

Dielectric relaxation behaviour of triethylene glycol [TEG]+water mixture as a function of composition and temperature using TDR technique

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The complex dielectric spectra of binary mixture of triethylene glycol [TEG] + water have been carried out at different concentrations and temperatures (0 °C, 5 °C, 10 °C, 15 °C, 20 °C and 25 °C) in the frequency range of 10 MHz to 30 GHz using time domain reflectometry technique. The static dielectric constant (ϵ_0), relaxation time (τ), Kirkwood correlation factor (g^{eff}), excess permittivity (ϵ_0^E), thermodynamic parameters (activation enthalpy and entropy) and Bruggeman factor (f_B) have been determined for binary mixtures. The Bruggeman model for the nonlinear case has been fitted to the dielectric data. These dielectric parameters confirm that the intermolecular homogeneous and heterogeneous hydrogen bonding vary significantly with the increase in concentration of the triethylene glycol in water mixtures.

Keywords: Triethylene glycol, Time domain reflectometry, Dielectric relaxation, Kirkwood correlation factor, Thermodynamic parameter

1 Introduction

It is known that in heteromolecular interactions of solutions of aliphatic compound with water an important role is played by number of hydroxyl groups in the alcohol. Aqueous solutions are fundamentally involved in the chemical processes of life and all of biological chemistry takes place in an aqueous environment and have found extensive applications, mostly because of their wide application in the field of biochemistry and biochemical engineering. Aqueous solutions are perplexing since they adopt some of the eccentric behaviour of water. The eccentricities of aqueous solutions are closely tied to the structure and dynamics of the liquid.

Triethylene glycol [TEG] [$C_6H_{14}O_4$] is a straight-chain. It has dihydric alcohol aliphatic compound on both ends by hydroxyl group. Due to the presence of ends hydroxyl groups, the molecules of these liquids can enter into intra and intermolecular hydrogen bonding giving rise to several conformations in water mixture¹⁻⁴. TEG molecules are soluble in water in a wide concentration range and are the most useful pharmaceuticals and industrial polymers. TEG is used in the oil and gas industry to dehydrate natural gas.

Although TEG compound finds important applications in the chemical industry, their structural behaviour and dielectric relaxation have not been systematically studied and only few authors reported concerning these aspects⁴. Dielectric spectroscopy is one of the most scientific method for studying hydrogen bonding in liquid mixtures and has great potential to investigate intermolecular interaction between them. The dielectric relaxation studies of ethylene glycol, diethylene glycol and their binary mixtures were investigated in water and 1,4-dioxane solutions to understand molecular interaction^{1,2}. Dielectric relaxation studies of binary mixtures of ethylene glycol-water carried out by Zahn *et al.*⁵. The same study was done by Shinyashiki *et al.*⁶. This work confirms the solute-solvent interaction and dynamical behaviour of water⁶⁻⁹. Also the dielectric studies carried out by Joshi *et al.*¹⁰ and Sastry *et al.*¹¹. Extensive dielectric relaxation studies were carried out in the frequency range from 10 MHz to 10 GHz on the associating molecules for their molecular conformations¹²⁻¹⁴. The dielectric parameters of EG-water and DEG-water mixtures predict that polymeric hydrogen bonded structures involving unlike molecules in DEG is more dominant than in EG¹⁵. No attempt, so far, seems to have been made to study the

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temperature dependent dielectric behaviour of TEG+ water mixture in the microwave region.

In the present paper, we comprise the detailed study of dielectric behaviour of triethylene glycol (TEG) and water mixtures using time domain reflectometry (TDR) at different temperatures in the frequency range of 10 MHz to 30 GHz. From the measured complex permittivity spectra, the static dielectric constant, permittivity at the high frequency, dielectric relaxation time were obtained by least squares fit method. Excess dielectric permittivity, Kirkwood correlation factor and Bruggeman factor are also determined to study the intermolecular interactions in dissimilar molecules through hydrogen bonding.

2 Materials and Method

2.1 Material

Triethylene glycol [TEG] was obtained from S. D. Fine-Chem. Ltd. India and used without further purification (99% purity). Double-distilled de-ionised water (high performance liquid chromatography grade) was used as a solvent for preparing mixtures. Binary mixtures of TEG and water prepared at eleven concentrations by volume. Assuming ideal mixing behaviour, the concentration was converted into the mole fraction of water in TEG.

