6.82	0.86	-28.66
	Excess inverse relaxation time			
25	0.02	0.27	-0.00	4.08
35	-0.43	2.33	0.22	12.94

2. For EG-2P system: It is observed that values of B_0 and B_1 get positive to negative values with decrease in molecular size of EG. The values of B_2 becomes positive for 25°C as liquid b changes from EG to 2P, whereas the values of B3 becomes smaller. This provides information regarding formation of multimers in (2P-nP) and (EG-2P) mixtures respectively. As the physical meanings for EG-2P system of B_0, B_1, B_2 and B_3 are correlated to rates for forming multimers as follows: B_0 represents rate for forming dimer 2P-EG, B_1 represents rate for forming trimer 2 2P-EG, B2 represents rate for forming quartermers 2 2P-2 EG, B_3 represents rate for forming pentamer 3 2P-2 EG respectively.

There is no report of theoretical molecular simulation study for the systems to support the finding. It will be interesting to perform the theoretical simulation on clusters to get detail structural information. However, in the absence of such theoretical work, the Kirkwood correlation factor may provide more additional information about clusters.

3.3. Kirkwood Parameter Model

The Kirkwood correlation factor g_f [14] 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.

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

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 2P and nP & EG in gas phase are taken as 1.68 D and 1.68 D respectively [4, 14]. In equation (6), 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, generally are greater than 1, except for pure solution of 2P. The effective values of the correlation factor for 2P are larger than the corresponding value in nP & EG. The g^{eff} decreases with increase in volume % of nP in 2P.

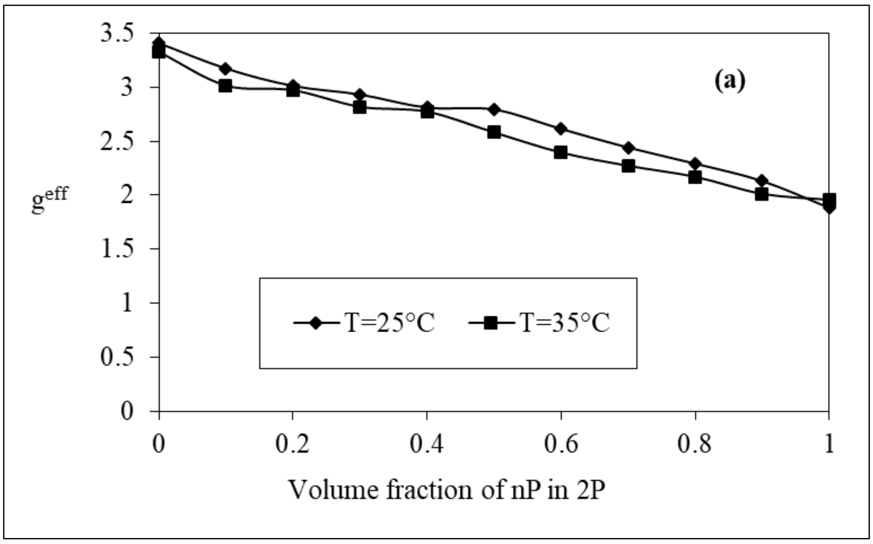

Fig 9(a): Variation of g^{eff} versus Volume fraction of nP in 2P at various temperatures.

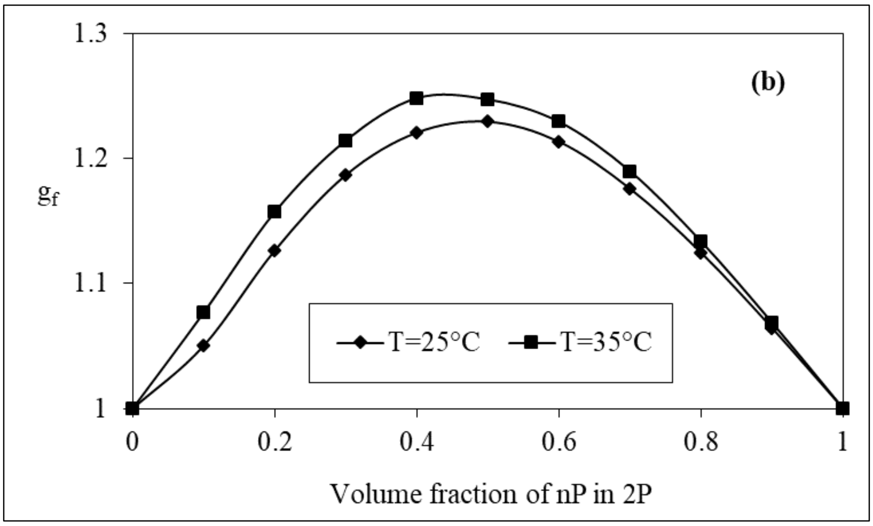

Fig 9(b): Variation of g_f versus Volume fraction of nP in 2P at various temperatures.

