Characterization of Heterogeneous Interaction Behaviour in Ternary Mixtures by Dielectric Analysis: The H-Bonded Binary Polar Mixture in Non-Polar Solvent

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Received January 31, 2006

The heterogeneous association behaviour of various concentration binary mixtures of mono alkyl ethers of ethylene glycol with ethyl alcohol were investigated by dielectric measurement in benzene solutions over the entire concentration range at 25 °C. The values of static dielectric constant ε_o of the mixtures were measured at 1 MHz using a four terminal dielectric liquid test fixture and precision LCR meter. The high frequency limiting dielectric constant ε_∞ values were determined by measurement of refractive index n_D ($\varepsilon_\infty = n_D^2$). The measured values of ε_o and ε_∞ were used to evaluate the values of excess dielectric constant ε^E, effective Kirkwood correlation factor g^{eff} and corrective correlation factor g_f of the binary polar mixtures to obtain qualitative and quantitative information about the H-bond complex formation. The non-linear behaviour of the observed ε_o values of the polar molecules and their mixtures in benzene solvent confirms the variation in the associated structures with change in polar mixture constituents concentration and also by dilution in non-polar solvents. Appearance of the maximum in ε^E values at different concentration of the polar mixtures suggest the formation of stable adduct complex, which depends on the molecular size of the mono alkyl ethers of ethylene glycol. Further, the observed $\varepsilon^E < 0$ also confirms the heterogeneous H-bond complex formation reduces the effective number of dipoles in these polar binary mixtures. In benzene solutions these polar molecules shows the maximum reduce in effective number of dipoles at 50 percent dilutions. But ethyl alcohol rich binary polar mixtures in benzene solvent show the maximum reduce in effective number of dipoles in benzene rich solutions.

Key Words : Heterogeneous interaction, Dielectric constant, Kirkwood correlation factor, Excess dielectric parameters

Introduction

The confirmation of H-bond complex formation between associating polar molecules and the change in their homogeneous structures with varying environmental conditions is one of the most interesting and challenging subject in chemical physics and physical chemistry. In last two decades, several investigators[1-17] have extensively investigated the heterogeneous interaction properties of the binary mixtures of hydrogen bonded molecules by dielectric measurements. In regards to H-bonded liquids, the molecules of the homologous series of mono alkyl ethers of ethylene glycol ($ROCH_2CH_2OH$) exist with intra and inter molecular hydrogen bonding in dynamic equilibrium in pure liquids state.[18] The molecules of ethyl alcohol (C_2H_5OH) also exist in H-bonded linear polymeric chain structure with switch-over type mechanism due to breaking and making of H-bonds.[19,20] The presence of H-bond sites in mono alkyl ethers of ethylene glycol and ethyl alcohol, the binary mixtures of these molecules can give rise to different conformations, and these conformations may vary with change in the concentration of the mixture constituents. Further the H-bonded heterogeneous structures formed in a particular concentration binary mixture of these molecules can also vary by dilution in non-polar solvent.

The mono alkyl ethers of ethylene glycol and ethyl alcohol are extensively used as solvents. In view of this, it will be highly informative to explore the formation of heterogeneous structures in different concentration solvent-cosolvent binary mixture of these molecules by precision dielectric measurements. In order to get insight into the formation of heterogeneous interaction and the elongation of the H-bonded structures in non-polar solvent, the dielectric behaviour of the binary mixtures of mono alkyl ethers of ethylene glycol and ethyl alcohol were investigated in benzene solutions over the entire concentration range at 25 °C.

Experimental Section

Materials. Grade reagent of mono methyl (MM), mono ethyl (ME) and mono butyl (MB) ether of ethylene glycol and ethyl alcohol (EA) were purchased from E. Merck, India. Benzene of spectroscopic grade obtained from BDH, India, was used as non-polar solvent. The binary mixtures of mono alkyl ethers of ethylene glycol and ethyl alcohol were prepared at 20, 40, 60 and 80 volume percent of the mixture constituents at room temperature, and simultaneously by weight measurements the mole fractions of the mixture constituents were determined. Using the polar binary mix-

ture as one system and non-polar solvent benzene as other system, the different concentration ternary mixtures were prepared over the entire concentration range by mixing them at seven different volume percent. By weight measurements the mole fraction of benzene X_B (X_3) in ternary mixture was determined using the relation

$$X_3 = \frac{m_3/M_3}{(m_1/M_1)+(m_2/M_2)+(m_3/M_3)} = \frac{m_3/M_3}{(m_{12}/M_{12})+(m_3/M_3)} \quad (1)$$

where m_1, m_2, m_3, and M_1, M_2 and M_3 are the weights and molecular weights of mono alkyl ether of ethylene glycol, ethyl alcohol and benzene respectively. m_{12} and M_{12} are the weight and molecular weight of polar binary mixture The mole fraction of the binary polar mixture is $X_{12} = 1-X_3$.

