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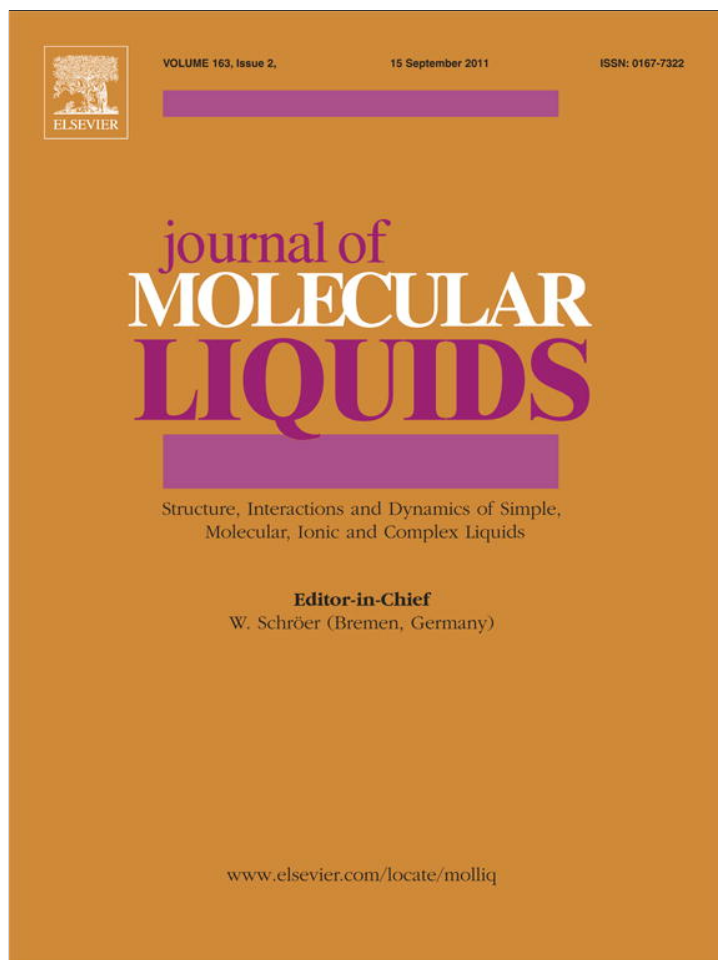


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The dielectric relaxation study of 2(2-alkoxyethoxy)ethanol–water mixtures using time domain reflectometry

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ABSTRACT

Complex permittivity spectra of 2(2-alkoxyethoxy)ethanol–water mixtures for the entire concentration range and at 25 °C have been measured using time domain reflectometry technique up to 30 GHz. The relaxation processes have been obtained by fitting the complex permittivity spectra of the binary mixtures in 2-Debye equation. In glycol ether–water mixtures except for pure water and its rich region the double relaxation times, primary process (τ_1) and secondary process (τ_2) have been observed. The primary relaxation process (τ_1) may be due to cooperative relaxation of the H-bond network of mixture constituents and the secondary relaxation process (τ_2) may be due to its flexible parts attached to the carbon chain. The intra and intermolecular hydrogen bonding of 2(2-alkoxyethoxy)ethanol in pure form as well as in binary mixtures of water have been discussed using Kirkwood correlation factor, Excess dielectric properties and the Bruggeman factor.

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1. Introduction

Dielectric studies have been carried out extensively on alcohols and its water mixtures to understand strong intra and intermolecular interactions through hydrogen bond, which play an important role in biochemistry, results in a peculiar dynamical property. The local structures of hydrogen bonding liquids are complicated due to molecular clusters and network structures through the hydrogen bond. Asymmetric shape of the loss peak was observed for the alcohol and its water mixtures, and the dielectric spectrum was described well by the Havriliak–Negami (HN) equation. The HN equation gives the complex permittivity as [1]

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

where ε_0 is the static dielectric constant, ε_∞ is the permittivity at high frequency, τ is relaxation time. α and β are the symmetric and asymmetric distribution of relaxation times, respectively. The model can be fitted in three ways: i) If $\alpha = 0$ and $\beta = 1$ then single Debye relaxation, ii) $0 \leq \alpha \leq 1$ then it would be a Cole–Cole model of symmetric distribution of relaxation times and iii) $\alpha = 0$ and β varied such that $0 \leq \beta \leq 1$, this behavior is identified as Cole–Davidson (CD) asymmetric distribution of relaxation times.

As earlier discussed, in the dielectric loss spectrum of long chain molecules or molecules in binary mixtures of two polar groups, the loss peak of these high frequency process hidden by the primary process and these process behave as high frequency wing of the primary process. The frequency range up to 30 GHz is sufficient to resolve the primary and secondary relaxation process in alcohols in pure and its rich region in aqueous solution. Therefore the complex permittivity spectra of these mixtures in glycol ether rich region can be described by sum of two Debye terms as follows [2]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_1}{1 + j\omega\tau_1} + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + j\omega\tau_2} \quad (2)$$

ε_1 is the dielectric constant at intermediate frequency. τ_1 and τ_2 are the relaxation times in picoseconds for the primary process and secondary process, respectively. Schrodle et al. have been already explain the superiority of 2-Debye over other models [2].

