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Study of dielectric relaxation and hydrogen bonding interaction in binary mixtures of methoxy polyethylene glycol and water

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The complex permittivity spectra of binary mixtures of methoxy polyethylene glycol (Polyethylene glycol monomethylether 350) and water over entire concentrations and at different temperatures have been measured using time domain technique in the frequency range of 10 MHz to 30 GHz. The spectra have been fitted to Cole-Davidson model using non linear least square fit method to obtain the dielectric parameters. The non linear behaviour of dielectric parameters suggest intermolecular interaction among the unlike molecules. Excess properties and Bruggeman factor confirm the contribution of hydrogen bonding interactions among the solute-solvent mixtures. Thermodynamic properties of these binary mixtures are also discussed.

Keywords: Complex permittivity, Dielectric relaxation, TDR, Thermodynamic properties

1 Introduction

Polyethylene glycol monomethylether (PEGME) 350 is a polymer having structural formula $CH_3(OCH_2CH_2)_nOH$ with '*n*' indicating average number of oxyethylene group. PEGME's also known as methoxy polyethylene glycols are addition of polymers of ethylene oxide and methanol. They are used in surfactants, polyester and polyurethane based paints. As polymer modifier they improve stability, wetting and linking characteristics in waterborne systems. In biological process it provides compatibility with physiological tissues and fluids. The study of dielectric absorption and dispersion spectra of binary liquid mixture provides information regarding molecular interaction through hydrogen bonding in the liquid mixture[1]. Therefore the dielectric relaxation spectroscopy (DRS) is an applicable system in which hydrogen bonds play an important role such as aqueous solutions[2]. DRS offers valuable insights into the microdynamics of fluctuating hydrogen bonded liquids[1-4]. Dielectric relaxation depends upon the molecular size, shape and molecular interactions and this study is useful to find out dipole-dipole interaction, complex structure formation and short range intermolecular interactions[5]. In literature, dielectric characterizations of some polymers in pure and binary form are carried out but that of polymer ether are rare[6-8]. In our previous work, we studied in detail the dielectric relaxations of ethylene glycol monoalkyl ethers (methoxyethanol (ME), ethoxyethanol (EE) and butoxyethanol (BE)) in aqueous solution[9-11]. The study gives insight into the molecular association among the glycol ether molecules with water molecules through hydrogen bonding. Also the dielectric parameters exhibit systematic change. The dielectric permittivity formerly known as static dielectric constant of ME > EE > BE whereas relaxation time of BE > EE > ME. The effect of chain length is observed from the excess dielectric permittivity plots. With increase in chain length, the values of ε_0^E were more negative and the minima shift towards water rich region. Since these glycol ethers having a strong molecular interaction with water, it is interesting to study the dielectric relaxation and molecular association among the polymer of glycol ethers and water. Recently, we studied the dielectric and electrical characterization over the frequency range 20 Hz to 2 MHz of binary mixture of polyethylene glycol monomethylether with water[12]. In present work, the complex permittivity spectra of PEGME 350 with water over the concentration range from $0 \leq X_W \leq 1$ (X_W is the mole fraction of water) have been measured using time domain technique in the frequency range of 10 MHz to 30 GHz at different temperatures. The dielectric parameters have been evaluated using non linear least square fit method. The intermolecular interactions among the PEGME 350 in presence of aqueous solutions have been discussed in subsequent

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sections using excess dielectric permittivity, Bruggeman factor and thermodynamic parameter.

2 Experimental

2.1 Materials

PEGME 350 was obtained from Alfa Aesar with purity 99% and water with HPLC grade made by Qualigens. They were used without further purification. The solutions were prepared at different weight percentage of PEGME 350 in water.

2.2 Measurements and data analysis

The measurements of complex permittivity spectra in the frequency range of 10 MHz to 30 GHz have been carried out by the time domain reflectometry technique. For the measurements, Tektronix model number DSA8200 digital serial analyzer with sampling module 80E08 has been used. The detailed data analysis to obtain the complex permittivity spectra $\varepsilon^*(\omega)$ and the dielectric parameters using nonlinear least squares fit method have been discussed in our previous work[13-15]. Figure 1 shows frequency dependent complex permittivity spectra for PEGME350–water mixtures at 298.15 K. The dielectric parameters viz. dielectric permittivity (ε_o), relaxation time (τ), dielectric permittivity at high frequency (ε_∞) and asymmetric distribution of relaxation (β) are evaluated using Cole-Davidson Model[16] and are given in Table 1. The dielectric parameters for pure water are in good agreement