Measurements. The values of static dielectric constant ε_o of the studied polar molecules and their binary and ternary mixtures were determined by using 'capacitive measurement method' at 1MHz. Agilent 4284A Precision LCR Meter and a four terminal cell Agilent 16452A Liquid Test Fixture were used for the determination of the accurate ε_o values of these mixtures. The capacitances of the Liquid Dielectric Test Fixture without and with samples were measured by using it for a short compensation. The Test Fixture correction coefficient was also considered to cancel the stray capacitance during the determination of the ε_o values. 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 wavelength of sodium light. All measurements were made at 25 °C and the temperature was controlled thermostatically.

Data Analysis

Excess dielectric constant. The excess dielectric constant ε^E for binary mixture is defined as[12,14,17]

$$\varepsilon^E = (\varepsilon_o - \varepsilon_\infty)_m - [(\varepsilon_o - \varepsilon_\infty)_1 X_1 + (\varepsilon_o - \varepsilon_\infty)_2 X_2] \quad (2)$$

where X is the mole fraction and subscripts m, 1 and 2 represent the binary mixture and components 1 and 2 of the binary mixture, respectively.

The excess dielectric constant ε^E for ternary mixture is determined by the relation

$$\varepsilon^E = (\varepsilon_o - \varepsilon_\infty)_m - [(\varepsilon_o - \varepsilon_\infty)_{12} X_{12} + (\varepsilon_o - \varepsilon_\infty)_3 X_3] \quad (3)$$

where subscripts m, 12 and 3 represent the ternary mixture and components of the ternary mixture *i.e.* binary mixture (12) and benzene (3) solvent, respectively. The excess dielectric constant provides qualitative information as follows:

(i) $\varepsilon^E = 0$ indicates that mixture constituents do not interact;

(ii) $\varepsilon^E < 0$ 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

(iii) $\varepsilon^E > 0$ indicates that the constituents of the binary mixture interact in such a way that the effective number of dipoles increases.

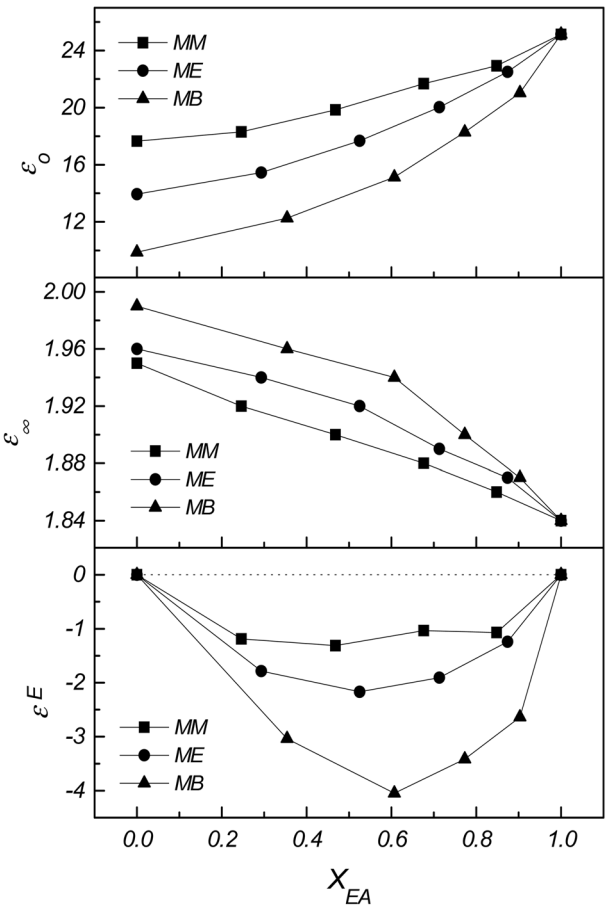

Figure 1. Plots of ε_o, ε_∞ and ε^E versus X_{EA} of the binary mixtures of mono alkyl ethers of ethylene glycol with ethyl alcohol.

The evaluated ε^E values of the polar binary mixture are plotted against mole fraction of ethyl alcohol X_{EA} in Figure 1. The ε^E values of polar molecules and their binary mixtures in benzene solvent were plotted against mole fraction of benzene in Figure 4.

Kirkwood correlation factor. The Kirkwood correlation factor[21] g is also a parameter, which gives the information regarding the formation of multimers and ordering of dipoles in pure liquid. In a pure liquid g is given by the expression

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

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. For the evaluation of g value from experimental data, we used the μ values of these molecules[16,22] in inert solvent *i.e.* carbon tetrachloride.

