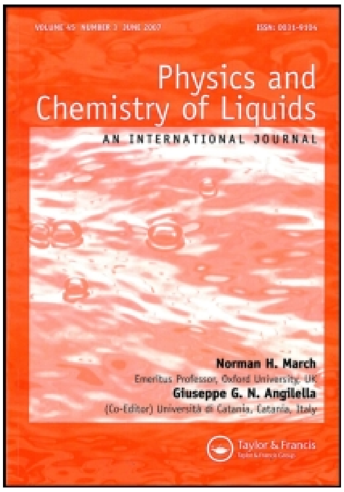

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H-bonded molecular interaction study on binary mixtures of mono alkyl ethers of ethylene glycol with different polar solvents by concentration dependent dielectric analysis

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Static dielectric constant measurements on binary mixtures of the homologous series of mono alkyl ethers of ethylene glycol with six different characteristic polar solvents i.e. ethyl alcohol, ethylene glycol, glycerol, water, dimethyl formamide and dimethyl sulphoxide over the entire concentration range were carried out using precision LCR meter and a four terminal liquid dielectric test fixture at 1 MHz and 25°C. The concentration dependent excess dielectric constant and Kirkwood correlation factor were determined for the confirmation of solvent–cosolvent heterogeneous molecular interactions. The values of stoichiometric ratio corresponding to maximum interactions between the mixtures constituents were also estimated from the concentration dependent values of ε^E. It is observed that the behaviour of heterogeneous interactions significantly varies with the increase in molecular size of the homologous series and also with the change in the mixture constituents. Comparative dielectric parameters values of the studied binary mixtures were applied to recognize the dipolar orientation due to heterogeneous interactions of mono alkyl ethers with hydroxyl group(s) containing solvents and non-hydroxyl group containing solvents.

Keywords: Polar binary mixtures; Dielectric constant; Kirkwood correlation factor; Excess dielectric parameters

1. introduction

The confirmations of the homogeneous and heterogeneous molecular interactions in polar binary mixtures are the central topics in liquid state physics and chemistry [1–18]. Alcohols–water mixtures [1–4,10,13] are very good probes for an investigation on these interaction phenomena. Alcohols strongly interact with water through hydrogen bonds and at the same time enhance the structural aspects of the solvent water surrounding the alkyl group. Dielectric constant and relaxation measurements [1–22] are among the most powerful methods providing information on molecular

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interaction and dynamical aspects of the binary systems in pure liquid state and also in dilute solutions of non-polar solvents. In addition, the dielectric measurements on the binary mixtures of associating molecules have aroused considerable interest under varying conditions of composition in formulating adequate new dielectric models of liquid mixtures.

Mono alkyl ethers of ethylene glycol are important solvents. Due to the presence of hydroxyl group in their molecular structure, these molecules form intramolecular and intermolecular H-bonded structures in dynamic equilibrium in their pure liquid state [23]. A survey of the available literature shows that, so far no attempt has been made as to confirm the heterogeneous molecular interaction of this homologous series with non-hydroxyl and hydroxyl group(s) containing polar solvents in pure binary mixtures. Earlier in this laboratory, Sengwa and co-authors [23–29] have extensively investigated the dielectric relaxation and dipole moment study of mono alkyl ethers of ethylene glycol and their binary mixtures with different polar solvents at different temperatures to confirm their molecular dynamics and dipole interactions in dilute solutions with different non-polar solvents.

Microwave dielectric relaxation measurements [24,27,28] established that the hindrance to the molecular reorientation increases with the increase in molecular size of the mono alkyl ethers of ethylene glycol in dilute solutions of benzene, dioxane and carbon tetrachloride solvents. Further, the higher density of non-polar solvent produces more hindrance to the molecular dynamics but the dioxane interactions mask the density effect. It has also been confirmed that in dilute solutions, these molecules exist in self-associated form in dynamical equilibrium with the breaking and reforming of hydrogen bonds due to intramolecular rotations of alkoxyl and hydroxyl group. The dielectric relaxation and dipole moment study [28,29] of the binary mixtures of mono alkyl ethers of ethylene glycol with ethyl alcohol, glycerol, dimethyl sulphoxide and dimethyl formamide in dilute solutions of dioxane proved that the hindrance to the molecular reorientations due to heterogeneous interactions is influenced by the nature of polar solvent and by the composition of the mixture constituents.

The goal of this work is to study the dielectric behaviour of mono methyl, mono ethyl and mono butyl ether of ethylene glycol with the mixtures of some common polar solvents over the entire concentration range in pure liquid state from the viewpoint of heterogeneous molecular interaction and the conformation changes originating as a consequence of these interactions. We also have a particular interest on the presentation of the accurate values of dielectric constant of the mixtures of mono alkyl ethers of ethylene glycol with water and alcohols having different number of hydroxyl group(s) (i.e. monohydric, dihydric and trihydric), and also with non-hydroxyl group containing solvents i.e. dimethyl formamide and dimethyl sulphoxide, which needs in formulating the dielectric models of associating binary mixtures.

2. Experimental

2.1. *Materials*

Mono methyl (MM), mono ethyl (ME) and mono butyl (MB) ether of ethylene glycol ($ROCH_2CH_2OH$), ethyl alcohol (EA) (C_2H_5OH), ethylene glycol (EG) ($HOCH_2CH_2OH$) and glycerol (Gly) ($HOCH_2CHOHCH_2OH$) of AR grade were obtained from E. Merck, India. Dimethyl sulphoxide (DMSO) (CH_3SOCH_3) and *N*,*N*-dimethyl formamide (DMF) ($HCON(CH_3)_2$) of LR grade were obtained from Qualigens Fine Chemicals, India. These samples were used for the preparation of different concentration binary mixtures. Double-distilled and deionized water (W) is used for the preparation of the binary mixtures of mono alkyl ethers of ethylene glycol with water. The binary mixtures were prepared at seven different volume percentages of the mixture constituents over the entire concentration range at room temperature, and simultaneously by weight measurements the mole fractions of the mixture constituents were determined.

2.2. *Measurements*

The static dielectric constant ε_o of the liquid samples was determined by using 'capacitive measurement method' at 1 MHz. Agilent 4284A Precision LCR Meter and a four terminal cell Agilent 16452A Liquid Dielectric Test Fixture were used for accurate evaluation of the dielectric constant ε_o of the mixture. By measuring the air capacitance C_o and liquid sample capacitance C_p, the values of ε_o of the samples were determined from the relation $\varepsilon_o = \alpha(C_p/C_o)$, where α is the liquid test fixture correction coefficient. The Test Fixture correction coefficient was considered to cancel the stray capacitance for accurate evaluation of the ε_o values of the liquids. The capacitances of the Liquid Dielectric Test Fixture without and with sample were measured by using it for a short compensation. The high frequency limiting dielectric constant ε_∞ was taken as the square of the refractive index n_D, which was measured with an Abbe refractometer at the wavelength of sodium light. All measurements were made at 25°C and the temperature was controlled thermostatically. The measured values of ε_o and ε_∞ of these systems are recorded in table 1.