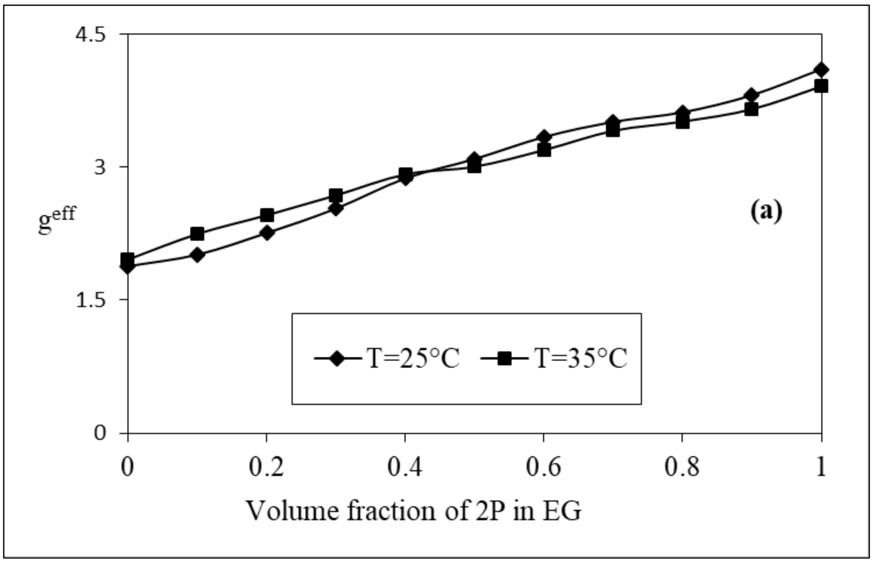

Fig 10(a): Variation of g^{eff} versus Volume fraction of 2P in EG at various temperatures.

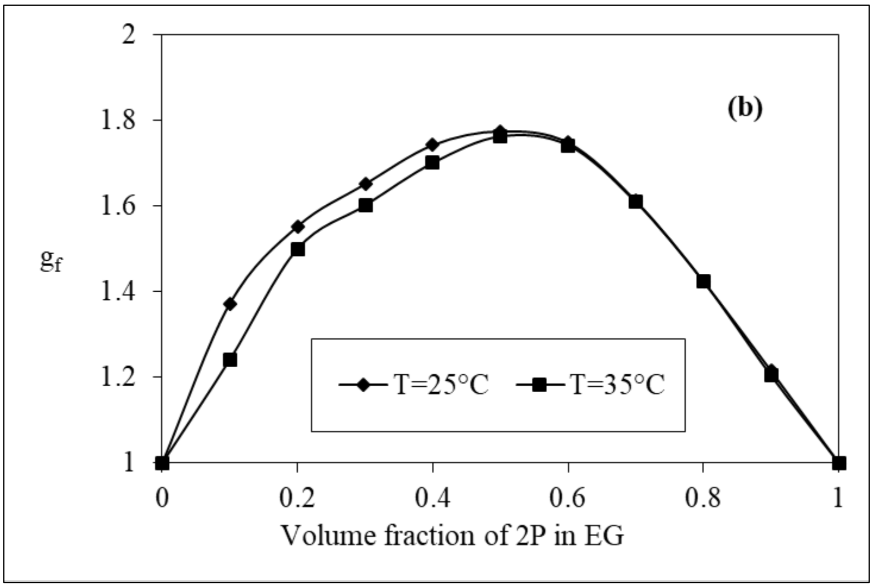

Fig 10(b): Variation of g_f versus Volume fraction of 2P in EG at various temperatures.

The value of ‘a’ greater than one indicates that the dipoles of 2P and nP & EG will be orientated in such a way that the effective dipole will be greater than corresponding values of pure liquids.

To fit the experimental data, the above equation has been modified [15]

$$f_B = 1-[a-(a-1)\,\phi_2]\,\phi_2 \qquad (7)$$

Where 'a' is numerical fitting parameter.

The parameters ‘a’ has been determined by the least squares fit method. The deviation from 1 relates to corresponding liquids 1 and 2 interactions. The values of a are 0.457, 0.519, 0.851 and 0.935 at 25°C and 35°C respectively. The small deviation of ‘a’ suggest that weaker interaction between 2P and nP & EG. The dipole moments for 2P, nP and EG in gas phase are taken to be as 1.68 D, 1.68 D and 2.2 D respectively. The calculated values of g^{eff} and g_f for the mixtures of the systems as (2P-nP), and (EG-2P) are shown in Figure 9 and Figure 10 respectively. The g_f values are close to unity for all the system studied, indicating weaker intermolecular interactions between components of the system.