In binary mixtures of polar solvents, the effective averaged angular Kirkwood correlation factor g^{eff} between heterogeneous molecules were evaluated by using the modified Kirkwood equation[23,24] for the mixture

$$\frac{4\pi N}{9kT}\left(\frac{\mu_1^2 d_1}{M_1}\phi_1+\frac{\mu_2^2 d_2}{M_2}\phi_2\right)g^{eff}=\frac{(\varepsilon_{om}-\varepsilon_{\infty m})(2\varepsilon_{om}+\varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m}+2)^2} \quad (5)$$

where ϕ_1 and ϕ_2 are the volume fractions of liquids 1 and 2 respectively.

If it is assumed that the Kirkwood correlation factor for the molecules of liquid 1 and 2 *i.e.* g_1 and g_2 in the mixture contribute to the g^{eff} values proportional to their pure –liquid values, then under this assumption the Kirkwood equation[14] for the binary mixture can be written as

$$\frac{4\pi N}{9kT}\left(\frac{\mu_1^2 d_1 g_1}{M_1}\phi_1+\frac{\mu_2^2 d_2 g_2}{M_2}\phi_2\right)g_f=\frac{(\varepsilon_{om}-\varepsilon_{\infty m})(2\varepsilon_{om}+\varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m}+2)^2} \quad (6)$$

where g_f is the corrective Kirkwood correlation factor for a binary mixture.

Discussion

Binary mixtures of polar liquids.

H-bonds in polar liquids: The Kirkwood correlation values greater than unity (Table 1) of mono alkyl ethers of ethylene glycol and ethyl alcohol in their pure liquid state confirms that these molecules exist in hydrogen bonded linear structures with parallel dipole alignment in dynamical equilibrium. The ethyl alcohol molecules have switch-over type mechanism in their linear H-bonded polymeric structure. In this mechanism, due to breaking of O–H ···O bond the EA molecule rotate 180° and make the new O–H ···O bond and the switch-over occurs cooperatively all along the multimer chain.[19,20] The g values of mono methyl, mono ethyl and mono butyl ethers are 1.68, 1.45 and 1.36 respectively, which confirms the decrease in the H-bond formation strength with increase in the size of the molecules of this homologous series. The g value of ethyl alcohol is 2.77, which shows the higher order H-bonded structure of ethylene glycol.

Table 1. Values of dipole moment μ (in Debye) and Kirkwood correlation factor for mono alkyl ethers of ethylene glycol and ethyl alcohol

Sample	μ (D)	g
Mono methyl (MM)[a]	2.23	1.68
Mono ethyl (ME)[a]	2.31	1.45
Mono butyl (MB)[a]	2.27	1.36
EA[b]	1.84	2.77

Values of μ [a][22] and [b][16]

Dielectric constant of binary mixtures. Table 2 shows the values of ε_o, ε_∞ and ε^E of the mono alkyl ethers-ethyl alcohol binary mixtures against the mole fraction of ethyl alcohol X_{EA}. The non-linear behaviour of ε_o and ε_∞ against X_{EA} (Figure 1) confirms that the structures of the molecules in binary mixture changes with the variation in mixture constituents concentration. The findings of non-zero ε^E suggest that the addition of EA in ethers acts as homogeneous structure breakers and simultaneously there is the formation of complexes between these molecules through H-bonds. The observed negative values of ε^E of ethers-ethyl alcohol mixtures also confirm that the effective number of dipoles reduces due to the formation of the heterogeneous species. Further, the increase in the magnitude of ε^E values with increase in the molecular size also confirms the more reduce in effective number of dipole from mono methyl to mono butyl ether with ethyl alcohol mixtures, which is due to the increase in H-bond connectivities between hetero molecules. Corradini *et al.*[25] has suggested that the minimum in ε^E values are corresponding to the stoichiometric ratio of stable adduct complexation. The MM–EA, ME–EA and MB–EA mixtures exhibit the minimum in ε^E values at $X_{EA} \approx 0.47$; $X_{EA} \approx 0.53$ and $X_{EA} \approx 0.61$, respectively, which is a reliable indication of the formation of maximum complexes at these concentration. This stoichiometric ratio of ethers to EA in MM–EA, ME–EA and MB–EA mixtures are 1 : 1, 1 : 1.2 and 1 : 1.3 respectively, and its value decreases with increase in molecular size of the mono alkyl ether molecules. Higher the magnitude of ε^E indicates the strengthening of H-bond connectivities, which is higher for MB–EA system, *i.e.* strength of heterogeneous H-bond connectivity increases with increase in molecular size of mono alkyl ethers, which may be due to the decrease in self-association with the increase in molecular size of this homologous series.