3. Results and discussion

3.1. *Static dielectric constant*

The values of static dielectric constant ε_o of the studied binary mixtures with mole fraction of mono alkyl ethers of ethylene glycol X at 25°C are plotted in figure 1. The ε_o values of the polar cosolvents used in binary mixtures i.e. EA, EG, Gly, Water, DMF and DMSO are higher than the ε_o values of the mono alkyl ethers of ethylene glycol (table 1). Because of this, the observed ε_o values decrease with increasing concentration of mono alkyl ethers of ethylene glycol (X) in all the studied binary mixtures (figure 1). In general, the ε_o value of H-bonded liquid at constant temperature is mainly dependent on the dipole moment μ, the number of molecules per unit volume and Kirkwood correlation factor g. In case of the binary mixture of hydroxyl group(s) containing cosolvents i.e. EA, EG and Gly, the value of ε_o decreases non-linearly with increase in X. But in case of water–ethers mixture, the large decrease in ε_o values were found with the increase in X value, which is more pronounced with increase in the molecular size of the mono alkyl ether in the water-rich region. This decrease is mainly attributed to the comparative larger decrease in number of water molecules per unit volume in the water–ether mixtures. The ε_o values of the mixtures of glycerol with mono methyl and mono ethyl ether shows small increase as compared to ε_o value of pure glycerol (at $X \approx 0.1$), which is interesting and may be due to significant variation

Table 1. Values of static dielectric constant ε_o, high frequency limiting dielectric constant ε_∞ and excess dielectric constant ε^E for various binary mixtures at different mole fraction X of mono alkyl ethers of ethylene glycol at 25°C.

X	ε_o	ε_∞	ε^E	X	ε_o	ε_∞	ε^E	X	ε_o	ε_∞	ε^E
MM–W				ME–W				MB–W			
0.000	78.76	1.77		0.000	78.76	1.77		0.000	78.76	1.77	
0.031	71.39	1.79	−5.49	0.026	72.35	1.79	−4.74	0.019	70.25	1.79	−7.22
0.070	65.47	1.82	−9.04	0.058	65.92	1.82	−9.12	0.044	59.96	1.83	−15.81
0.119	58.98	1.85	−12.56	0.100	58.83	1.86	−13.51	0.076	49.99	1.86	−23.60
0.184	51.70	1.88	−15.88	0.156	50.42	1.89	−18.32	0.120	40.13	1.89	−30.45
0.273	43.78	1.90	−18.38	0.236	41.85	1.91	−21.71	0.186	31.63	1.92	−34.42
0.401	34.87	1.92	−19.46	0.357	31.11	1.94	−24.61	0.291	24.06	1.95	−34.77
0.611	26.82	1.93	−14.66	0.565	23.68	1.95	−18.53	0.489	16.98	1.97	−28.19
1.000	17.65	1.95		1.000	13.94	1.96		1.000	9.87	1.99	
MM–EA				ME–EA				MB–EA			
0.000	25.13	1.84		0.000	25.13	1.84		0.000	25.13	1.84	
0.095	23.72	1.85	−0.70	0.079	23.18	1.85	−1.07	0.060	22.81	1.85	−1.41
0.196	22.72	1.86	−0.95	0.167	21.79	1.87	−1.48	0.129	20.90	1.87	−2.27
0.305	21.75	1.88	−1.11	0.265	20.45	1.88	−1.73	0.211	19.06	1.89	−2.87
0.422	20.78	1.90	−1.21	0.376	18.95	1.90	−1.99	0.308	17.19	1.91	−3.27
0.549	19.81	1.91	−1.22	0.501	17.52	1.92	−2.02	0.426	15.15	1.94	−3.51
0.687	18.95	1.92	−1.05	0.644	16.07	1.93	−1.87	0.571	13.15	1.96	−3.30
0.837	18.13	1.94	−0.74	0.808	14.78	1.95	−1.32	0.757	11.22	1.98	−2.38
1.000	17.65	1.95		1.000	13.94	1.96		1.000	9.87	1.99	
MM–EG				ME–EG				MB–EG			
0.000	41.12	2.04		0.000	41.12	2.04		0.000	41.12	2.04	
0.091	37.55	2.02	−1.42	0.076	36.88	2.02	−2.17	0.057	35.97	2.02	−3.35
0.189	34.83	2.01	−1.84	0.161	33.39	2.01	−3.35	0.124	31.90	2.02	−5.33
0.295	31.67	2.00	−2.51	0.257	30.09	2.00	−4.03	0.203	27.67	2.01	−7.09
0.411	28.65	1.99	−2.81	0.365	26.40	2.00	−4.79	0.298	23.49	2.00	−8.30
0.538	25.71	1.98	−2.77	0.490	22.90	1.99	−4.89	0.414	19.59	2.00	−8.58
0.677	22.87	1.97	−2.35	0.633	19.64	1.98	−4.26	0.560	15.94	2.00	−7.66
0.830	20.06	1.96	−1.57	0.801	16.57	1.97	−2.77	0.748	12.54	1.99	−5.19
1.000	17.65	1.95		1.000	13.94	1.96		1.000	9.87	1.99	
MM–Gly				ME–Gly				MB–Gly			
0.000	44.06	2.15		0.000	44.06	2.15		0.000	44.06	2.15	
0.119	45.76	2.08	4.89	0.100	45.06	2.08	4.06	0.076	43.30	2.09	1.89
0.240	42.05	2.06	4.37	0.206	40.75	2.07	2.93	0.161	37.48	2.08	−1.03
0.362	38.02	2.05	3.55	0.319	35.97	2.06	1.56	0.257	31.61	2.06	−3.62
0.486	33.93	2.03	2.73	0.438	31.20	2.04	0.36	0.365	26.38	2.05	−5.16
0.612	29.64	2.01	1.76	0.565	26.63	2.02	−0.39	0.490	21.61	2.04	−5.66
0.740	25.32	1.99	0.82	0.701	21.96	2.00	−0.97	0.633	17.16	2.02	−5.23
0.869	21.68	1.97	0.58	0.845	17.88	1.98	−0.72	0.801	13.48	2.01	−3.18
1.000	17.65	1.95		1.000	13.94	1.96		1.000	9.87	1.99	
MM–DMSO				ME–DMSO				MB–DMSO			
0.000	47.13	2.18		0.000	47.13	2.18		0.000	47.13	2.18	
0.121	44.86	2.13	1.31	0.095	44.13	2.14	0.09	0.072	43.29	2.15	−1.15
0.243	42.44	2.11	2.49	0.197	41.26	2.11	0.55	0.153	39.74	2.12	−1.66
0.366	39.73	2.08	3.40	0.306	37.93	2.08	0.79	0.246	35.72	2.10	−2.21
0.490	36.38	2.05	3.71	0.424	34.02	2.06	0.77	0.352	31.31	2.08	−2.67
0.616	32.34	2.02	3.38	0.551	29.59	2.04	0.56	0.475	26.36	2.06	−3.04
0.743	27.74	2.00	2.53	0.688	24.49	2.01	0.02	0.620	20.90	2.03	−3.10
0.871	23.02	1.97	1.57	0.837	19.64	1.99	0.17	0.792	15.52	2.02	−2.08
1.000	17.65	1.95		1.000	13.94	1.96		1.000	9.87	1.99	
MM–DMF				ME–DMF				MB–DMF			
0.000	37.65	2.03		0.000	37.65	2.03		0.000	37.65	2.03	
0.113	35.64	2.01	0.26	0.102	34.82	2.01	0.52	0.077	34.26	2.02	−1.24

(*Continued*)

Table 1. Continued.