2.2 Measurement

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique^{16,17}. The Tektronix model no. DSA8200 digital serial analyzer sampling mainframe along with the sampling module 80E08 was used for the time domain reflectometer. A repetitive fast rise pulse with 18 ps incident pulse rise time and 20 ps reflected pulse rise time was fed through coaxial line system impedance of 50 ohm. Sampling oscilloscope monitors change in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 2 ns and digitized in 2000 points. The Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra $\epsilon^*(\omega)$ using nonlinear least squares fit method¹⁷⁻¹⁹. The temperature of the sample was controlled with an accuracy ± 1 °C.

3 Results and Discussion

Figure 1 shows an example of the frequency dependent complex permittivity for TEG at different

temperatures and Fig. 2 shows TEG-water mixtures at different concentrations. It can be seen from the values of $\epsilon'(\omega)$ are decreasing with increasing concentration of TEG in mixture, and there is one single loss peak $\epsilon''(\omega)$ for each concentration in the entire composition range, and as we go from lower concentrations to higher concentrations of TEG in mixture, the peak shifts towards lower frequency side, which shows that relaxation time increases with concentration of TEG in mixture.

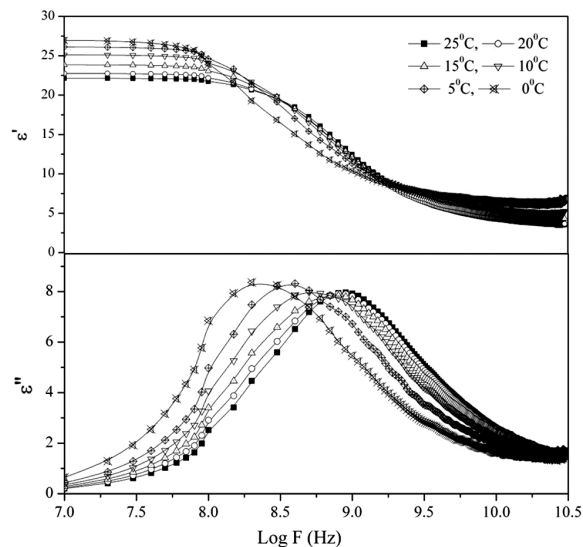


Fig. 1 — Complex permittivity spectra (ϵ' and ϵ'') of triethylene glycol (TEG) at different temperature range (0 °C, 5 °C, 10 °C, 15 °C, 20 °C and 25 °C).

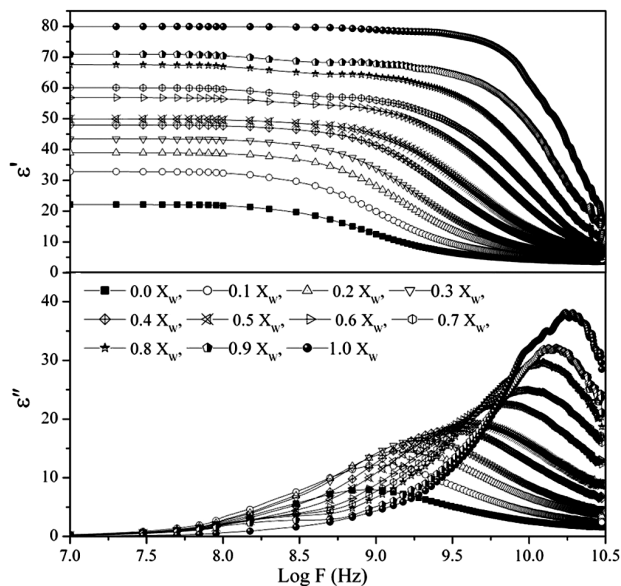


Fig. 2 — Complex permittivity spectra (ϵ' and ϵ'') of TEG+ water mixture at 25 °C.