Kirkwood correlation factor of binary mixtures: The value of effective Kirkwood correlation factor g^{eff} of polar binary mixtures at different volume fraction of ethyl alcohol ϕ_{EA} are recorded in Table 3. Figure 2 shows the plots of g^{eff} values against volume fraction of ethyl alcohol ϕ_{EA}. The g^{eff}

Table 2. 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 of ethyl alcohol X_{EA} at 25 °C

X_{EA}	ε_o	ε_∞	ε^E	X_{EA}	ε_o	ε_∞	ε^E	X_{EA}	ε_o	ε_∞	ε^E
MM - EA mixture				ME - EA mixture				MB - EA mixture			
0.000	17.65	1.95		0.000	13.94	1.96		0.000	9.87	1.99	
0.246	18.30	1.92	−1.19	0.293	15.45	1.94	−1.78	0.354	12.26	1.96	−3.04
0.468	19.84	1.90	−1.31	0.525	17.67	1.92	−2.17	0.607	15.13	1.94	−4.05
0.676	21.68	1.88	−1.03	0.713	20.03	1.89	−1.91	0.773	18.28	1.90	−3.41
0.848	22.93	1.86	−1.07	0.874	22.50	1.87	−1.24	0.903	21.03	1.87	−2.64
1.000	25.13	1.84		1.000	25.13	1.84		1.000	25.13	1.84	

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 of ethyl alcohol ϕ_{EA} at 25 °C

ϕ_{EA}	g^{eff}	g_f	g^{eff}	g_f	g^{eff}	g_f
	MM - EA mixture		ME - EA mixture		MB - EA mixture	
0.0	1.68	1.00	1.45	1.00	1.36	1.00
0.2	1.79	0.95	1.63	0.94	1.61	0.92
0.4	2.00	0.96	1.89	0.94	1.90	0.93
0.6	2.25	0.97	2.16	0.96	2.20	0.94
0.8	2.45	0.96	2.45	0.97	2.41	0.94
1.0	2.77	1.00	2.77	1.00	2.77	1.00

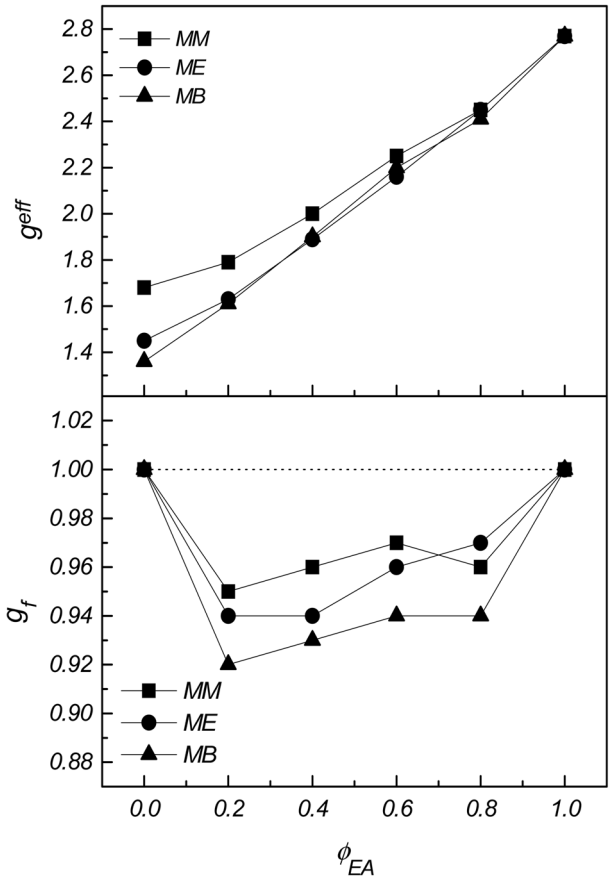

Figure 2. Plots of g^{eff} and g_f versus ϕ_{EA} of the binary mixtures of mono alkyl ethers of ethylene glycol with ethyl alcohol.

values increase from the g value of pure mono alkyl ether of ethylene glycol to the g value of pure ethyl alcohol with increase in ϕ_{EA} in their binary mixtures. The deviation in g^{eff} values from linearity confirms that the formation of heterogeneous interactions with the dipole orientation of the mixture constituents. The evaluated values of the corrective correlation factor g_f of these mono alkyl ethers of ethylene glycol-ethyl alcohol mixtures deviate from unity (less than unity), which also confirm the formation of the heterogeneous structures in these mixtures. Further the anomalous variation in g_f with ϕ_{EA} suggests the variation in size of the heterogeneous structures with the change in the concentration of the mixture constituents.