X	ε_{o}	ε_{∞}	ε^{E}	X	ε_{o}	ε_{∞}	ε^{E}	X	ε_{o}	ε_{∞}	ε^{E}
0.229	33.70	2.00	0.64	0.209	32.49	2.01	1.61	0.163	31.22	2.01	−1.89
0.349	31.76	1.99	1.10	0.322	30.23	2.00	2.88	0.260	27.94	2.01	−2.47
0.472	29.42	1.98	1.22	0.442	27.47	1.99	3.73	0.369	24.84	2.01	−2.55
0.598	26.88	1.98	1.20	0.569	24.45	1.98	4.29	0.494	21.18	2.00	−2.74
0.728	23.89	1.97	0.81	0.704	21.08	1.98	4.28	0.637	17.53	2.00	−2.42
0.862	21.61	1.96	1.20	0.847	17.78	1.97	3.59	0.804	13.76	2.00	−1.55
1.000	17.65	1.95		1.000	13.94	1.96		1.000	9.87	1.99	

in the three-dimensional hydrogen-bonded network of glycerol (trihydric alcohol) molecules in the presence of small amount of ether molecules.

3.2. *High frequency limiting dielectric constant*

The variation of the high frequency limiting dielectric constant ε_{∞} of the polar binary mixtures with mole fraction of ethers X is shown in figure 2. In case of the binary mixtures of water–ethers and EA–ethers, the ε_{∞} value increases with increase in X, but for other binary mixtures, the decrease in ε_{∞} is observed with increase in X. The large decrease in ε_{∞} is observed in case of glycerol–ethers mixtures at $X \approx 0.1$, which also supports the large increase in ε_{o} value in the same concentration range and confirms the significant structural enhancement of trihydric alcohol molecules due to its large interactions with ether molecules in binary mixtures at very small concentrations of ether.

3.3. *Excess dielectric constant*

The excess dielectric constant ε^{E} is defined as [30]

$$\varepsilon^{\mathrm{E}} = (\varepsilon_{\mathrm{o}} - \varepsilon_{\infty})_{\mathrm{m}} - \left[(\varepsilon_{\mathrm{o}} - \varepsilon_{\infty})_{\mathrm{A}} X_{\mathrm{A}} + (\varepsilon_{\mathrm{o}} - \varepsilon_{\infty})_{\mathrm{B}} X_{\mathrm{B}}\right] \tag{1}$$

where X is the mole fraction and subscripts m, A and B represent mixture and constituents A and B of the mixture, respectively. The excess dielectric constant provides qualitative information as follows [5,12,18]:

(a) $\varepsilon^{\mathrm{E}} = 0$ indicates that mixture constituents do not interact;
(b) $\varepsilon^{\mathrm{E}} < 0$ indicates that mixture constituents interact so as to reduce the total number of effective dipoles (this suggests that the constituents of the mixtures may form multimers regarding to less effective dipoles); and
(c) $\varepsilon^{\mathrm{E}} > 0$ indicates that the constituents of the binary mixture interact in such a way that the effective number of dipoles increases.

The evaluated ε^{E} values of the binary mixtures are listed in table 1 and plotted in figure 3. The non-zero ε^{E} values over entire mixture concentration range confirm the formation of heterogeneous structures in these binary mixtures. From the comparative study of ε^{E} values, it seems that the heterogeneous interaction strength of mono alkyl ethers of ethylene glycol vary with the nature of cosolvent and these interactions are considerably affected by the size of the ethers molecule of the homologous series. First, we consider the interactions of ether molecules with the hydroxyl group(s) containing solvents. The negative ε^{E} value of hydroxyl group(s) containing solvents

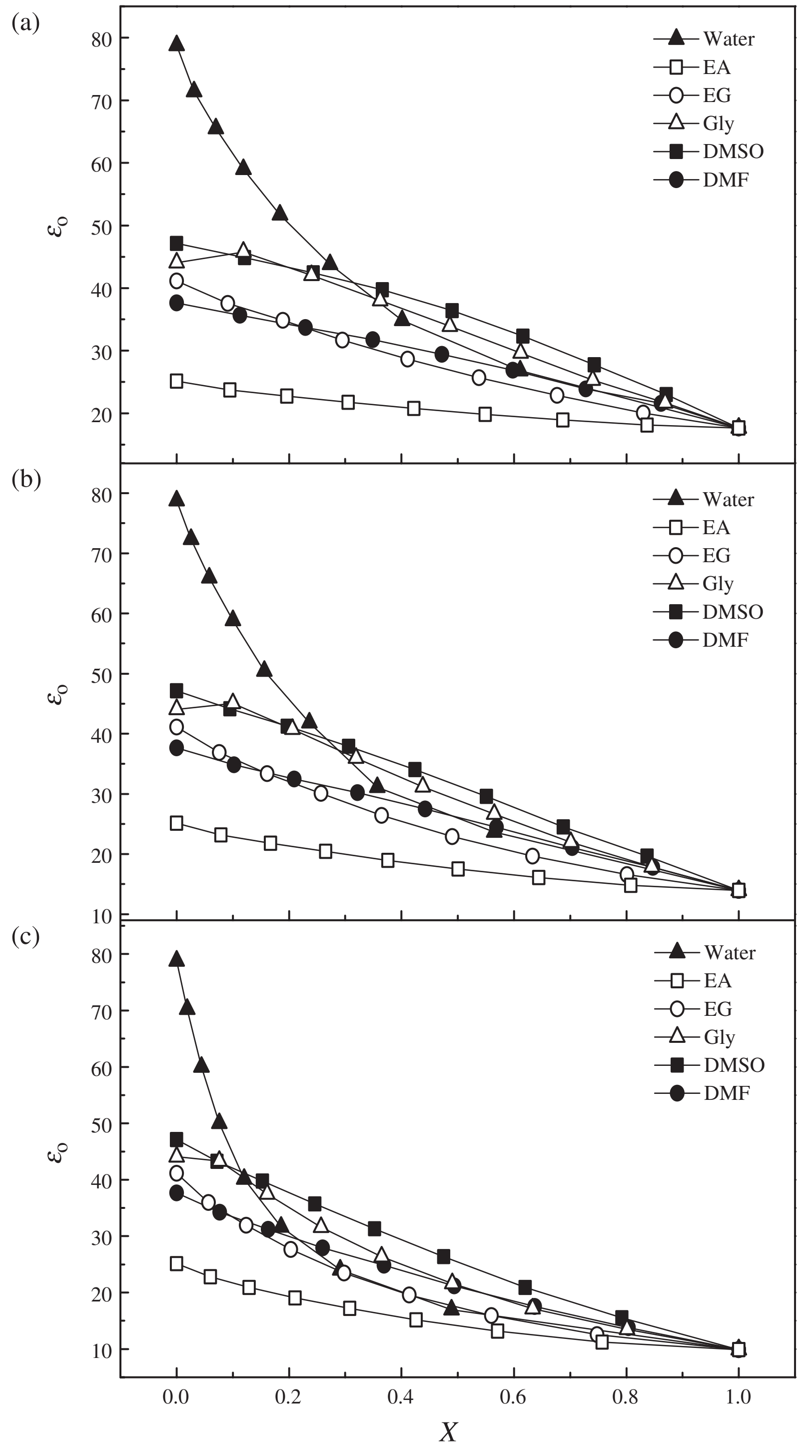

Figure 1. Plots of ε_o for various binary mixtures against mole fraction of mono alkyl ethers of ethylene glycol X at 25°C. (a) Binary mixtures of mono methyl ether of ethylene glycol, (b) binary mixtures of mono ethyl ether of ethylene glycol and (c) binary mixtures of mono butyl ether of ethylene glycol.