2(2-alkoxyethoxy)ethanols are the monoalkyl ethers of diethylene glycol (glycol ether). They are also known as carbitols having proton donor and acceptor sites in same molecule. These monoalkylethers of diethylene glycol have structural formula $\text{ROCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ where R is an alkyl group. The chemical structure of long hydrocarbon chain resist to solubility in water, while ether or alcohol groups introduce the promoted hydrophilic solubility performance. This surfactant-like structure provides the compatibility between water and a number of organic solvents, and the ability to couple unlike phases. These hydrophilic/hydrophobic balances in glycol ethers make the dielectric relaxation study interesting. Dielectric relaxation

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spectroscopy (DRS) probes the response of the total dipole moment of the system, $M(t) = \sum \mu_j(t)$, to a time dependent external electric field [3]. This inherent ability to monitor the cooperative motion of molecular ensemble distinguishes dielectric relaxation from methods like NMR or Raman spectroscopy which yield information on the motions of individual molecules [4]. It makes the DRS a powerful tool for investigating liquids whose structure and dynamics are dominated by intermolecular hydrogen bonds [5]. Literature survey indicates that the monoalkylethers of ethylene and diethylene glycol have been studied in pure form and nonpolar solvents such as dioxane, benzene and carbon tetrachloride but dielectric relaxation behavior of these systems in aqueous solution is scarce [6–13]. The molecules of these compounds have several hydrogen bonding sites which may leads to different conformations through intra and intermolecular interactions.

Recently dielectric relaxation study of polymers and binary mixtures of 2-methoxyethanol-water have been successfully carried out in our laboratory [14,15]. In the present study the complex permittivity spectra of 2(2-methoxyethoxy)ethanol (MEE), 2(2-ethoxyethoxy)ethanol (EEE) and 2(2-butoxyethoxy)ethanol (BEE) with water have been measured at 25 °C. The dielectric parameters such as static dielectric constant, relaxation time have been calculated. The dielectric behavior of these associating liquid have been discussed in terms of Bruggeman factor, Kirkwood correlation factor and excess properties.

2. Experimental

2.1. Materials

MEE, EEE and BEE were obtained from Loba Chemie, India and were used without further purification. The water used in the preparations of mixtures was obtained by double distillation procedure. The solutions were prepared at different mole fractions of water.

2.2. Measurements

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 has been used for the time domain reflectometer (TDR). A repetitive fast rising voltage pulse with 18 ps incident pulse rise time and 20 ps reflected pulse rise time was fed through coaxial line system of impedance 50 Ω . Sampling oscilloscope monitors changes 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 non linear least squares fit method [17,18].

3. Results and discussion

In general, the dielectric loss spectrum of pure water in this frequency range is usually described by a single Debye relaxation [19]. From Fig. 1 it is observed that the Cole–Cole Plots for the pure glycol ethers at 25 °C exhibit the skewed arc curve and the value of ϵ''_{\max} is less than $(\epsilon_0 - \epsilon_\infty)/2$ which indicate that the dielectric behavior deviate from the single Debye relaxation. This deviation is usually explained by assuming there is not just one relaxation time but a continuous distribution. Also the dielectric spectrum of polyalcohol shows an asymmetric shape and it is described by Havriliak–Negami spectral function or double Debye relaxation model [20]. Therefore the complex permittivity spectra $\epsilon^*(\omega)$ of the glycol ether–water

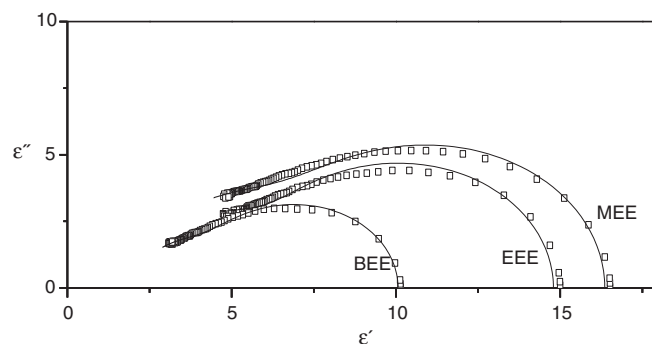


Fig. 1. Cole–Cole plot for pure 2(2-alkoxyethoxy)ethanol at 25 °C.

mixtures have been fitted in 2-Debye model using least squares fit method to determine the dielectric relaxation parameters.