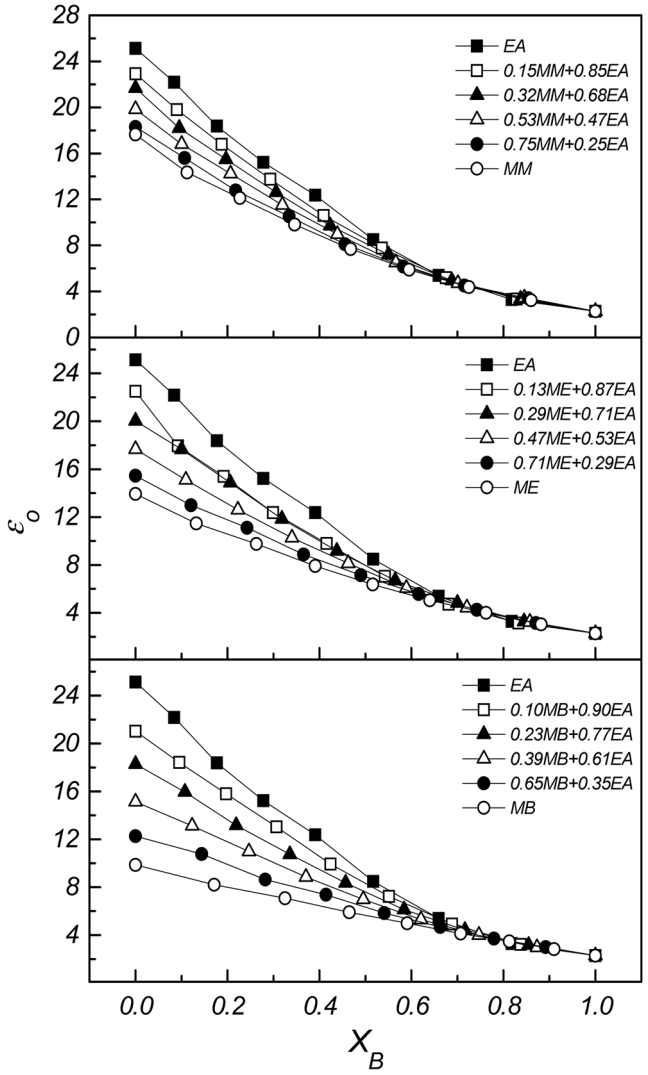

Figure 3. Plots of ε_o versus X_B of mono alkyl ethers of ethylene glycol, ethyl alcohol and their binary mixtures in benzene solution.

Binary mixture of polar liquids in non-polar solvent. To explore the change in the homogeneous and heterogeneous structures of the mono alkyl ethers of ethylene glycol – ethyl alcohol binary mixtures due to dilution in non-polar solvent over the entire concentration range, the comparative change in the dielectric parameters of binary mixtures and ternary mixtures were considered.

Dielectric constant of ternary mixture: Table 4 shows the values of ε_o, ε_∞ and ε^E of the polar molecules and the binary polar mixtures in benzene solutions. Figure 3 shows the variation in ε_o values of mono alkyl ethers, ethyl alcohol and their binary mixture in benzene solvent with mole fraction of benzene X_B. These plots have non-linear behaviour in polar solvent rich region but shows linear behaviour in benzene rich region. From these plots behaviour, it is inferred that addition of the benzene molecules acts as 'structures breaker' of the polar molecules H-bonded structures. In polar solvent or polar binary mixture rich region in benzene solvent, the molecules of benzene penetrate into the H-bonded homogeneous/heterogeneous polar molecules

Table 4. Values of static dielectric constant ε_o, high frequency limiting dielectric constant ε_∞ and excess dielectric constant ε^E of polar molecules and the various concentration polar binary mixture in benzene solutions at different mole fraction of benzene X_B at 25 °C