3.1 Dielectric constant and relaxation time

The complex permittivity is given as $\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega)$ where, $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the dielectric constant and dielectric loss, respectively. To calculate static dielectric constant ϵ_0 , molecular reorientation relaxation time τ (ps) and distribution parameters α and β , the complex permittivity $\epsilon^*(\omega)$ data were fitted by the non-linear least squares method to the Havriliak-Negami expression²⁰:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad \dots (1)$$

where $\epsilon^*(\omega)$ is complex permittivity at an angular frequency ω , ϵ_0 is the static dielectric constant, ϵ_∞ is permittivity at high frequency, τ is the dielectric relaxation time, α is the shape parameter representing symmetrical distribution of relaxation time and β is shape parameter of an asymmetric relaxation curve and are the fitting parameters. The Havriliak- Negami expression includes the Cole-Cole ($\beta=1$), Davison-Cole ($\alpha=0$) and Debye ($\alpha= 0, \beta=1$) relaxation models. In this study water and TEG mixture shows Debye type dispersion. Therefore, the complex permittivity spectra have been fitted in Debye type model using non-linear least square fit method to determine dielectric parameters. The value of static dielectric constant (ϵ_0) and relaxation time (τ) of binary mixtures of TEG-water mixture at various temperatures and concentrations are reported in Table 1 and they are plotted against volume fraction of water (V_w) in Fig. 3. It can be seen from Fig. 3 that static dielectric constant is continuously increasing with increasing concentration of water in mixture which shows the increase in dipole moment of complex molecules with increasing concentration of water, and on the other hand, relaxation time is decreasing with increasing concentration of water in mixture, the decrease in relaxation time is more for lower volume fractions (<0.5) and less for higher volume fraction of water in mixture. This may be due to the increase in concentration of water in mixture, resulting in a reduction in TEG-water interaction. Also the temperature effect on dielectric parameters of all the compositions can be seen from Fig. 3. The values of static dielectric constant and the values of relaxation time increase with decreasing temperatures.

3.2 Kirkwood correlation factor

The Kirkwood correlation factor ‘g’ provides valuable information about the orientation of the dipoles in polar liquids²¹. For the pure liquid, the value of Kirkwood factor can be obtained by using the Kirkwood-Frochlich equation as follows²¹:

$$g\mu^2 \frac{4\pi N\rho}{9kTM} = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad \dots (2)$$

where ‘g’ is Kirkwood correlation factor, N is Avogadro’s number, μ is dipole moment of liquid, M is molecular weight, ρ is density of the liquid, ϵ_0 is static dielectric constant and ϵ_∞ is dielectric constant at high frequency and k is the Boltzmann constant and T is the temperature.

For calculation of Kirkwood correlation factor for binary mixture, the modified form of above equation can be used to study the orientation of dipoles due to heterogeneous interactions in binary mixtures and can be expressed as follows²¹:

$$\frac{4\pi N}{9kT} \left[\frac{\mu_w^2 \rho_w V_w}{M_w} + \frac{\mu_A^2 \rho_A (1-V_w)}{M_A} \right] \times g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad \dots (3)$$

where g^{eff} is the Kirkwood effective correlation factor, μ_w is the dipole moment of water, μ_A is the dipole moment of TEG. ρ_w and ρ_A are the densities of water and TEG, respectively, at 25 °C. V_w represents the volume fraction of water in TEG. The calculated g^{eff} values of TEG are reported in Table 2. For calculating Kirkwood correlation factor we have taken dipole moment of TEG (2.99 D), dipole moment of water (1.84 D), density of TEG (1.12 gcm⁻³), densities of water^{22,23} (1.0 gcm⁻³). The Kirkwood correlation factor ‘g’ for water is 2.83 at 25 °C, which is higher than the value of TEG. The deviation of Kirkwood correlation factor from unity is the measure of degree of dipolar orientation due to hydrogen bonding.

3.3 Excess permittivity

The contribution of hydrogen bonds to the dielectric properties of the mixture is also studied in terms of the excess dielectric permittivity. The excess permittivity (ϵ_0)^E can be written as^{24,25}.

$$(\epsilon_0)^E = (\epsilon_0)_M - [(\epsilon_0)_W X_W + (\epsilon_0)_{\text{TEG}}(1-X_W)] \quad \dots (4)$$

where the subscripts M and W represent mixture and water, respectively, and X_w represents the mole

Table 1 — The dielectric relaxation parameters for TEG-water mixtures at different temperatures.