The dielectric permittivity spectra have been shown in Fig. 2 a), b), c) and dielectric loss spectra in Fig. 2d), e), f) for MEE, EEE and BEE, respectively at 25 °C. The symbol shows experimental values whereas solid lines represent the fit values determined from Eq. (2). The high frequency dielectric constant ϵ_∞ for pure liquids have been determined from the square of refractive index [21] and for the intermediate concentrations $\epsilon_{\infty m}$ has been calculated by simple additive equation as used by Sato et al. to choose the fitting model for methanol-water [22]. The values of dielectric parameters (ϵ_{0m} , ϵ_{1m} , τ_1 and τ_2) are reported in Table 1. The relaxation time τ_1 increases for pure glycol ether as carbon chain length increases such that the τ_1 of MEE < EEE < BEE and the relaxation time τ_2 is approximately same for all glycol ethers in pure and in their aqueous solutions. The dielectric loss spectra for pure 2(2-alkoxyethoxy) ethanol at 25 °C with primary and secondary dielectric losses have been shown in Fig. 3.

3.1. Static dielectric constant

The values of dipole moment in gas phase for MEE, EEE and BEE are very similar but the static dielectric constant are in decreasing order such that MEE > EEE > BEE. As the chain length increases from MEE to BEE the dielectric constant goes on decreasing. Fig. 4 shows the dielectric constant vs. mole fraction of water (X_W). Here the dielectric constants for binary mixtures show deviation from ideal mixing behavior. The straight lines indicates the ideal behavior calculated from the simple additive equation as,

$$\epsilon_{0m} = X_W \epsilon_{0W} + (1 - X_W) \epsilon_{0S} \quad (3)$$

where ϵ_{0m} , ϵ_{0W} and ϵ_{0S} are the dielectric constants of mixture, water and solute, respectively. The deviation from ideal behavior suggests the molecular interactions in glycol ether and water molecules. By using the static dielectric constants of binary mixtures the heterogeneous intermolecular interactions in water-glycol ether molecules would be described by following factors:

3.2. Bruggeman factor

The static permittivity of binary mixtures can be obtained by using the Bruggeman mixture formula [23]

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0W}}{\epsilon_{0S} - \epsilon_{0W}} \right) \left(\frac{\epsilon_{0S}}{\epsilon_{0m}} \right)^{1/3} = 1 - V_W \quad (4)$$

where, ϵ_{0m} , ϵ_{0W} , ϵ_{0S} are the static dielectric constant of mixture, water and solute (glycol ethers) respectively. V_W is the volume fraction of water. Bruggeman expression predicts a linear relationship between f_B and the volume fraction of water but the experimental values of f_B