X_B	ε_o	ε_∞	ε^E	X_B	ε_o	ε_∞	ε^E	X_B	ε_o	ε_∞	ε^E
EA–Benzene											
0.000	25.13	1.84									
0.084	22.18	1.87	−1.03								
0.177	18.38	1.91	−2.71								
0.278	15.22	1.96	−3.57								
0.391	12.38	1.99	−3.83								
0.517	8.49	2.06	−4.85								
0.659	5.39	2.12	−4.71								
0.818	3.29	2.17	−3.17								
1.000	2.28	2.22									
(0.15 MM + 0.85 EA)–Benzene				(0.12 ME + 0.88 EA)–Benzene				(0.10 MB + 0.90 EA)–Benzene			
0.000	22.93	1.86		0.000	22.50	1.87		0.000	21.03	1.87	
0.090	19.81	1.90	−1.27	0.092	17.94	1.90	−2.69	0.095	18.42	1.91	−0.83
0.187	16.80	1.94	−2.28	0.192	15.39	1.94	−3.24	0.197	15.81	1.95	−1.54
0.293	13.76	1.98	−3.12	0.299	12.37	1.99	−4.09	0.306	13.04	1.99	−2.26
0.409	10.60	2.03	−3.90	0.416	9.79	2.03	−4.32	0.424	9.93	2.04	−3.17
0.536	7.77	2.07	−4.12	0.542	7.06	2.08	−4.50	0.551	7.23	2.08	−3.50
0.678	5.19	2.12	−3.82	0.681	4.74	2.12	−4.02	0.688	4.92	2.13	−3.22
0.829	3.33	2.17	−2.49	0.833	3.15	2.17	−2.53	0.837	3.22	2.18	−2.13
1.000	2.28	2.22		1.000	2.28	2.22		1.000	2.28	2.22	
(0.32 MM + 0.68 EA)–Benzene				(0.28 ME + 0.72 EA)–Benzene				(0.23 MB + 0.77 EA)–Benzene			
0.000	21.68	1.88		0.000	20.03	1.89		0.000	18.28	1.90	
0.095	18.19	1.91	−1.65	0.100	17.66	1.92	−0.59	0.107	15.96	1.93	−0.61
0.197	15.49	1.95	−2.38	0.206	14.86	1.96	−1.52	0.219	13.17	1.97	−1.61
0.306	12.62	1.99	−3.14	0.318	11.85	2.00	−2.54	0.335	10.74	2.01	−2.18
0.423	9.71	2.03	−3.76	0.438	9.16	2.04	−3.11	0.457	8.36	2.05	−2.62
0.550	7.20	2.07	−3.81	0.565	6.70	2.09	−3.32	0.584	6.13	2.10	−2.82
0.688	4.94	2.12	−3.41	0.700	4.83	2.13	−2.78	0.716	4.41	2.14	−2.42
0.837	3.35	2.17	−2.10	0.845	3.27	2.18	−1.77	0.855	3.17	2.18	−1.45
1.000	2.28	2.22		1.000	2.28	2.22		1.000	2.28	2.22	
(0.53 MM + 0.47 EA)–Benzene				(0.47 ME + 0.53 EA)–Benzene				(0.39 MB + 0.61 EA)–Benzene			
0.000	19.84	1.90		0.000	17.67	1.92		0.000	15.13	1.94	
0.100	16.80	1.92	−1.27	0.109	15.10	1.95	−0.88	0.123	13.12	1.97	−0.43
0.207	14.24	1.97	−1.97	0.223	12.61	1.98	−1.63	0.247	10.98	2.00	−0.97
0.319	11.51	2.01	−2.73	0.340	10.27	2.02	−2.16	0.371	8.85	2.04	−1.52
0.439	8.98	2.05	−3.17	0.462	8.13	2.06	−2.42	0.495	6.98	2.07	−1.79
0.566	6.51	2.10	−3.41	0.589	6.06	2.10	−2.55	0.621	5.30	2.11	−1.86
0.701	4.72	2.13	−2.82	0.721	4.43	2.14	−2.15	0.746	3.99	2.15	−1.55
0.846	3.44	2.17	−1.55	0.858	3.23	2.18	−1.24	0.873	2.98	2.19	−0.94
1.000	2.28	2.22		1.000	2.28	2.22		1.000	2.28	2.22	
(0.75 MM + 0.25 EA)–Benzene				(0.71 ME + 0.29 EA)–Benzene				(0.65 MB + 0.35 EA)–Benzene			
0.000	18.30	1.92		0.000	15.45	1.94		0.000	12.26	1.96	
0.107	15.61	1.96	−0.98	0.121	12.99	1.97	−0.87	0.144	10.77	1.99	−0.05
0.218	12.77	1.99	−2.04	0.243	11.11	2.00	−1.14	0.282	8.64	2.03	−0.80
0.334	10.53	2.02	−2.41	0.366	8.87	2.04	−1.76	0.414	7.37	2.05	−0.74
0.456	8.11	2.07	−2.90	0.490	7.14	2.07	−1.85	0.541	5.84	2.09	−1.01
0.582	6.16	2.10	−2.81	0.616	5.58	2.11	−1.77	0.663	4.68	2.12	−0.95
0.715	4.52	2.14	−2.33	0.742	4.25	2.15	−1.43	0.779	3.71	2.16	−0.76
0.854	3.40	2.17	−1.21	0.871	3.16	2.18	−0.83	0.892	3.00	2.19	−0.36
1.000	2.28	2.22		1.000	2.28	2.22		1.000	2.28	2.22	
MM–Benzene				ME–Benzene				MB–Benzene			
0.000	17.65	1.95		0.000	13.94	1.96		0.000	9.87	1.99	
0.112	14.35	1.98	−1.58	0.132	11.47	1.99	−0.93	0.171	8.21	2.02	−0.35
0.227	12.12	2.01	−2.04	0.263	9.76	2.02	−1.10	0.325	7.08	2.04	−0.29
0.346	9.81	2.04	−2.52	0.391	7.92	2.05	−1.45	0.465	5.91	2.07	−0.41
0.468	7.69	2.08	−2.77	0.516	6.36	2.08	−1.55	0.591	4.99	2.10	−0.36
0.595	5.89	2.11	−2.62	0.640	5.05	2.11	−1.41	0.707	4.12	2.13	−0.36
0.725	4.38	2.14	−2.13	0.762	4.00	2.13	−1.04	0.813	3.47	2.16	−0.21
0.860	3.24	2.18	−1.20	0.882	3.04	2.19	−0.61	0.910	2.83	2.19	−0.13
1.000	2.28	2.22		1.000	2.28	2.22		1.000	2.28	2.22	