V_w	ϵ_∞	ϵ_0	τ (ps)
		25 °C	
0.0	2.27(1)	23.29(8)*	171.05(1)
0.1	3.25(9)	34.10(9)	143.45(1)
0.2	3.34(1)	40.31(9)	97.77(1)
0.3	3.26(1)	44.77(8)	76.98(1)
0.4	2.76(1)	48.85(5)	49.68(1)
0.5	2.34(1)	50.60(5)	36.57(9)
0.6	1.53(9)	56.33(3)	23.23(2)
0.7	2.64(9)	59.69(1)	16.52(1)
0.8	1.81(3)	64.92(8)	14.20(3)
0.9	3.49(4)	67.37(1)	11.54(2)
1.0	2.83(1)	78.73(1)	8.57(5)
		20 °C	
0.0	2.84(1)	23.93(8)	191.04(2)
0.1	3.21(1)	34.12(1)	148.79(1)
0.2	3.43(1)	40.99(9)	109.45(1)
0.3	3.23(1)	45.07(9)	79.97(1)
0.4	2.71(1)	49.75(7)	53.87(1)
0.5	2.35(1)	51.38(5)	38.75(9)
0.6	1.90(1)	56.91(4)	24.66(3)
0.7	5.15(3)	60.55(8)	20.38(2)
0.8	1.43(3)	65.51(7)	14.51(2)
0.9	5.45(4)	68.84(1)	11.52(2)
1.0	.72(1)	80.01(1)	8.85(1)
		15 °C	
0.0	3.37(1)	25.18(9)	219.78(2)
0.1	3.64(1)	35.72(1)	174.89(2)
0.2	3.80(1)	42.92(1)	124.64(1)
0.3	3.46(2)	46.80(1)	88.93(1)
0.4	2.67(2)	51.41(1)	58.41(1)
0.5	2.21(1)	52.34(7)	39.84(1)
0.6	2.97(1)	58.82(4)	26.10(4)
0.7	1.23(7)	61.56(9)	21.53(1)
0.8	2.17(4)	69.96(1)	17.24(2)
0.9	2.72(4)	70.64(1)	13.45(2)
1.0	2.83(1)	81.48(1)	9.50(1)
		10 °C	
0.0	4.13(1)	26.82(1)	273.73(4)
0.1	4.51(2)	38.30(1)	223.69(3)
0.2	4.43(2)	44.84(1)	147.06(1)
0.3	3.88(2)	49.20(1)	105.49(1)
0.4	3.03(3)	54.39(1)	68.53(1)
0.5	1.98(3)	54.52(1)	43.57(1)
0.6	2.82(2)	61.00(4)	28.47(4)
0.7	1.59(8)	64.84(9)	22.95(1)
0.8	2.95(2)	71.32(9)	19.45(2)
0.9	1.76(5)	75.04(1)	16.25(5)
1.0	2.12(1)	84.66(2)	10.02(4)
		5 °C	
0.0	4.99(1)	28.38(1)	331.32(9)
0.1	5.36(2)	40.22(1)	247.96(5)
0.2	5.18(3)	47.71(1)	202.54(3)

(contd.)

Table 1 — The dielectric relaxation parameters for TEG-water mixtures at different temperatures.— (contd.)

V_w	ϵ_∞	ϵ_0	τ (ps)
0.3	4.77(3)	52.35(1)	144.54(2)
0.4	3.51(4)	58.38(1)	93.03(1)
0.5	2.59(4)	58.72(1)	58.23(1)
0.6	2.40(2)	65.41(7)	34.77(8)
0.7	1.08(5)	68.19(7)	28.86(1)
0.8	1.10(2)	71.45(3)	21.63(2)
0.9	2.07(5)	77.08(1)	18.25(5)
1.0	2.04(6)	88.05(3)	12.01(2)
		0 °C	
0.0	3.40(1)	28.95(1)	399.1(1)
0.1	5.96(2)	40.63(1)	296.53(5)
0.2	5.99(3)	49.11(1)	212.69(3)
0.3	5.43(3)	54.59(1)	200.14(3)
0.4	4.63(4)	61.26(1)	136.45(2)
0.5	3.16(4)	61.73(1)	81.09(1)
0.6	2.25(5)	70.38(1)	74.83(1)
0.7	2.21(4)	71.84(6)	38.69(1)
0.8	2.07(3)	75.62(9)	26.84(3)
0.9	3.66(6)	79.15(1)	20.36(5)
1.0	2.12(4)	90.98(6)	18.05(1)

Number in bracket indicates that the last significant digit obtained by the least Square fit method. e.g.: 23.29(8)* means 23.29 ± 0.8 .

fraction of water in solute. The plot for the variation of excess permittivity with respect to mole fraction of water in mixture for different temperatures is shown in Fig. 4. The plot exhibits a pronounced maximum and it remains negative for whole concentration range. These negative values for TEG –water mixtures show the experimental evidence of a certain interaction among the unlike molecules through hydrogen bonding. The negative values of excess permittivity suggest that the breaking of homogenous structures of TEG and water due to the hydrogen bonding between solute and solvent results in the formation of multimers with the reduction in effective total number of dipoles^{26,27}. The temperature effect on the values of excess permittivity of concentrations also can be seen from Fig. 4.