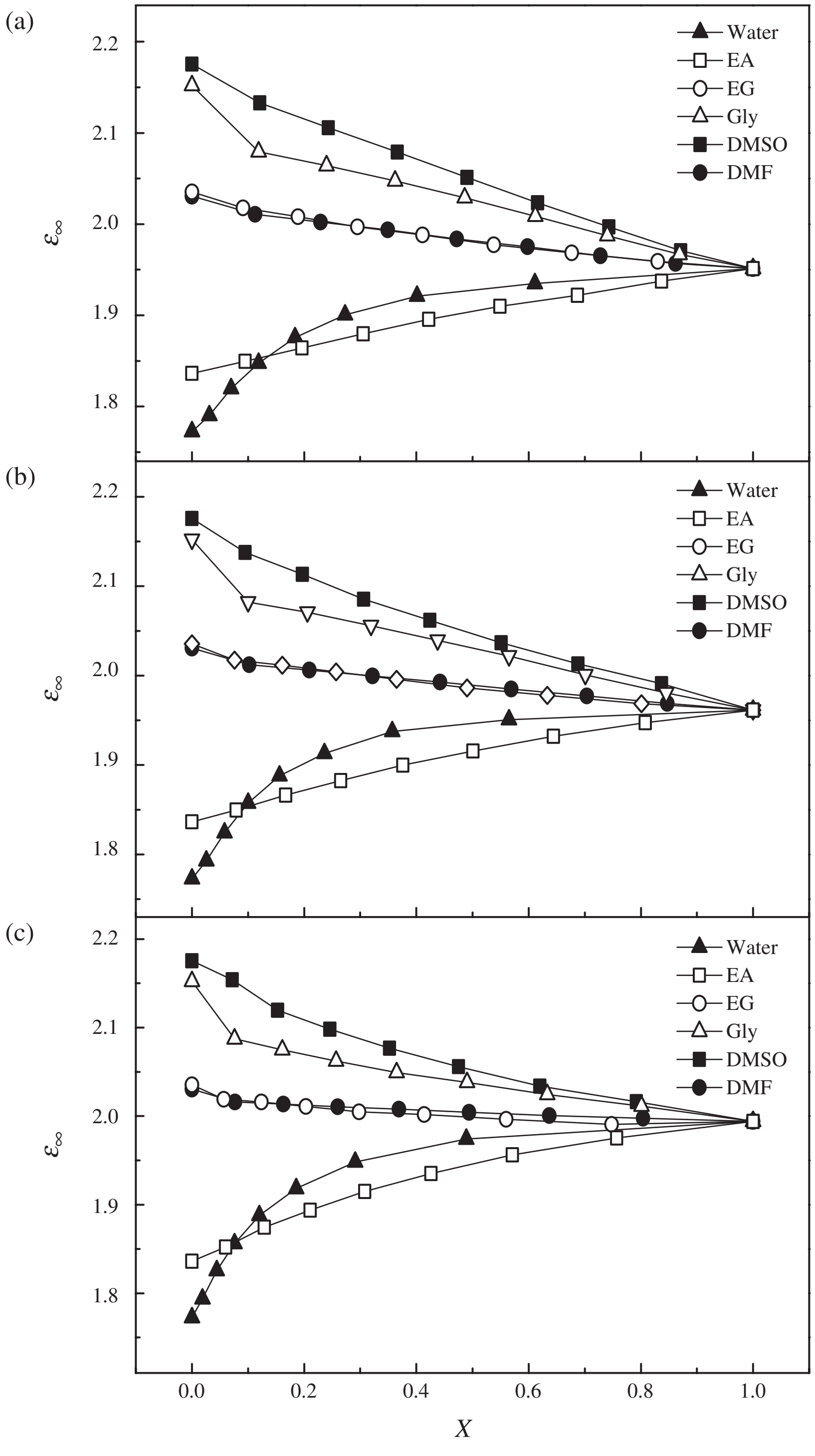

Figure 2. Plots of ε_∞ for various binary mixtures against mole fraction of mono alkyl ethers of ethylene glycol X at 25°C. (a) Binary mixtures of mono methyl ether of ethylene glycol, (b) binary mixtures of mono ethyl ether of ethylene glycol and (c) binary mixtures of mono butyl ether of ethylene glycol.