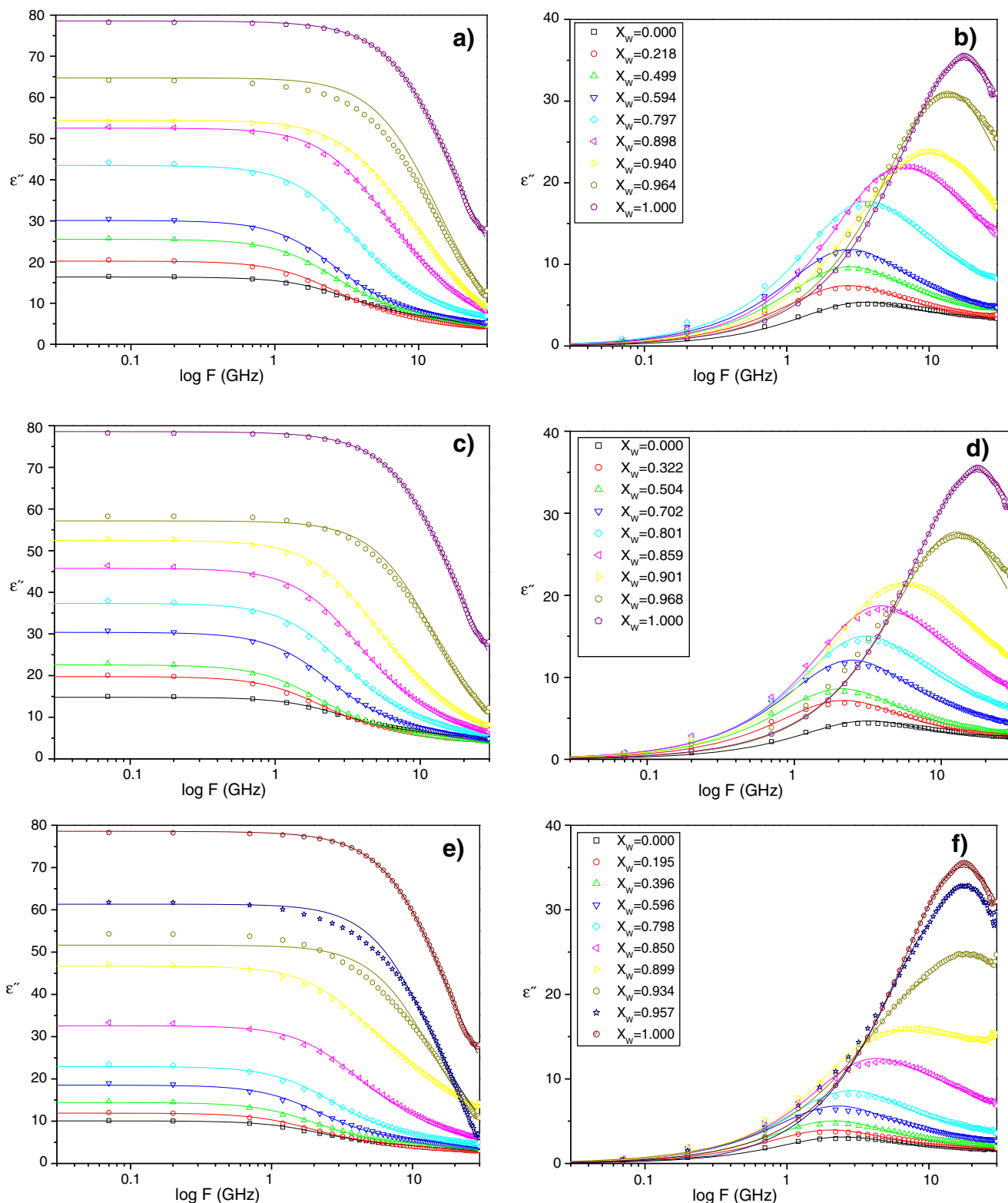


Fig. 2. a), b) & c) are the dielectric permittivity whereas c), d) & e) are dielectric loss spectra for MEE, EEE and BEE, respectively. The solid lines are the best fit theoretical values from Eq. (2).

shows a non linear behavior (Fig. 5). To explain the non linear relationship the Eq. (4) is modified as follows [24]

$$f_B = \left(\frac{\epsilon_{0m} - \epsilon_{0w}}{\epsilon_{0s} - \epsilon_{0w}} \right) \left(\frac{\epsilon_{0s}}{\epsilon_{0m}} \right)^{1/3} = 1 - [a - (a-1)V_W]V_W \quad (5)$$

Here Eq. (4) is modified by factor $[a - (a-1)V_W]$. This modification in volume may be due to the structural rearrangement of solvent molecules in the mixture. The value of 'a' contains the information regarding the change in the orientation of solvent molecule in the mixture. In Fig. 5 solid lines represents according to Eq. (4). Experimental values represent the deviation from ideal behavior of

Table 1
Dielectric relaxation parameters for 2(2-alkoxyethoxy)ethanol–water mixtures at 25 °C.

X_W	MEE–water				
	ϵ_{0m}	ϵ_{1m}	$\epsilon_{\infty m}$	τ_1 (ps)	τ_2 (ps)
0.000	16.35(2)	6.71(2)	2.04	50.1(3)	5.59(4)
0.120	18.22(2)	6.87(2)	2.01	52.4(2)	5.24(4)
0.218	20.22(3)	6.39(4)	1.98	62.8(4)	6.85(8)
0.398	23.18(3)	6.75(2)	1.93	60.3(2)	5.56(5)
0.499	25.54(3)	7.17(3)	1.90	60.8(2)	6.05(5)
0.594	30.11(3)	7.44(3)	1.87	59.9(2)	5.46(4)
0.701	32.71(3)	6.42(3)	1.84	50.8(1)	6.20(7)
0.797	43.47(5)	10.20(7)	1.82	45.8(2)	5.87(6)
0.850	47.49(5)	12.23(10)	1.80	40.1(1)	6.89(7)
0.898	52.54(5)	18.28(29)	1.79	31.2(2)	8.67(10)
0.940	54.47(6)	33.65(65)	1.78	29.5(6)	10.92(11)
0.964	63.40(10)	–	1.77	12.39(3)	–
1.000	78.32(2)	–	1.76	8.21(1)	–
X_W	EEE–water				
	ϵ_{0m}	ϵ_{1m}	$\epsilon_{\infty m}$	τ_1 (ps)	τ_2 (ps)
0.000	14.79(1)	6.10(1)	2.04	53.6(2)	4.29(3)
0.132	15.38(3)	5.45(2)	2.00	65.9(5)	5.76(6)
0.187	16.62(2)	5.50(2)	1.99	72.2(4)	6.64(6)
0.322	19.75(3)	6.00(2)	1.95	76.2(4)	5.63(6)
0.424	21.15(3)	5.94(2)	1.91	77.6(3)	6.29(6)
0.504	22.57(3)	5.96(2)	1.89	78.3(3)	5.73(6)
0.604	26.57(3)	6.59(3)	1.87	71.1(3)	5.97(6)
0.702	30.38(4)	7.17(3)	1.84	66.8(2)	6.11(6)
0.801	37.34(5)	8.86(6)	1.82	54.5(2)	5.98(7)
0.859	45.75(5)	11.35(9)	1.79	44.7(2)	7.03(7)
0.901	52.46(5)	16.01(16)	1.78	35.4(2)	7.76(7)
0.968	57.14(8)	–	1.77	12.52(3)	–
1.000	78.32(2)	–	1.76	8.21(1)	–
X_W	BEE–water				
	ϵ_{0m}	ϵ_{1m}	$\epsilon_{\infty m}$	τ_1 (ps)	τ_2 (ps)
0.000	10.06(1)	4.28(1)	2.05	70.1(5)	7.29(7)
0.087	10.68(1)	4.36(1)	2.02	71.3(5)	7.05(7)
0.195	11.90(2)	4.47(2)	1.99	82.7(7)	7.88(9)
0.308	13.07(2)	4.62(2)	1.96	78.8(5)	7.12(7)
0.396	14.42(2)	4.81(2)	1.94	78.0(5)	6.21(7)
0.498	16.02(2)	5.13(2)	1.90	73.6(4)	5.85(6)
0.596	18.53(3)	5.53(2)	1.88	72.7(4)	5.84(6)
0.696	21.70(3)	6.50(3)	1.85	59.9(3)	5.88(6)
0.798	22.93(3)	6.61(3)	1.82	59.7(3)	5.52(6)
0.850	32.58(4)	10.70(8)	1.80	42.6(2)	6.85(7)
0.899	46.69(7)	22.40(14)	1.79	37.1(3)	5.70(4)
0.934	51.65(14)	–	1.78	13.1(1)	–
0.957	62.47(26)	–	1.77	12.1(1)	–
1.000	78.32(2)	–	1.76	8.21(1)	–