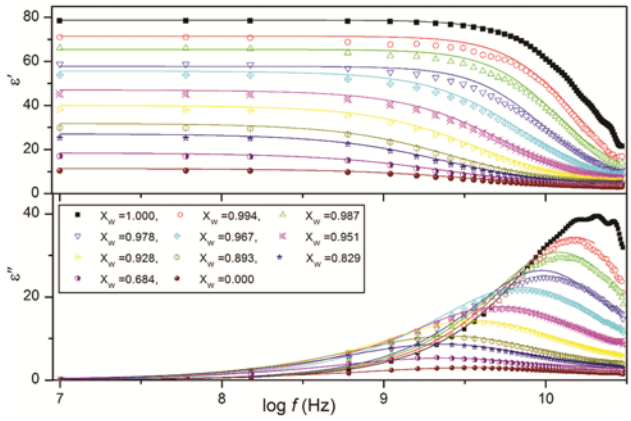

Fig. 1 — Frequency dependent dielectric permittivity (ε') and dielectric loss (ε'') for PEGME 350-water over entire concentrations at 298.15 K. Solid lines are drawn from CD fit values.

Table 1 — Dielectric relaxation parameters of PEGME350+ water mixtures at various temperatures.

X_W	298.15 K					288.15 K				278.15 K			
	ε_0	ε_∞	τ (ps)	β	n_D	ε_0	ε_∞	τ (ps)	β	ε_0	ε_∞	τ (ps)	β
0.000	11.06 (2) [11.21]	1.96 (7)	44.01 (34)	0.729 (2)	1.3320	11.55 (2)	2.10 (1)	50.26 (41)	0.717 (2)	13.72 (4)	2.95 (1)	70.96 (91)	0.67 (3)
0.684	18.15 (5) [19.11]	2.36 (1)	68.47 (60)	0.744 (2)	1.3465	19.47 (6)	2.64 (1)	89.35 (98)	0.728 (3)	21.35 (10)	4.09 (1)	135.01 (248)	0.713 (4)
0.829	26.86 (5) [26.71]	2.65 (1)	68.92 (42)	0.782 (2)	1.3595	28.44 (7)	3.03 (1)	88.71 (71)	0.774 (2)	30.71 (13)	4.27 (2)	132.67 (187)	0.76 (3)
0.893	31.57 (5) [33.51]	2.68 (1)	62.33 (27)	0.798 (2)	1.3765	33.06 (7)	2.98 (1)	74.62 (44)	0.790 (2)	36.09 (12)	4.28 (2)	116.56 (125)	0.781 (3)
0.928	39.77 (3) [40.91]	2.56 (1)	43.54 (9)	0.829 (1)	1.3865	41.37 (4)	2.80 (1)	51.00 (14)	0.824 (1)	45.68 (10)	3.83 (2)	77.56 (47)	0.803 (2)
0.951	46.74 (2) [48.21]	2.25 (7)	30.51 (3)	0.851 (1)	1.4010	49.34 (3)	2.53 (1)	36.71 (5)	0.842 (1)	54.71 (8)	3.21 (2)	53.69 (20)	0.819 (1)
0.967	55.31 (2) [54.21]	1.73 (1)	22.51 (2)	0.882 (1)	1.4145	57.29 (2)	1.77 (1)	25.21 (2)	0.876 (1)	62.61 (4)	1.47 (1)	32.11 (5)	0.852 (1)
0.978	57.41 (13) [59.11]	4.85 (5)	16.86 (7)	1.000	1.4260	60.29 (15)	4.85 (6)	18.84 (8)	1.000	66.16 (21)	4.85 (6)	23.24 (12)	1.000
0.987	65.05 (9) [65.31]	3.73 (4)	13.17 (4)	1.000	1.4335	68.12 (10)	3.39 (4)	14.78 (4)	1.000	73.92 (14)	1.23 (5)	17.46 (5)	1.000
0.994	71.12 (9) [70.21]	2.58 (5)	10.68 (3)	1.000	1.4440	76.41 (7)	0.65 (4)	12.14 (2)	1.000	82.63 (8)	1.83 (10)	14.93 (10)	1.000
1.000	78.32 (2) [77.96] 78.36[a]	1.98 (2)	8.21 (1) 8.27[a]	1.000	1.4505	82.01 (6) 82.05[a]	2.07 (2)	10.56 (1) 10.83[a]	1.000	85.24 (4) 85.83[a]	2.56 (1)	14.43 (1) 14.91[a]	1.000

Numbers in bracket denotes uncertainties in the last significant digits obtained by least square fit method e.g. 11.06 (2) means 11.06 ± 0.02. Values in square brackets are from frequency domain measurements Ref.[12]. [a] Literature values for pure water from Ref.[17,18]

with literature values[17,18]. Figure 2 shows an example of complex permittivity spectra for 40% PEGME 350 + 60% water mixtures by weight (corresponding to X_W =0.967) for different temperatures studied here. Refractive indices (n_D) of those binary mixtures have been measured by Abbe's refractometer with an accuracy $\pm 5\times10^{-4}$ and are reported in Table 1.