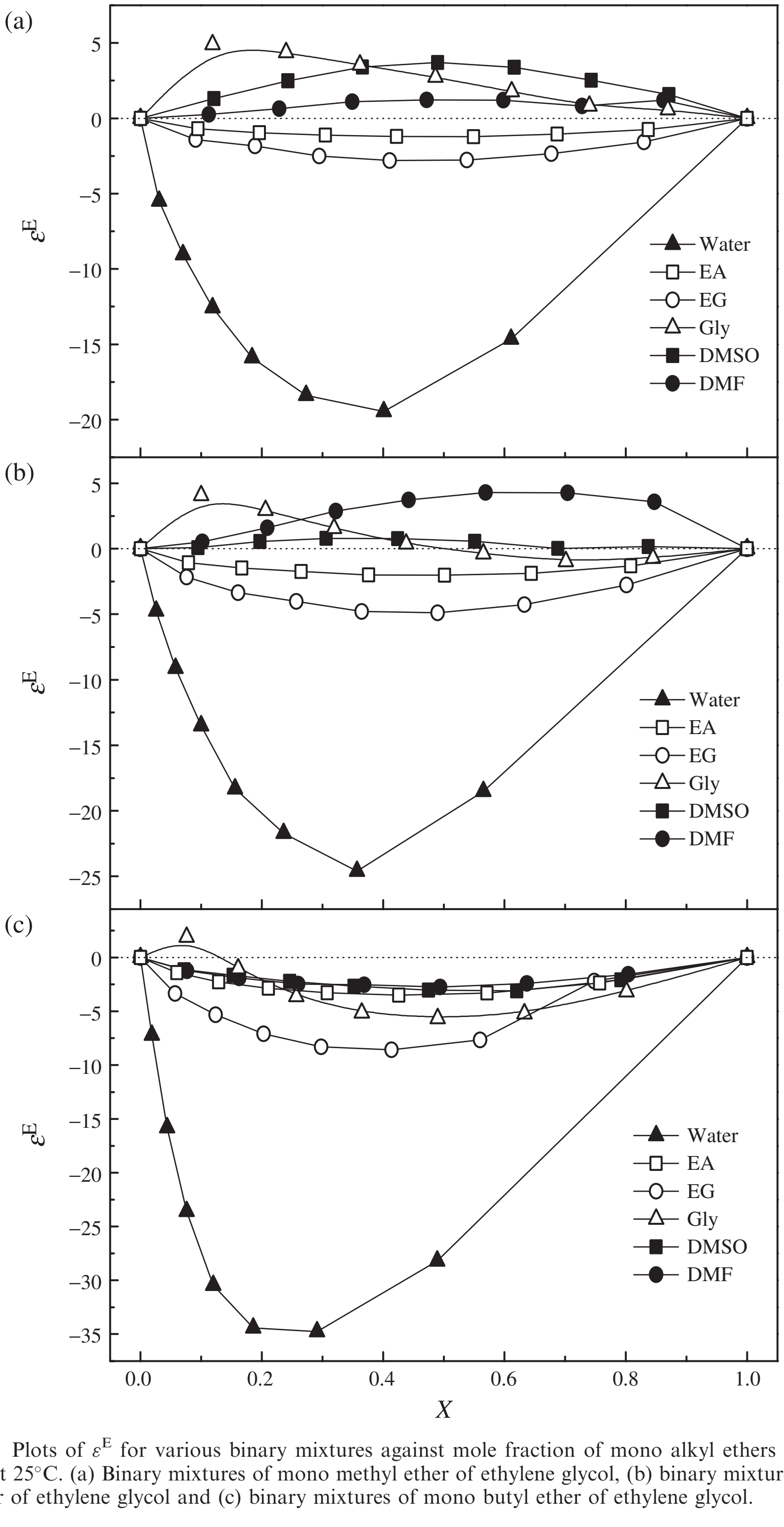

Figure 3. Plots of ε^{E} for various binary mixtures against mole fraction of mono alkyl ethers of ethylene glycol X at 25°C. (a) Binary mixtures of mono methyl ether of ethylene glycol, (b) binary mixtures of mono ethyl ether of ethylene glycol and (c) binary mixtures of mono butyl ether of ethylene glycol.

confirm that the heterogeneous interactions of water, EA (monohydric alcohol) and EG (dihydric alcohol) with ether molecules reduces the effective number of dipoles in the mixtures. Further, the decrease in total number of effective dipoles is more pronounced from mono methyl to mono butyl ether, which is evidenced by increase in the magnitude of negative ε^E values of these mixtures. The molecular interactions of monoalkyl ethers of ethylene glycol with water, EA and EG results the formation of the heterogeneous cooperative domains through $O{-}H\cdots O$ complexation and simultaneously alters the homogeneous cooperative domains of these molecules with a change in the effective number of dipoles in the mixture. Further, in case of water–ether mixtures, the molecular, concentration of ethers corresponding to maximum negative value of ε^E decreases from mono methyl to mono butyl ether (figure 3), which confirms that heterogeneous interaction of the homologous series are molecular size dependent. The positive ε^E values for glycerol–mono methyl ether over entire concentration range indicate the formation of heterogeneous interaction with increase in the total number of dipoles, which is higher in glycerol-rich region. But observed ε^E values changes from positive to negative at concentration $X \approx 0.50$ in case of glycerol–mono ethyl ether mixtures, and $X \approx 0.12$ for glycerol–mono butyl ether mixtures. These results indicate that in glycerol-rich region, the total number of dipoles increases due to heterogeneous interactions but in mono ethyl and mono butyl-rich regions, it seems that there is an opposite alignment of the dipoles of the two interacting polar solvent molecules, which results in the negative ε^E values. The comparative observations on hydroxyl group(s) containing cosolvents binary mixture with mono alkyl ethers confirms that the three-dimensional self-associated homogeneous structure of glycerol (trihydric alcohol) molecules influences more when compared to the homogeneous structures of ethyl alcohol (monohydric alcohol) and of ethylene glycol (dihydric alcohol) in presence of mono alkyl ethers molecules. This is expected because of the presence of three hydroxyl sites in glycerol molecules, which results in the three-dimensional $O{-}H\cdots O$ heterogeneous cooperative domains as compared to the formation of linear polymeric chain type structures of ethyl alcohol and ethylene glycol with ether molecules.

The ε^E values of mono methyl and mono ethyl ethers with DMSO and DMF mixtures were found positive at all the concentrations (figure 3), which confirms that the net number of dipoles increases due to heterogeneous interactions. Further, the comparative value of ε^E suggest that the increase in effective number of dipoles due to heterogeneous interactions is higher in DMSO–mono methyl ether mixture as compared to the DMSO–mono ethyl ether mixture. But opposite trends in ε^E values were observed in DMF–mono methyl ether and DMF–mono ethyl ether mixtures as compared to their mixtures with DMSO. In case of binary mixtures of mono butyl ether with DMSO and DMF, the negative ε^E values confirm the decrease in number of dipoles due to heterogeneous molecular interactions. From these observations it can be concluded that the size of alkoxyl group of the mono alkyl ethers of ethylene glycol also affects the nature of heterogeneous molecular interactions with non-hydroxyl group containing polar solvents and the interaction behaviour is also influenced by concentration variation of the mixture constituents.

Corradini *et al.* [31] working on associating behaviour of mixed liquids concluded that the maximum magnitude of ε^E values is corresponding to the stoichiometric ratio of a stable adduct complex formation between the mixture constituents. This stoichiometric ratio is estimated for the studied mixtures from the ε^E values

Table 2. Values of dipole moment μ (in Debye) for mono alkyl ethers of ethylene glycol and other polar liquids in dilute solutions of non-polar solvents.

Stoichiometric ratio (ether to cosolvent)		
MM–W	ME–W	MB–W
1 : 1.5	1 : 1.8	1 : 2.5
MM–EA	ME–EA	MB–EA
1 : 1	1 : 1.2	1 : 1.3
MM–EG	ME–EG	MB–EG
1 : 1.3	1 : 1.4	1 : 1.4
MM–Gly	ME–Gly	MB–Gly
1 : 7.3*	1 : 9.0*	1 : 11.5*
–	1 : 0.4	1 : 1
MM–DMSO	ME–DMSO	MB–DMSO
1 : 1*	1 : 1.8*	1 : 0.8
MM–DMF	ME–DMF	MB–DMF
1 : 1*	1 : 0.7*	1 : 1
Dipole moment μ (Debye)		
MM[a]	ME[a]	MB[a]
2.23	2.31	2.27
EA[b]	EG[c]	Gly[d]
1.84	2.38	2.86
W[e]	DMSO[d]	DMF[d]
1.82	4.34	4.09

* Complex formation with increase in effective number of dipoles.
Values of μ Refs: [a][26], [b][28], [c][34], [d][29] and [e][32].

and recorded in table 2. Table 2 shows that the stoichiometric ratio corresponding to maximum interactions (i.e. for the formation of stable adduct) decreases with increasing molecular size of mono alkyl ethers in ethers–water and ethers–EA mixtures. This ratio remains almost same in case of ethers–EG mixtures, which may be due to the gauche conformation of EG molecules. In case of ethers–Gly mixtures, the observed stoichiometric ratio for maximum interactions decreases with increase in molecular size of mono alkyl ethers for the complex formation with increase in effective number of dipoles and also for the complex formation with decrease in effective number of dipoles. This is interesting and may be due to the presence of secondary –OH group in Gly structure. Further, in case of ethers–DMSO and ethers–DMF, the stoichiometric ratio corresponding to maximum interactions varies anomalously with increase in molecular size of ether molecules. Further, the magnitude of ε^E values is direct evidence of the H-bond connectivities. The higher magnitude of ε^E is corresponding to stronger H-bond heterogeneous connectivities between the constituents of the mixture [31]. The comparative magnitudes of ε^E (figure 3) confirm that the H-bond heterogeneous connectivities between the studied mixtures constituents significantly vary with the size of mono alkyl ethers and also with the change in mixture cosolvent. In these binary mixtures, the H-bond connectivities between ether and water molecules were found to be comparatively very strong.