For (2P-nP) & (2P-EG) system: The g^{eff} increases with increase in volume % of nP & EG in 2P. The values of g_f are greater than or equal to unity for all temperature. As $g>1$ indicates parallel alignment of dipoles in multimers. This value of g_f greater than or equal to unity indicates interaction between 2P and nP. This indicates that the effective dipoles in the mixture will be less than the corresponding average value in pure liquids 2.

3.5. Thermodynamic Parameters

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 [16] by least square fit method as

$$\tau = \frac{h}{KT} \exp{(\Delta H - T\Delta S)/RT} \qquad (8)$$

Table 3: Molar energy of activation ΔH and entropy of activation ΔS for polar liquid systems.

Volume % of 2P	**ΔH KJ mol^{-1}**	**ΔS J mol^{-1} K^{-1}**	**ΔH KJ mol^{-1}**	**ΔS J mol^{-1} K^{-1}**
	2P + nP		2P + EG	
1.0	17.21	0.2267	17.22	0.2267
0.9	15.28	0.2199	19.52	0.2349
0.8	14.24	0.2163	19.71	0.2359
0.7	14.37	0.2167	19.16	0.2346
0.6	14.05	0.2155	18.56	0.2333
0.5	13.84	0.2148	18.45	0.2335
0.4	13.73	0.2144	18.26	0.2335
0.3	13.68	0.2142	19.15	0.2369
0.2	13.37	0.2131	19.07	0.2373
0.1	13.65	0.2139	18.23	0.2350
0.0	13.35	0.2125	17.36	0.2340

The values of activation energies ΔH and ΔS are tabulated in Table 3. Thermodynamic properties may be used to access the dipole under the influence of applied field. Enthalpy refers to the total energy content of the system. The increase in enthalpy suggests that there is more hydrogen bonding. Entropy, is a term for disorder in a system and that the overall entropy in a system always increases.

4. Conclusion

The study has provided the dielectric parameters for the mixtures of binary polar liquids, viz 2P-nP and EG-2P systems. The experimental values observed are in good agreement with the literature values. Also 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 have a wide range of applications. These are used as industrial solvents, surfactants, detergents, wetting agents, a solvent, as a cleaning fluid, an antifreeze, and EG is mainly used as a precursor to polymers. Due to great industrial applications of these molecules, it is very important to investigate the molecular dynamics of these molecules in dilute solutions to understand the role of hydrogen bonds and the number of carbon atoms present in the chain.

References

1. Debye P. *Polar molecules*. New York: Chemical Catalog; 1929.
2. Cole RH, Berbarian JG, Mashimo S, Cryssikos G, Burns A, Tombari E. Time domain reflection methods for dielectric measurements to 10 GHz. *J. Appl. Phys.* 1989;66:793-802.
3. Davidson DW, Cole RH. Dielectric relaxation in glycerine. *J. Chem. Phys.* 1950;18:1417.
4. Puranik SM, Kumbharkhane AC, Mehrotra SC. Dielectric relaxation of tert-butyl alcohol-water mixtures using a time domain technique. *J. Chem. Soc., Faraday Trans.* 1991;87:1569-1773.
5. Hosamani MT, Fattepur RH, Deshpande DK, Mehrotra SC. Temperature and frequency-dependent dielectric studies of p-fluorophenyl acetonitrile-methanol mixtures using time domain reflectometry. *J. Chem. Soc., Faraday Trans.* 1995;91(4):623-6.
6. Pawar VP, Mehrotra SC. Dielectric relaxation study of chlorobenzene-dimethylformamide using TDR technique. *J. Mol. Liq.* 2002;95:63-74.
7. Khirade PW, Mehrotra SC. Temperature-dependent dielectric relaxation of 2-ethoxyethanol, ethanol, and 1-propanol in dimethylformamide solution using the time domain technique. *J. Sol. Chem.* 1999;28(8):1031.
8. Kumbharkhane AC, Puranik SM, Mehrotra SC. Dielectric properties of 2 Propanol-water mixtures using a time domain spectroscopy. *J. pure and Applied physics* 1992;4(2):196.
9. Shannon CE. Communication in the presence of noise. *Proc. IRE* 1949.
10. Samulon HA. Spectrum analysis of transient response curves. *Proc. IRE* 1951;39:175-86.
11. Cole KS, Cole RH. Dispersion and absorption in dielectrics. *J. Chem. Phys.* 1941;9:341-5.
12. Frolhich H. *Theory of dielectrics*. London: Oxford University press; 1949.
13. Mehrotra SC, Boggs JE. Effect of collison-induced phase shifts on the line widths and line shifts of rotational spectral lines. *J. Chem. Phys.* 1977;66:5306-12.
14. *Catalog handbook of fine chemicals*. USA: Aldrich chemical co., Inc.; 1990.
15. Frolhich H. *Theory of dielectrics*. London: Oxford University Press; 1949.
16. Eyring H. *J. Chem. Phys.* 1936;4:283.