3 Results and Discussion

3.1 Dielectric parameters

Dielectric permittivity values of binary mixtures of PEGME 350 -water against the mole fraction of water are plotted in Fig. 3. Dielectric permittivity values obtained using time domain technique is in good agreement with our previous measurement[12] using LCR at frequency 2 MHz. Here, on diluting the mixture, the values of static dielectric permittivity are slowly increasing up to $X_W \approx 0.8$. Above this concentration, the value of ε_o abruptly increases towards the high value of dielectric permittivity of water. In comparison with water the dielectric permittivity of pure PEGME 350 is low. The plot suggests the two regions of ε_o values, below X_W=0.8 solute molecules (PEGME) have more influence on dielectric permittivity value therefore rise in ε_o value is very small. Above this concentration, the rise in the ε_o values is rapid indicating the effect of solvent molecules (water) in the binary mixtures. The discussion for dielectric behaviour for the binary mixtures of PEGME-water is continued further using the plot of relaxation time of PEGME – water binary mixtures (Fig. 4). Both the plots exhibit non-linear nature (Figs 3 and 4), attributed as certain intermolecular interactions among the solute and solvent molecules. Also this non-linear nature of dielectric parameters is a function of temperature and it increases with decrease in temperature. It may be due to more favorable conditions for solute and solvent interactions. Molecular interactions and dynamics in the medium among the PEGME-water molecules are discussed using excess properties, bruggeman factor and thermodynamic parameters in subsequent sections.

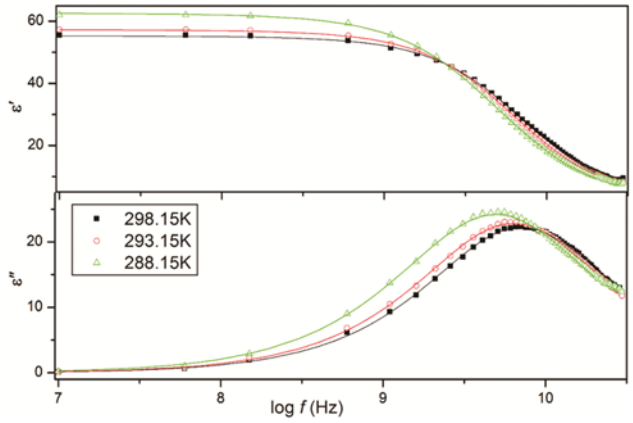

Fig. 2 — Frequency dependent dielectric permittivity (ε′) and dielectric loss (ε″) for X_W= 0.967 for different temperatures. Solid lines are drawn from CD fit values.

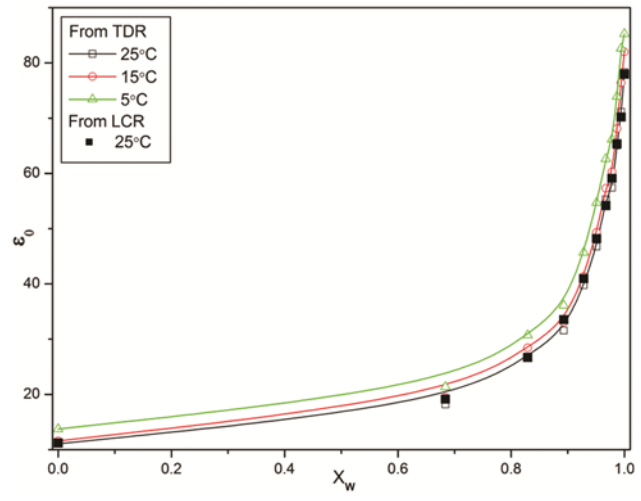

Fig. 3 — Dielectric permittivity (ε_0) versus mole fraction of water (X_W) for PEGME350- water mixtures.