3.4. *Kirkwood correlation factor*

The Kirkwood correlation factor g is also a parameter, which gives the information regarding the formation of multimers and ordering of dipoles in pure liquid. For pure liquid g is given by the expression [32]

$$\frac{4\pi Nd}{9kTM} g\mu^2 = \frac{(\varepsilon_o - \varepsilon_\infty)(2\varepsilon_o + \varepsilon_\infty)}{\varepsilon_o(\varepsilon_\infty + 2)^2} \tag{2}$$

where μ is the dipole moment, d is the density at temperature T, M is the molecular weight, k is the Boltzmann constant and N is the Avagadro's number. In associating liquids, there is a significant departure of g value from unity which is a measure of those short-range intermolecular forces, such as intermolecular hydrogen bonding, that lead to specific dipole–dipole reorientation. When the molecules tend to orient themselves with parallel dipole moments the g value will be greater than unity. When the molecules prefer an ordering with antiparallel dipoles, g value will be smaller than unity.

For the determination of g value from experimental data, we used the μ values of these molecules recorded in table 2 [26,28,29,33,34]. Table 3 shows that the observed g_f values of DMSO and DMF are 0.97 and 1.02 respectively, which are very close to unity and suggest the non-self associative behaviour of these molecules. But the g values of water, ethyl alcohol, ethylene glycol and glycerol are 2.90, 2.77, 2.37 and 2.25, respectively, confirms the existence of H-bonded multimers with parallel dipole orientation in their pure liquid state. Regarding the self-association behaviour of water, EA, EG and Gly molecules, we consider the concluding remarks on these molecules established by microwave dielectric relaxation measurements at 25°C. The dielectric relaxation studies [5,13,22,35–37] of water molecules confirmed that a self-associated cluster of five to six water molecules contributed to its molecular dynamics. The evaluated relaxation time $\tau_o \approx 8.3\,\text{ps}$ for water was assigned to the reorientation of the self-associated water cluster. In case of EA and EG, their τ_o values are 146.2 and 92.4 ps, respectively [7,8,38,39] established the fact that there is switch-over type molecular orientation in the long-chain self-associated polymeric structures due to breaking and making of H-bonds. The switch-over type dynamics in self-associated EA structures takes more time due to higher self-association strength of EA molecules as compared to EG molecules. Comparatively very large τ_o value of glycerol molecules ($\tau_o = 1247$ ps) [38] is due to the formation of its three-dimensional self-association structures, which results in the slow mode of large cluster dynamics. The g values of mono methyl, mono ethyl and mono butyl ether are also greater than unity i.e. 1.68, 1.45 and 1.36, respectively, which confirms the existence of intermolecular association with parallel dipole orientation in their pure liquid state. The self-association strength of the molecules of the homologous series of mono alkyl ethers in pure liquid state reduces with the increase in molecular size i.e. increase in size of the alkoxyl group. On mixing of these molecules with the other self-associating molecules, significant variation occurs in their local structures due to heterogeneous interactions. Further, such structures also change with the variation in the concentration of the mixture constituents. To confirm the structure variations due to heterogeneous interactions, generally the Kirkwood correlation factor of the mixture is evaluated.

In binary mixtures of polar solvents, the effective averaged angular correlation g^{eff} between heterogeneous molecules can be evaluated by using the modified Kirkwood equation for the mixture [40,41]

$$\frac{4\pi N}{9kT}\left(\frac{\mu_A^2 d_A}{M_A}\phi_A + \frac{\mu_B^2 d_B}{M_B}\phi_B\right)g^{\text{eff}} = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} + \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2} \tag{3}$$

Table 3. Values of effective averaged Kirkwood correlation factor g^{eff} and corrective Kirkwood correlation factor g_{f} for various binary mixtures at different volume fraction ϕ of mono alkyl ethers of ethylene glycol at 25°C.

ϕ	g^{eff}	g_{f}	g^{eff}	g_{f}	g^{eff}	g_{f}
	MM–W		ME–W		MB–W	
0.000	2.90	1.00	2.90	1.00	2.90	1.00
0.125	2.84	1.00	2.89	1.02	2.84	0.99
0.250	2.82	1.01	2.86	1.03	2.67	0.95
0.375	2.77	1.03	2.80	1.04	2.48	0.91
0.500	2.68	1.03	2.68	1.04	2.27	0.86
0.625	2.55	1.04	2.52	1.04	2.08	0.83
0.750	2.33	1.02	2.18	0.98	1.91	0.83
0.875	2.11	1.03	2.00	1.04	1.72	0.87
1.000	1.68	1.00	1.45	1.00	1.36	1.00
	MM–EA		ME–EA		MB–EA	
0.000	2.77	1.00	2.77	1.00	2.77	1.00
0.125	2.56	0.98	2.54	0.97	2.58	0.98
0.250	2.41	0.97	2.38	0.97	2.43	0.97
0.375	2.26	0.97	2.22	0.97	2.28	0.97
0.500	2.12	0.96	2.04	0.96	2.12	0.96
0.625	1.99	0.96	1.87	0.95	1.92	0.95
0.750	1.87	0.96	1.70	0.95	1.71	0.94
0.875	1.75	0.97	1.55	0.95	1.50	0.93
1.000	1.68	1.00	1.45	1.00	1.36	1.00
	MM–EG		ME–EG		MB–EG	
0.000	2.37	1.00	2.37	1.00	2.37	1.00
0.125	2.29	0.99	2.27	0.98	2.26	0.97
0.250	2.24	1.00	2.19	0.98	2.18	0.96
0.375	2.16	0.99	2.11	0.98	2.07	0.95
0.500	2.08	0.99	1.98	0.97	1.94	0.93
0.625	1.99	0.98	1.86	0.96	1.80	0.92
0.750	1.89	0.98	1.72	0.96	1.66	0.91
0.875	1.77	0.98	1.58	0.96	1.49	0.91
1.000	1.68	1.00	1.45	1.00	1.36	1.00
	MM–Gly		ME–Gly		MB–Gly	
0.000	2.25	1.00	2.25	1.00	2.25	1.00
0.125	2.56	1.16	2.54	1.16	2.48	1.12
0.250	2.51	1.16	2.46	1.16	2.35	1.09
0.375	2.42	1.15	2.35	1.14	2.19	1.05
0.500	2.33	1.14	2.21	1.12	2.04	1.02
0.625	2.19	1.11	2.06	1.09	1.89	0.99
0.750	2.03	1.08	1.87	1.06	1.71	0.96
0.875	1.89	1.06	1.68	1.03	1.57	0.97
1.000	1.68	1.00	1.45	1.00	1.36	1.00
	MM– DMSO		ME–DMSO		MB–DMSO	
0.000	0.97	1.00	0.97	1.00	0.97	1.00
0.125	1.05	1.05	1.03	1.04	1.01	1.03
0.250	1.12	1.09	1.09	1.09	1.07	1.08
0.375	1.20	1.14	1.16	1.13	1.12	1.11
0.500	1.29	1.16	1.22	1.16	1.17	1.14
0.625	1.37	1.17	1.28	1.17	1.21	1.16
0.750	1.45	1.15	1.32	1.14	1.24	1.14
0.875	1.56	1.11	1.40	1.12	1.29	1.11
1.000	1.68	1.00	1.45	1.00	1.36	1.00
	MM–DMF		ME–DMF		MB–DMF	
0.000	1.02	1.00	1.02	1.00	1.02	1.00
0.125	1.07	1.02	1.04	1.01	1.04	1.01

(*Continued*)

Table 3. Continued.