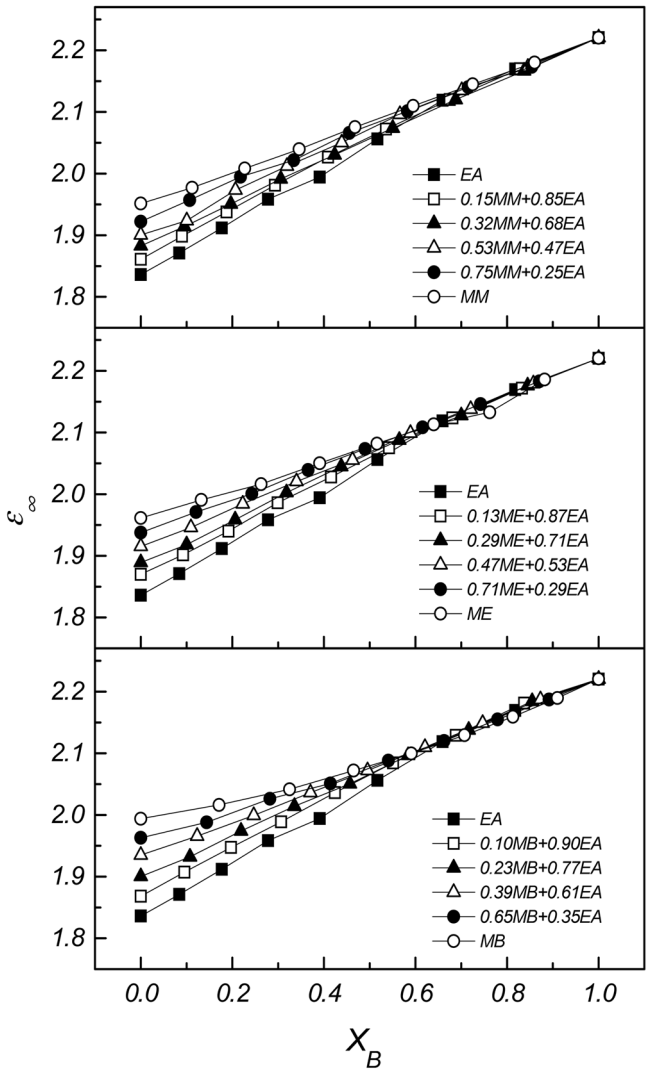

Figure 4. Plots of ε_∞ versus X_B of mono alkyl ethers of ethylene glycol, ethyl alcohol and their binary mixtures in benzene solution.