3.2 Excess properties

The contribution of hydrogen bonds to the dielectric properties of the mixture can be studied in terms of the excess dielectric permittivity. The excess

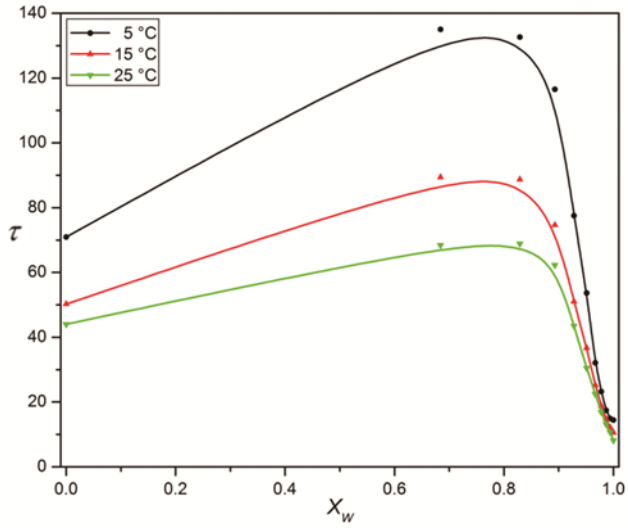

Fig. 4 — Relaxation time (τ) versus mole fraction of water (X_W) for PEGME350- water mixtures.

dielectric permittivity (ε_0^E) values for the PEGME 350 – water binary mixtures are evaluated using the same formula studied earlier elsewhere[19-21]. It gives qualitative information about multimers formation in the binary mixtures. In Fig. 5 the excess dielectric values are negative for entire concentrations. These negative ε_0^E values show (Fig. 5) the experimental evidence of the formation of H-bonding complexes and the strength of H-bond connectivity among the unlike molecules in the binary mixture[22]. This information may be attributed as the formation of complex structure in PEGME 350–water through H-bonds such that the effective dipole moment get reduced. The plot exhibit pronounced minima at X_W =0.8 which suggests the stoichiometric ratio of complex structure, water: PEGME is 4:1. As studied earlier[9], the pronounced minima of ε_0^E for water: EGME occurs at X_W=0.6. Dielectric permittivity at high frequency of binary mixtures is determined from the square of refractive index (n_D). Figure 6 shows the plot of excess permittivity at high frequency (ε_∞^E). The values of ε_∞^E give information about the magnitude of electronic polarization in binary mixtures[23,24]. From Fig. 6 the values of $\varepsilon_\infty^E > 0$ for entire binary mixtures studied here. It indicates a net increase in the magnitude of the electronic polarization due to H-bond interactions between unlike molecules (PEGME 350 + water) in these binary systems.

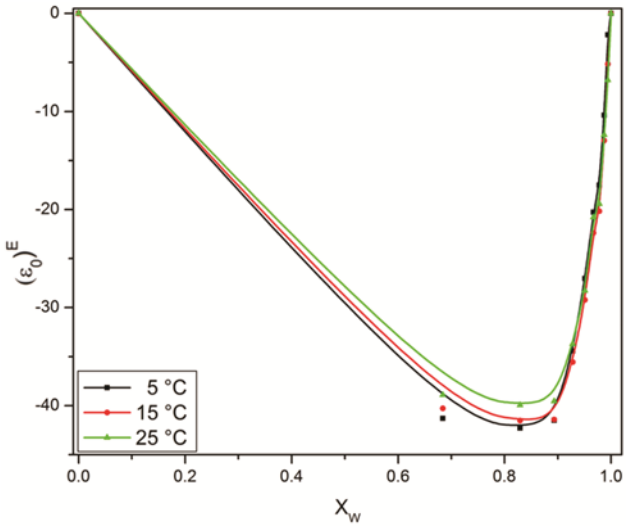

Fig. 5 — Excess dielectric permittivity (ε_0^E) versus mole fraction of water at various temperatures.

3.3 Bruggeman factor (f_B)

The Bruggeman expression predicts a linear relationship between the Bruggeman factor and the volume fraction of solvent[25]. But the experimental values of f_B show a non linear behaviour. To explain the non linear relationship, modified Bruggeman mixture formula has been used[26]. In Bruggeman mixture formula '*a*' is arbitrary parameter, if the value of '*a*' is unity then it indicates the ideal mixture with no molecular interaction between solute and solvent. Ideal behaviour according to Bruggeman mixture formula is shown by solid line in Fig. 7. But the experimental values represent the deviation from ideal behaviour of mixture which shows the solute-solvent molecular interaction between PEGME-water mixtures. The calculated value of '*a*' is determined using least square fit