ϕ	g^{eff}	g_{f}	g^{eff}	g_{f}	g^{eff}	g_{f}
0.250	1.12	1.04	1.09	1.03	1.06	1.03
0.375	1.19	1.07	1.14	1.06	1.09	1.04
0.500	1.26	1.08	1.19	1.08	1.13	1.06
0.625	1.33	1.08	1.25	1.09	1.16	1.06
0.750	1.41	1.07	1.30	1.08	1.20	1.06
0.875	1.58	1.09	1.38	1.06	1.26	1.04
1.000	1.68	1.00	1.45	1.00	1.36	1.00

where μ, d, M and ϕ are the dipole moment, density, molecular weight and volume fractions of the mixture constituents A and B, respectively. The evaluated g^{eff} values of the studied mixtures are recorded in table 3. These values change from the Kirkwood correlation factor value of one pure liquid to that of the second liquid.

The g^{eff} values of the studied binary mixtures with volume fraction of mono alkyl ethers ϕ are plotted in figure 4. From these plots it is found that the g^{eff} values of mono alkyl ethers of ethylene glycol with the binary mixtures of EA and EG vary non-linearly from the g value of one solvent to that of the second cosolvent. But in case of water mixtures with mono alkyl ethers of ethylene glycol the deviation of g^{eff} from linearity is high. This suggests the change in dipolar alignment due to heterogeneous interactions. The g^{eff} values of glycerol–ethers mixtures initially increases as compared to the g value of pure glycerol in glycerol-rich region and finally approaches to the g value of corresponding ether molecules. This finding is interesting and suggests that the small amount of ether molecules in glycerol helps in the parallel alignment of the large number of glycerol dipoles in the mixtures. The linear behaviour of g values against ether concentration X (figure 4) in the binary mixtures of DMSO–ethers and DMF–ethers indicates that the alignments of ether molecules dipoles due to heterogeneous interaction are unaffected in these non-hydroxyl group containing cosolvent mixtures. The dipole moment and microwave dielectric relaxation studies [28,29] of binary mixtures of mono alkyl ethers of ethylene glycol with EA, Gly, DMSO and DMF in dilute solutions of dioxane also established the fact that in most of the mixtures, heterogeneous interaction produces a field such that it facilitates the molecular dynamics. The dipole moment study of ethers–Gly mixtures in non-polar solvent [29] has confirmed that the interactions of the ether molecules of the homologous series with Gly molecules at all the concentrations greatly affects the Gly homogeneous structures, which is analogous to the inferences drawn from the g^{eff} values of pure liquid binary mixtures. Although, it is difficult to correlate the behaviour of heterogeneous molecular structures present in dilute solutions of non-polar solvent and in pure liquid state because on dilution of the binary mixture by non-polar solvent changes the heterogeneous structures and keeps them in quasi-isolated state.

If it is assumed that the Kirkwood correlation factor for molecules of liquid A and B in the mixture contribute to the g^{eff} values proportional to their pure liquid values g_{A} and g_{B}, respectively, then under this assumption the Kirkwood equation for the mixture can be written as [12,42]

$$\frac{4\pi N}{9kT}\left(\frac{\mu_{\text{A}}^2 d_{\text{A}} g_{\text{A}}}{M_{\text{A}}}\phi_{\text{A}} + \frac{\mu_{\text{B}}^2 d_{\text{B}} g_{\text{B}}}{M_{\text{B}}}\phi_{\text{B}}\right) g_{\text{f}} = \frac{(\varepsilon_{\text{om}} - \varepsilon_{\infty\text{m}})(2\varepsilon_{\text{om}} + \varepsilon_{\infty\text{m}})}{\varepsilon_{\text{om}}(\varepsilon_{\infty\text{m}} + 2)^2}, \tag{4}$$