3.4 Thermodynamic properties

The thermodynamic parameters evaluated using Eyring equation is as follows²⁸:

$$\tau = (h/kT) \exp(\Delta H/RT) \exp(-\Delta S/R) \quad \dots (5)$$

where ΔS are the entropy of activation, ΔH is the activation energy in kJ/mole, τ is the relaxation time in ps and T is the temperature in degree Kelvin, h is the Planck's constant and R is the gas constant. The temperature dependence of relaxation time is

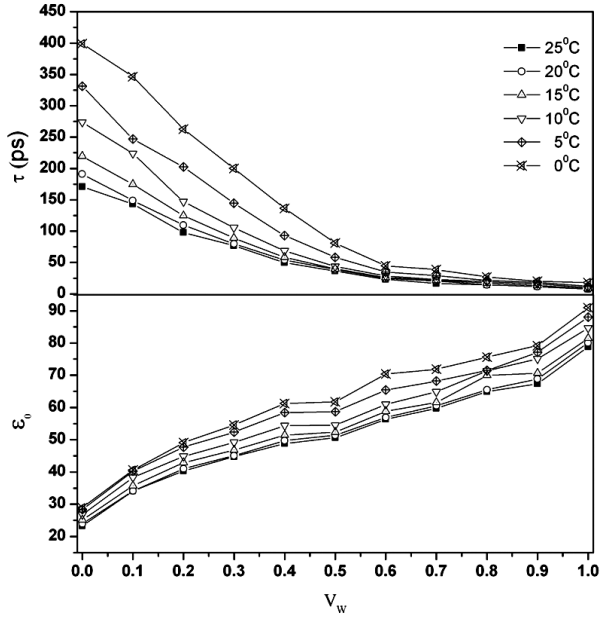


Fig. 3 — Dielectric parameters (ϵ_0 and τ) versus volume fraction of water (V_w) at different temperatures for TEG+water mixture.

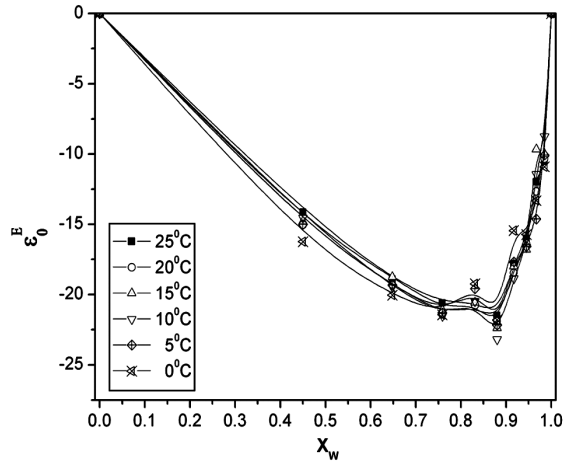


Fig. 4 — Excess permittivity (ϵ_0^E) versus mole fraction of water (X_w) for TEG+water mixture at different temperatures.

described by Arrhenius plot and is shown in Fig. 5 for TEG-water mixtures. The results of thermodynamic parameters of TEG-water mixtures are obtained by least square fit method and are reported in Table 3.

3.5 Bruggeman factor

The static permittivity of binary (TEG- water) mixtures can be obtained using the Bruggeman mixture formula²⁹:

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0wat}}{\epsilon_{0A} - \epsilon_{0wat}} \right) \left(\frac{\epsilon_{0A}}{\epsilon_{0m}} \right)^{1/3} = 1 - V_w \quad \dots(6)$$

where, ϵ_{0m} , ϵ_{0A} and ϵ_{0wat} are the static dielectric constant of mixture, TEG and water respectively, V_w is the volume fraction of water in TEG. Bruggeman equation predicts a linear relationship between f_B and volume fraction of water. In the present work experimental values of f_B shows nonlinear behaviour. To explain the nonlinear relationship Eq. (6) is modified. The experimental data can be well fitted with the modified form of Bruggeman equation as follows^{24,30}:

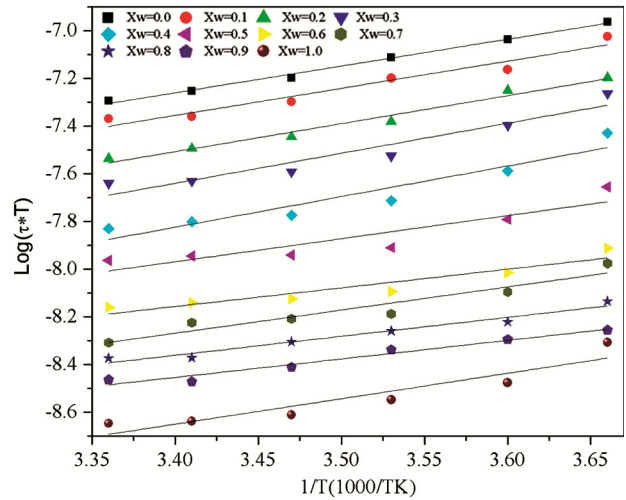


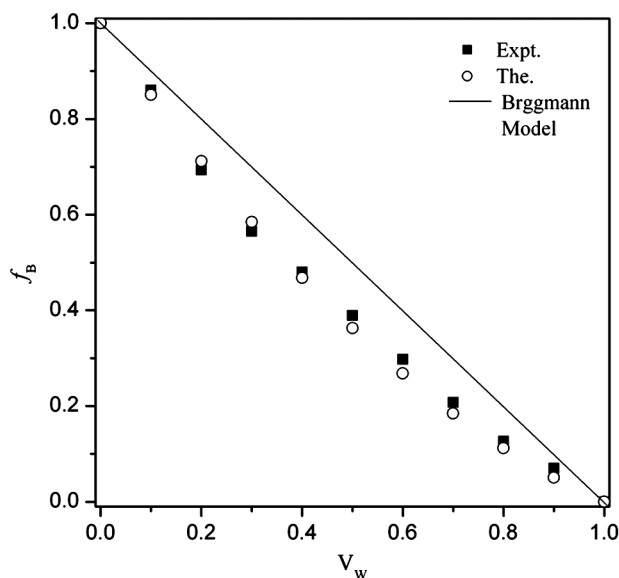
Fig. 5 — Arrhenius plot for TEG+water mixture.

Table 2 — Kirkwood correlation factor (g^{eff}) for TEG-water mixtures at different temperatures.

V_w	25 °C	20 °C	15 °C	10 °C	5 °C	0 °C
0.0	1.76	1.36	1.13	1.23	0.90	0.70
0.1	2.27	1.76	1.49	1.21	0.97	1.60
0.2	2.40	1.94	1.67	1.35	1.12	1.80
0.3	2.42	1.98	1.72	1.44	1.21	1.89
0.4	2.43	2.06	1.81	1.56	1.36	2.04
0.5	2.33	2.02	1.79	1.56	1.39	2.00
0.6	2.44	2.16	1.99	1.77	1.61	2.25
0.7	2.44	2.23	2.07	1.92	1.77	2.28
0.8	2.53	2.37	2.36	2.19	1.99	2.41
0.9	2.51	2.45	2.40	2.42	2.34	2.55
1.0	2.83	2.83	2.83	2.89	2.95	3.00

Table 3 — Thermodynamic parameters for TEG-water mixtures.

V_w	ΔH (kJ/mol)	ΔS (J/mol)
0.0	21.27(1)	0.243(1)
0.1	21.65(2)	0.246(1)
0.2	24.63(2)	0.259(1)
0.3	23.81(3)	0.259(1)
0.4	24.31(2)	0.264(1)
0.5	18.29(4)	0.246(1)
0.6	24.92(7)	0.272(1)
0.7	18.45(2)	0.253(1)
0.8	15.08(1)	0.243(1)
0.9	14.72(1)	0.244(1)
1.0	17.05(8)	0.254(1)

Fig. 6 — Bruggeman factor (f_B) versus volume fraction of water (V_w) for TEG+water mixture at 25 °C.