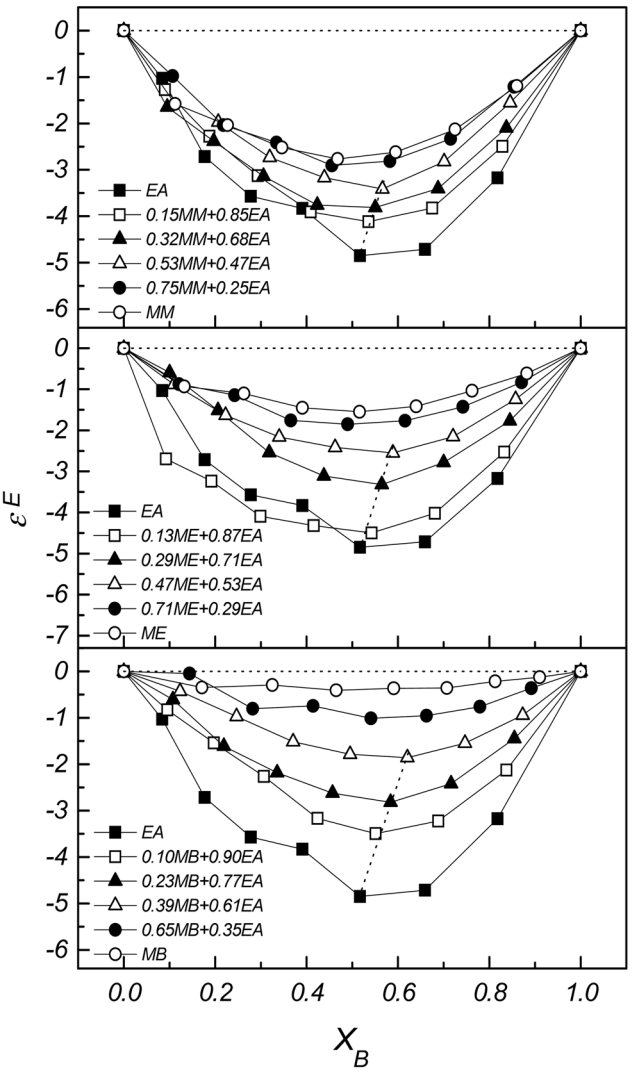

Figure 5. Plots of ε^E versus X_B of mono alkyl ethers of ethylene glycol, ethyl alcohol and their binary mixtures in benzene solution.

structures, due to which the structures elongation takes place and, hence there is large change in ε_o values at lower concentration X_B. Figure 4 shows the variation of ε_∞ against X_B. Most of the studied systems show almost linear behaviour, which confirms that the electronic polarization (*i.e.* orientation and atomic polarization) of these molecules is not affected by dilution in non-polar solvent benzene.

Excess dielectric constant of ternary mixture: Table 4 shows the values of excess dielectric constant ε^E of the polar molecules and their binary mixtures with ethyl alcohol, in benzene solutions over the entire concentration range. The ε^E values for all the studied systems were found negative. Figure 5 shows the variation of ε^E values against the benzene concentration X_B. In case of mono alkyl ethers of ethylene glycol, there is decrease in the magnitude of negative ε^E values with increase in molecular size from mono methyl ether to mono butyl ether. Further ethyl alcohol also has negative ε^E value and its magnitude is much higher than the ε^E values of mono alkyl ethers. From comparative ε^E values, it is inferred that in benzene solvent there is larger decrease in number of effective dipoles for the higher self-associated (H-bonded) molecules as compared to the molecules those have lower associating range. In these polar molecules the order of Kirkwood correlation factor g values are $g_{EA} > g_{MM} > g_{ME} > g_{MB}$ and their ε^E magnitudes have the same order *i.e.* $\varepsilon^E_{EA} > \varepsilon^E_{MA} > \varepsilon^E_{ME} > \varepsilon^E_{MB}$. Further all these polar molecules shows the minimum in ε^E values at $X_B \approx 0.5$, which is interesting. The sharp minimum in ε^E values of these polar molecules near 50 percent dilution in benzene confirms the maximum decrease in the number of effective dipoles at this concentration.

All the binary mixtures of mono alkyl ethers with ethyl alcohol have negative ε^E values Figure 1, and hence the observed ε^E values of each binary polar mixture in benzene solutions are also found negative. Further these values vary in the range of the ε^E values of the individual polar molecule of the mixture, which is expected from the g^{eff} values of the polar binary mixtures. The interesting observation observed from Figure 5 is the shift in the magnitude of maximum ε^E values of the polar binary mixtures in benzene rich region,

which is found at 50% concentration for individual polar molecules in benzene solution. This shift is indicated by the dotted line in Figure 5. It is found that for binary mixture of ethers-ethyl alcohol of $X_{EA} > 0.5$ in benzene solutions, the maximum magnitude of ε^E value is found in benzene rich solution, and its position shifted towards higher X_B values with decrease in X_{EA} in the binary mixtures (Figure 5). But for the ethers-rich polar binary mixtures, there is almost insignificant change in the concentration corresponding to the maximum magnitude of ε^E values as compared to their individual constituent maximum ε^E concentration. These findings concludes that in the binary mixtures of mono alkyl ethers with ethyl alcohol, the maximum decrease in effective number of dipoles in their homogeneous and heterogeneous structures are in benzene rich region, when the ethyl alcohol concentration is higher as compared to the concentration of mono alkyl ethers in their binary mixtures.

Conclusions

The comparative dielectric study of the binary mixtures of mono alkyl ethers of ethylene glycol with ethyl alcohol confirms the H-bond complex formation in these mixtures, which vary with the variation in mixture constituents concentration. The formation of heterogeneous interactions reduces the effective number of dipoles in the mixtures. The stoichiometric ratio of ethers-ethyl alcohol corresponding to the formation of stable adduct also depends on the molecular size of mono alkyl ethers. The homogeneous structures of the molecules of mono alkyl ethers of ethylene glycol with ethyl alcohol exists in benzene solutions with maximum reduce in effective number of dipoles when they are diluted by benzene at 50 percent concentration. The ethyl alcohol rich binary mixtures of these polar solvents in benzene solution exist with maximum reduce in effective number of dipoles due to the increase in heterogeneous H-bond connectivities in benzene rich region of these ternary mixtures.

Acknowledgments. The authors are grateful to the University Grants Commission, New Delhi for financial assistance.

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