Numbers in bracket denote uncertainties in the last significant digits obtained by the least square fit method. e.g. 10.06(1) means 10.06 ± 0.01 .

mixture which shows the solute–solvent molecular interaction between glycol ether–water mixtures. The calculated value of 'a' for MEE, EEE and BEE–water mixture is determined using least square fit method and it is found to be 1.73, 1.78 and 1.82, respectively at 25 °C. The larger value of 'a' suggests that effective volume fraction of solute in water reduced very much.

3.3. Excess dielectric properties

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

$$\epsilon_0^E = \epsilon_{0m} - [\epsilon_{0W}X_W + \epsilon_{0S}(1-X_W)] \quad (6)$$

where the subscripts m, W and S represents mixture, water and glycol ether respectively and X_W represent the mole fraction of water. The excess dielectric constant may provide qualitative information about multimers formation in the mixtures as follows:

- $\epsilon_0^E = 0$ indicates that mixture constituents do not interact.

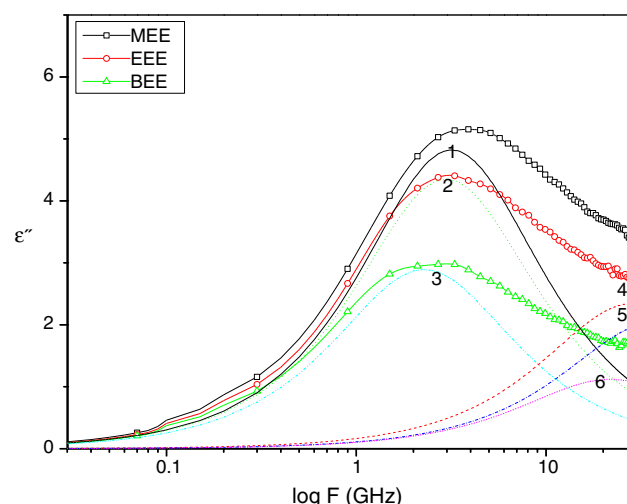


Fig. 3. Dielectric loss spectra for 2(2-alkoxyethoxy)ethanol with a sum of 2-Debye terms. The lines 1, 2 & 3 show the primary process whereas lines 4, 5 & 6 show the secondary process for MEE, EEE and BEE respectively.

- $\epsilon_0^E < 0$ indicates that mixture constituents interact such that the total number of effective dipoles contributed in the mixture ϵ_0 values get reduced.
- $\epsilon_0^E > 0$ indicates that the constituents of a mixture interact such that there is an increase in number of effective dipoles contributed in the mixture ϵ_0^E values.
- Higher the magnitude of ϵ_0^E represents the stronger and long-range H-bond interaction between unlike molecules and vice versa.

The plot of excess permittivity vs. X_W shown in Fig. 6. The plot exhibits a pronounced minimum and it remains negative for whole concentration range. These negative ϵ_0^E values for glycol ether–water mixtures shows the experimental evidence of a molecular interaction among the unlike species through hydrogen bonding so that the total number of effective dipoles get reduced. It also suggests the formation of complex structure in glycol ether–water through H-bonds. The mole fraction of water (X_W) corresponding to the minimum in ϵ_0^E value provides the stoichiometric ratio of stable adduct complexation. From Fig. 6 the minimum in ϵ_0^E values for MEE < EEE < BEE indicates as