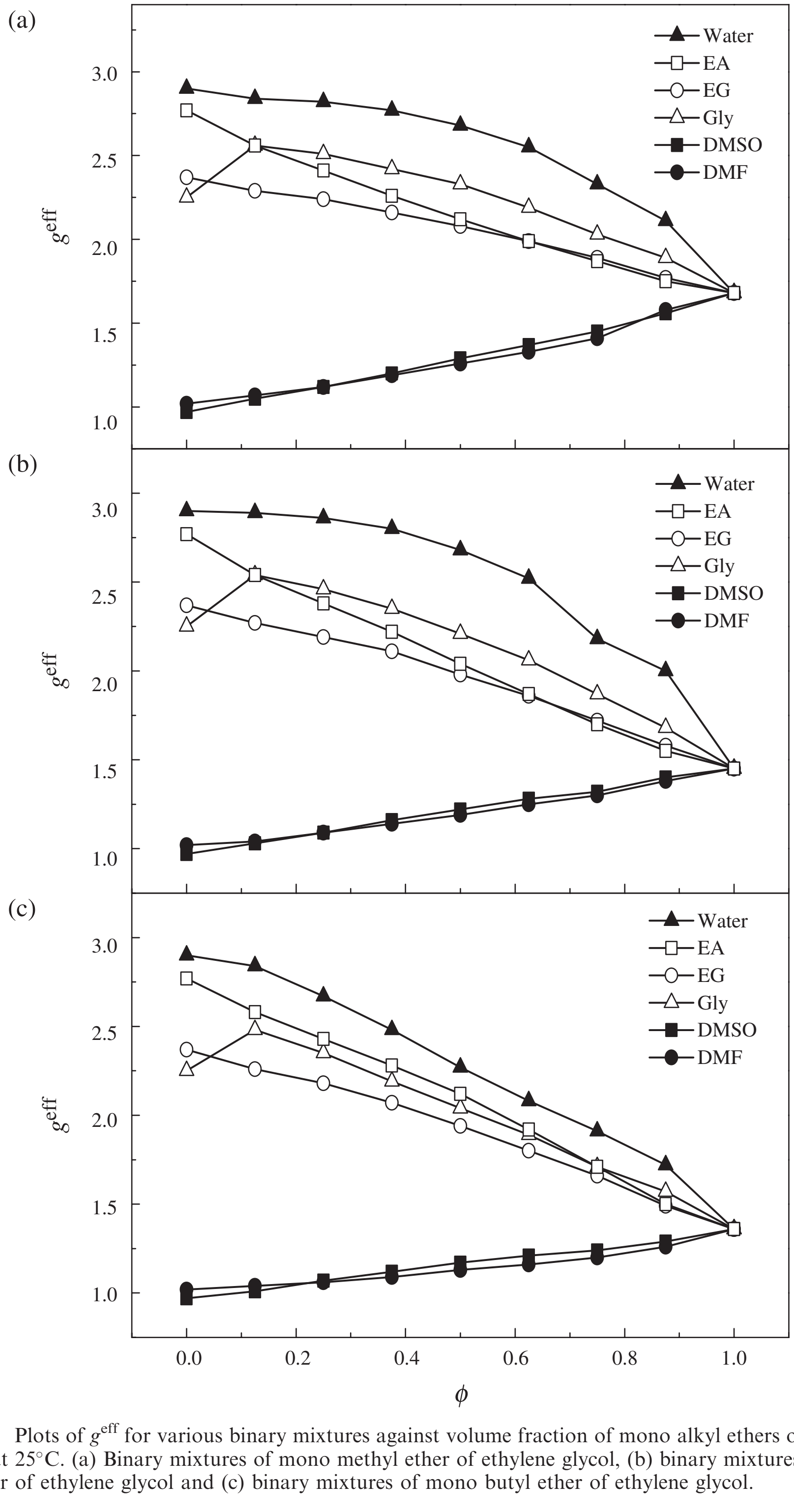

Figure 4. Plots of g^{eff} for various binary mixtures against volume fraction of mono alkyl ethers of ethylene glycol ϕ at 25°C. (a) Binary mixtures of mono methyl ether of ethylene glycol, (b) binary mixtures of mono ethyl ether of ethylene glycol and (c) binary mixtures of mono butyl ether of ethylene glycol.

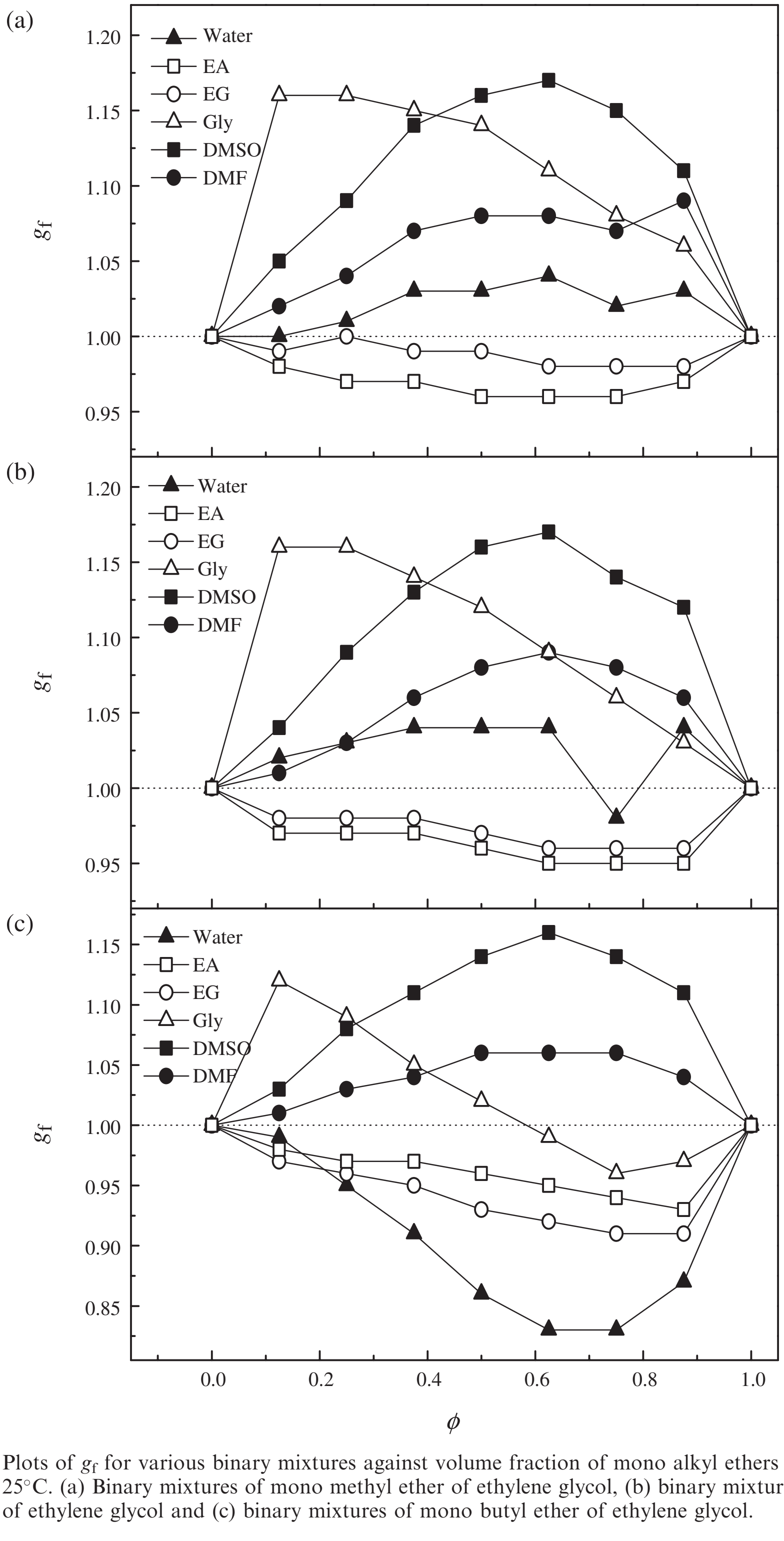

Figure 5. Plots of g_f for various binary mixtures against volume fraction of mono alkyl ethers of ethylene glycol ϕ at 25°C. (a) Binary mixtures of mono methyl ether of ethylene glycol, (b) binary mixtures of mono ethyl ether of ethylene glycol and (c) binary mixtures of mono butyl ether of ethylene glycol.

where g_f is the corrective Kirkwood correlation factor for a binary mixture. The evaluated values of g_f for the studied mixtures are given in table 3 and these values are also plotted in figure 5. The deviation in g_f values from unity supports the formation of heterogeneous structures by the participation of both the mixture constituents in the interactions. Further, the anomalous behaviour of g_f values confirm that the contribution of the mixture constituents in the formation of heterogeneous interactions changes with the variation in the concentration of the mixture constituents and also with the increase in the molecular size of the mono alkyl ethers of ethylene glycol.

4. Conclusions

This article reports the concentration dependent high accuracy dielectric data of the binary mixtures of homologous series of mono alkyl ethers of ethylene glycol with six different characteristic polar solvents. The reported high accuracy dielectric data can be applied to formulate more accurate dielectric models of the solvent–cosolvent mixtures of different associating molecules under varying conditions of composition. The type of heterogeneous interactions with various solvents, effects of constituents concentration, the number of hydroxyl groups and the size of the alkoxyl group of the mono alkyl ethers on the formation of heterogeneous interaction were confirmed. The major conclusion of this investigation is that, judging from the binary mixture dielectric data and the interpretation based on dielectric parameters presented herein on the dipolar alignment, the formation of concentration dependent homogeneous and heterogeneous structures can also be applied to estimate the interaction behaviour of similar type of homologous series molecules with the polar cosolvent used in the present study.

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