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0wat}}{\epsilon_{0A} - \epsilon_{0wat}} \right) \left(\frac{\epsilon_{0A}}{\epsilon_{0m}} \right)^{1/3} = 1 - [a - (a - 1)V_w] V_w \quad \dots (7)$$

where 'a' is an arbitrary parameter, the value of $a=1$ means the ideal mixture with no interaction between solute and solvent. The value ' $a=1$ ' leads to the Bruggeman Eq. (6). In Fig. 6 solid line represents the ideal behaviour according to Eq. (6). The deviation of 'a' from unity indicates the molecular interaction within the mixture resulting in deviation in actual volume effectively occupied by the solute in the presence of solvent. The value of 'a' for binary mixture of TEG and water at all temperature are found to be greater than unity, which indicate that the effective microscopic volume of water get more than actual volume. The value of 'a' can be

determined by least square fit method. The calculated value of 'a' for TEG in water mixture is determined using least squares fit method and it is found to be 1.55.

4 Conclusions

The complex permittivity spectra of TEG with water have been studied using time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. The negative values of excess dielectric constant confirms that the hydrogen bond interaction with different molecules. The modified Bruggeman equation is well fitted to experimental values of static dielectric constant and confirms the interaction between constituents of solution.

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References

- 1 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Sol Chem*, 21 (1992) 201.
- 2 Kumbharkhane A C, Sudo S, Oshiki N, Shinyashiki N, Yagihara S & Mehrotra S C, *J Phys Chem A*, 111 (2007) 2993.
- 3 Sengwa R J, Kaur K & Chaudhary R, *Polym Int*, 49 (2000) 599.
- 4 Sengwa R J, *Polym Int*, 45 (1998) 43.
- 5 Zahn M, Ohki Y, Fenneman D B, Gripshover R J & Gehman V H, *Proc IEEE*, 74 (1986) 1182.
- 6 Shinyashiki N, Sudo S, Abe W & Yagihara S, *J Chem Phys*, 109 (1998) 9843.
- 7 Shinyashiki N, Ashaka N, Mashimo S & Yagihara S, *J Chem Phys*, 93 (1990) 760.
- 8 Shinyashiki N, Arita I, Yagihara S & Mashimo S, *J Chem Phys*, 102 (1998) 3429.
- 9 Shinyashiki N & Yagihara S, *J Phys Chem*, 103 (1999) 4481.
- 10 Joshi Y S, Kanse K S, Rander D N & Kumbharkhane A C, *Indian J Pure Appl Phys*, 54 (2017) 621.
- 11 Vishwam T, Sarma N K S P S, Murthy V R K & Sastry S S, *Indian J Pure Appl Phys*, 55 (2017) 403.
- 12 Kumbharkhane A C, Kanse K S, Chavan S D & Mehrotra S C, *J Polym Mat*, 23(2006) 47.
- 13 Kumbharkhane A C, Puranik S M & Mehrotra S C, *Indian J Phys*, 67 (1993) 9.
- 14 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Chem Phys*, 99 (1993) 2405.
- 15 Chavan S D, Watode B D, Hudge P G, Suryawanshi D B, Akode C G, Kumbharkhane A C & Mehrotra S C, *Indian J Phys*, 84 (2010) 275.
- 16 Hasted J B, *Aqueous dielectric*, (London: Chapman and Hall), 1973.

- 17 Cole R H, Berberian J G, Mashimo S, Chryssikos G, Burns A, & Tombari E, *J Appl Phys*, 66 (1989) 793.
- 18 Lin C P, *Soil Sci Soc Am J*, 67 (2003) 720.
- 19 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Chem Soc Faraday Trans*, 87 (1991) 1569.
- 20 Havriliak S & Negami S, *J Polym Sci C*, 14 (1966) 99.
- 21 Kirkwood J G, *J Chem Phys*, 7 (1939) 911.
- 22 Kinart C M, Maj M, Cwiklinska A & Kinart W J, *J Mol Liq*, 139 (2009) 1.
- 23 Lide D R, *Handbook of chemistry and physics*, 87th Edn, (CRC Press), 1284, 2006-07.
- 24 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Sol Chem*, 22 (1993) 219.
- 25 Sengwa R J, Khatri V & Sankhla S, *J Mol Liq*, 144 (2009) 89.
- 26 Chaudhary A, Ahire A S & Mehrotra S C, *J Mol Liq*, 94 (2001) 17.
- 27 Parthipan G & Thenappan T, *J Sol Chem*, 36 (2007) 1231.
- 28 Glasstone S, Laidler K J & Eyring H, *Theory of rate processes*, (McGraw Hill: New York), 1941.
- 29 Bruggeman D A G, *Ann Phys*, 5 (1935) 636.
- 30 Kumbharkhane A C, Puranik S M & Mehrotra S C, *J Mol Liq*, 59 (1994) 173.