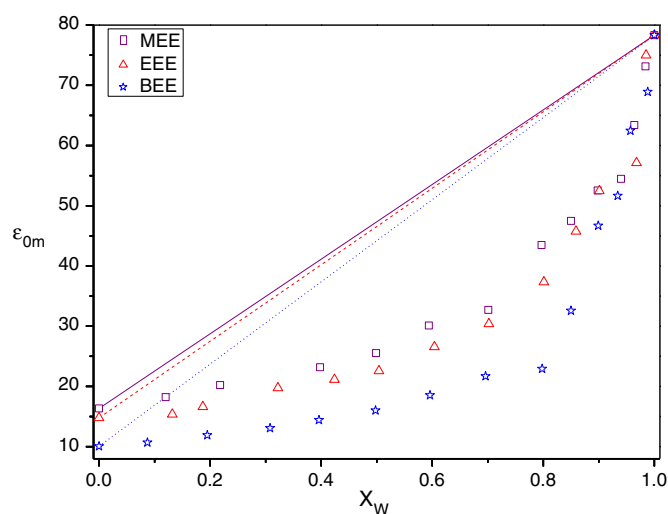


Fig. 4. Static dielectric constant vs. mole fraction of water (X_W) for 2(2-alkoxyethoxy) ethanol–water mixtures. Straight lines show the behavior of ideal mixture.

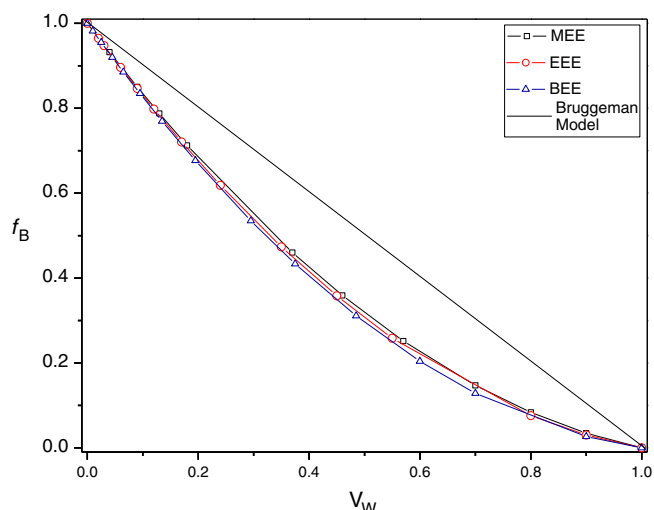


Fig. 5. Bruggeman factor (f_B) vs. V_W for 2(2-alkoxyethoxy)ethanol–water mixtures at 25 °C.

increase in chain length, the heteromolecular H-bond interaction reduces the number of effective dipoles. Dhondge et al. have been studied some thermodynamic and optical properties of ethylene glycol ethers in aqueous solution and shown that maxima/minima in the deviation of density, isentropic compressibility, refractive index and volume[21]. The excess molar volume remains negative over entire concentration range whereas the excess refractive index remains positive. The magnitude of minima or maxima increases on addition of CH₂ group in glycol ether molecule. It is attributed as the extensive volume contraction takes place due to strong solute–solvent interactions [26]. The pronounced minima of ϵ_0^E value for MEE & EEE is found approximately at $X_W \approx 0.7$ and for BEE at ≈ 0.8 which gives the stable adduct formation as water : MEE and EEE in the mole ratio of 1:2.3 and for water : BEE in the mole ratio of 1:4.

3.4. Kirkwood correlation factor

The Kirkwood Frohlich equation for pure liquid gives the useful information regarding the orientation of electric dipole. The departure of g value from unity is a measure of degree of short

range dipolar ordering due to hydrogen bond interactions. It can be represented as [27],

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9kTM} \quad (7)$$

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 kT has usual meaning. ϵ_∞ is considered as n^2 (n is refractive index) at 25 °C.

The molecular interaction between associating polar liquids can be described by effective Kirkwood correlation factor (g^{eff}) in binary mixtures by modified Kirkwood equation [27]

$$\frac{4\pi N}{9kT} \left[\frac{\mu_W^2 \rho_W}{M_W} X_W + \frac{\mu_S^2 \rho_S}{M_S} (1 - X_W) \right] g^{\text{eff}} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \quad (8)$$

where μ_W and μ_S are the dipole moments of water and glycol ether respectively, at 25 °C. ρ_W and ρ_S are corresponding densities. X_W is the mole fraction of water in glycol ether. The g^{eff} values for pure liquids, i.e. for water, MEE, EEE and BEE are 2.82, 1.46, 1.44 and 1.27, respectively. The significance of association effects according to decreasing order is as follows MEE>EEE>BEE. The g^{eff} values for water and glycol ethers are greater than unity, which suggest that the molecular dipoles have parallel orientation among themselves. Also water has higher correlation factor as compared to glycol ether indicates the strong intermolecular interaction in water molecules through hydrogen bonding whereas the g^{eff} for glycol ethers in pure form are such that, MEE>EEE>BEE. The values of Kirkwood correlation factor for entire binary mixtures of glycol ether–water are reported in Table 2. The addition of small amount of water, g^{eff} values glycol ether increases. This value gives significance of association in the mixtures and orientation of dipoles in the liquids.