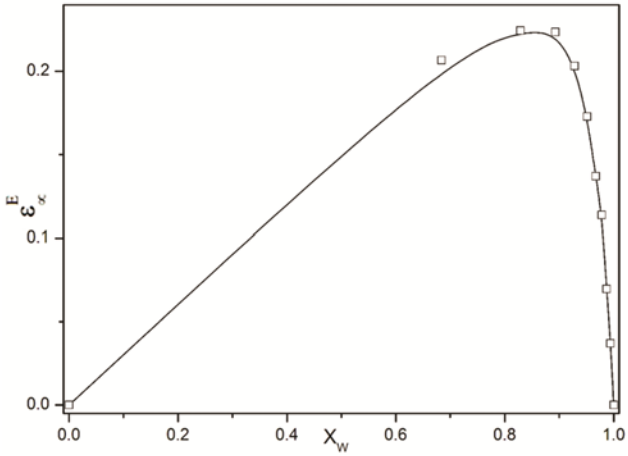

Fig. 6 — Excess dielectric permittivity at high frequency (ε_∞^E) versus mole fraction of water at 298.15 K.

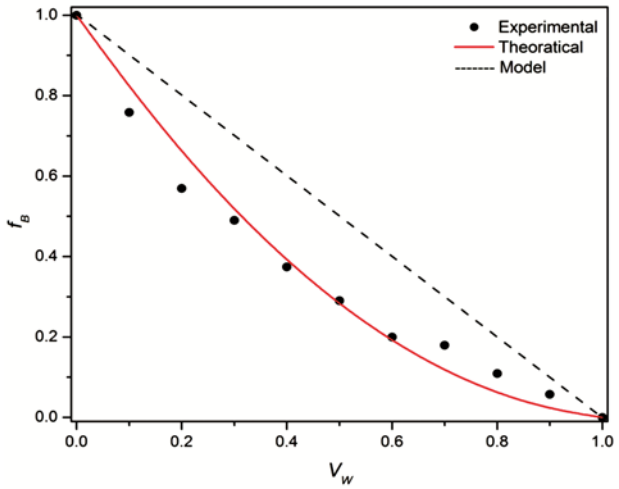

Fig. 7 — Bruggeman factor (f_B) versus V_W at 298.15 K.

Table 2 — Bruggeman factor for PEGME 350 + water.

Temperature (K)	*a* value
278.15	1.919
288.15	1.885
298.15	1.876

Table 3 — Thermodynamic parameters for water and PEGME 350 binary mixtures.

X_W	ΔH (kJ/mol)	ΔS (J/mol/k)
0.000	14.13 (391)	0.230 (13)
0.684	21.04 (246)	0.250 (8)
0.829	20.21 (255)	0.247 (8)
0.893	19.26 (493)	0.245 (17)
0.928	17.58 (481)	0.242 (16)
0.951	17.14 (351)	0.243 (12)
0.967	9.88 (233)	0.222 (8)
0.978	8.69 (175)	0.220 (6)
0.987	7.31 (83)	0.217 (2)
0.994	9.17 (135)	0.225 (4)
1.000	17.04 (83)	0.254 (2)

Numbers in bracket denote uncertainties in the last significant digits obtained by the least square fit method e.g. 17.04 (83) means 17.04 ± 0.83.

method and are given in Table 2 at various temperature ranges.

3.4 Thermodynamic parameters

The thermodynamic parameters were evaluated using Eyring equation[27]. The values of ΔH and ΔS are reported in Table 3. The values ΔH give information about the amount of activation energy require to rotation of H–bond in the mixtures[28]. From Table 3, on addition of small amount of PEGME 350 in water, the values of ΔH are suddenly fall in the region $1 \leq X_W \leq 0.967$. It can be attributed as change in H-bond strength or decrease in number of H-bond in the mixtures[29]. In this region the dipoles requires less energy for rotation than it requires in pure water. In the region $0.967 \leq X_W \leq 0.684$, there is increase in the values of activation energy (ΔH). This may be due to formation of H-bonds among the unlike molecules, i.e., PEGME 350 – water molecules. It means that the H-bond strength or average number of hydrogen bonds increases in this region and attributed as the water structure gets modified in presence of PEGME 350 molecules and forms a co-operative structure in unlike molecules.

4 Conclusions

The dielectric relaxation study of PEGME350 in aqueous solutions has been studied using time domain technique in the frequency range of 10 MHz to 30 GHz. The dielectric parameters studied here exhibit non linear behaviour attributed as hetero molecular interactions among the polymer–water molecules through hydrogen bonding. The intermolecular interactions among these unlike molecules are confirmed by the excess dielectric, Bruggeman factor and thermodynamic parameters. The negative values of excess dielectric values suggest that the hydrogen bonding interactions among the PEGME-water mixtures such that the effective dipole moments get reduced.

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