3.5. Relaxation time

The relaxation time is a function of molecular size and relaxation time τ increases from MEE to BEE which are reported in Table 1. The relaxation time is related to the apparent activation free energy of the rearrangement of dipoles by the Eyring formula [28]

$$\tau = \frac{h}{k_B T} \exp\left(\frac{\Delta G}{RT}\right) \quad (9)$$

Table 2
Kirkwood correlation factor (g^{eff}) for 2(2-alkoxyethoxy)ethanol–water mixtures at 25 °C.

g^{eff}					
X_W	MEE	X_W	EEE	X_W	BEE
0.000	1.46(9)	0.000	1.44(9)	0.000	1.27(8)
0.120	1.59(9)	0.132	1.44(9)	0.087	1.32(8)
0.218	1.70(10)	0.187	1.53(9)	0.195	1.42(8)
0.398	1.81(11)	0.322	1.74(10)	0.308	1.48(9)
0.499	1.87(12)	0.424	1.77(10)	0.396	1.56(9)
0.594	2.08(12)	0.504	1.80(11)	0.498	1.62(10)
0.701	1.99(12)	0.604	1.97(12)	0.596	1.72(10)
0.797	2.42(14)	0.702	2.05(12)	0.696	1.79(10)
0.850	2.43(14)	0.801	2.21(13)	0.798	1.59(9)
0.898	2.44(14)	0.859	2.44(14)	0.850	2.04(12)
0.940	2.31(13)	0.901	2.56(15)	0.899	2.57(15)
0.964	2.58(15)	0.968	2.31(13)	0.934	2.52(15)
1.000	2.82(16)	1.000	2.82(16)	0.957	2.79(16)
				1.000	2.82(16)

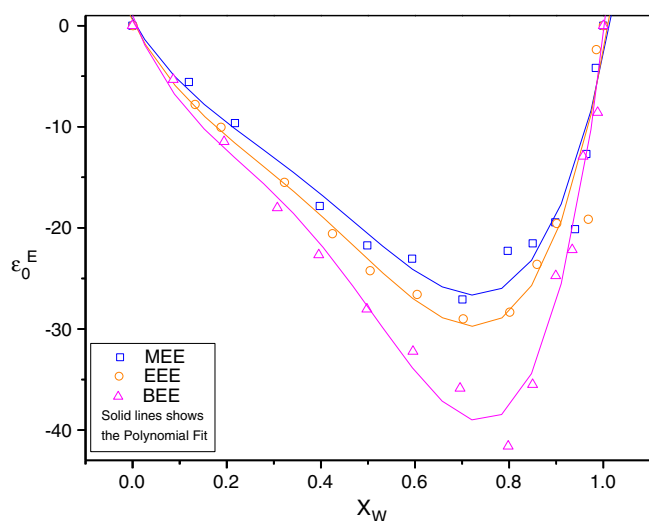


Fig. 6. Excess permittivity (ϵ_0^E) vs. mole fraction of water for 2(2-alkoxyethoxy)ethanol–water mixtures.

Here, h is Planck constant, k_B is the Boltzmann constant, T is the absolute temperature, R is gas constant and ΔG is the apparent activation free energy which relates to the relaxation rate in the molecular environment. If the glycol ether–water mixture considered as ideal mixture, the free energy of the mixed environment is equal to the arithmetic mean of the free energies of the pure liquids, and the apparent activation free energy, ΔG_{mix} , is given by [29]

$$\Delta G_{\text{mix}} = X_W \Delta G_W + (1-X_W) \Delta G_S \quad (10)$$

where ΔG_W and ΔG_S are the apparent free energies for pure water and solute (glycol ethers), respectively. Fig. 7 displays the free energy of activation for different glycol ether–water mixtures with against X_W . We can observe that these ΔG_{mix} values show extremely non linear dependence on X_W and ideal values of ΔG_{mix} indicate linear behavior by a straight line. This behavior indicates the existence of strong interactions between glycol ether and water molecules. Similarly, the relaxation time in the ideal case, τ_{ideal} , for the mixture is given by,

$$\tau_{\text{ideal}} = \frac{h}{k_B T} \exp\left(\frac{\Delta G_{\text{mix}}}{RT}\right) = \tau_W^{X_W} \tau_S^{(1-X_W)} \quad (11)$$

where τ_W and τ_S are the relaxation times of water and solute, respectively. This equation gives linear dependence of the logarithm of τ_{ideal} vs. X_W . In our results that are shown in Fig. 8, it is observed that, the experimental relaxation time increases slowly with increase in mole fraction of water in glycol ether, shows pronounced maxima and then rapidly decreases towards the relaxation time of water with further addition of water in glycol ether. These relaxation times deviate from τ_{ideal} in the entire concentration range and for all the system. The disagreement between τ_{ideal} and the observed τ_1 reflects the apparent activation free energy for the structural rearrangement of glycol ether and water unlike species. τ_{ratio} is defined as the ratio of $\tau_1/\tau_{\text{ideal}}$. Fig. 9 shows the plots of the τ_{ratio} against X_W for the glycol ether–water binary mixtures. The value of τ_{ratio} shows the maximum at $X_W = 0.7$ for MEE and EEE whereas at $X_W = 0.8$ for BEE.

4. Conclusions

The dielectric complex permittivity spectra of 2(2-alkoxyethoxy)ethanol in aqueous solution have been studied using two 2-Debye

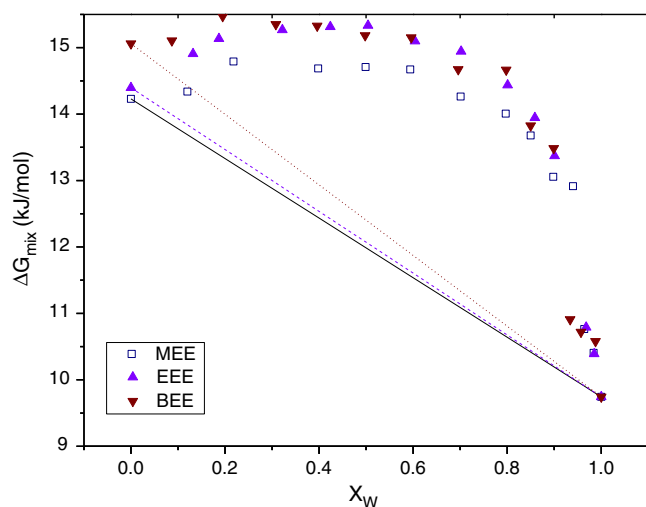


Fig. 7. Free energy of activation (ΔG_{mix}) for the dielectric relaxation process in 2(2-alkoxyethoxy)ethanol–water mixtures as a function of X_W at 25 °C. Straight lines show the behavior of ideal mixture.

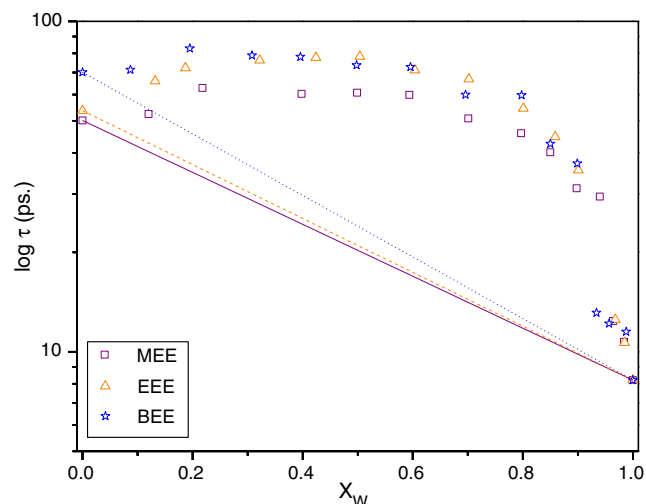


Fig. 8. $\log \tau$ (ps) vs. mole fraction of water (X_W) for 2(2-alkoxyethoxy)ethanol–water mixtures. Straight lines show the behavior of ideal mixture.

model by time domain reflectometry technique in the frequency range 10 MHz to 30 GHz. The deviation in dielectric constant of the mixtures from ideality attributed as increase in heterogeneous interaction in glycol ether–water mixtures. The modified Bruggeman equation is well fitted with experimental dielectric constant. The Kirkwood correlation factor is greater than unity shows that glycol ether molecules in aqueous solution form a multimers with parallel ordering of their dipole moment. The negative values of excess dielectric constant confirm that the hydrogen bond interaction of unlike molecules. The pronounced minimum in ϵ_0^E values provides the information regarding formation maximum stable adduct mixtures constituents.

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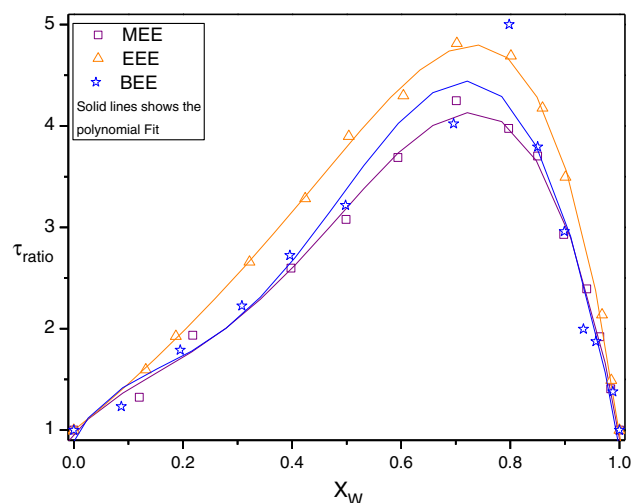


Fig. 9. τ_{ratio} vs. mole fraction of water for 2(2-alkoxyethoxy)ethanol–water mixtures at 25 °C.

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