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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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First published on: 05 June 2009

To cite this Article Sengwa, R. J. , Sankhla, Sonu and Shinyashiki, N.(2010) 'Dielectric properties of binary and ternary mixtures of some aliphatic alcohols: analysis of H-bonded interaction in complex systems', *Physics and Chemistry of Liquids*, 48: 1, 29 – 40, First published on: 05 June 2009 (iFirst)

To link to this Article: DOI: 10.1080/00319100802641740

URL: <http://dx.doi.org/10.1080/00319100802641740>

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Dielectric properties of binary and ternary mixtures of some aliphatic alcohols: analysis of H-bonded interaction in complex systems

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(Received 29 November 2006; final version received 22 November 2008)

The formation of the heterogeneous H-bonded interactions in binary mixtures of ethyl alcohol (EA) with ethylene glycol (EG), (EA + EG), and glycerol, (Gly) (EA + Gly); EG with Gly (EG + Gly); and ternary mixtures of equimolar EA + EG, EA + Gly and EG + Gly systems with Gly, EG and EA, respectively, have been investigated at 21 concentrations by precision dielectric measurements at 25°C. The concentration-dependent values of excess dielectric parameter, ϵ_o^E , and effective Kirkwood correlation factor, g^{eff} , were determined using the measured values of the static dielectric constant, ϵ_o , at 1 MHz, and the high-frequency limiting dielectric constant, $\epsilon_\infty = n_D^2$, at optical frequency. The observed ϵ_o^E values of EA + EG and EA + Gly systems were found to be negative over the entire concentration range, which indicates the decrease of the total number of same direction-aligned effective dipoles due to heterogeneous H-bond interactions. In contrast to these binary systems, the ϵ_o^E values of the EG + Gly system were found to be positive, which confirms the increase in total number of effective dipoles aligned in the same direction due to H-bond interactions. In (EA + EG) + Gly ternary mixtures, the observed positive ϵ_o^E values also indicate the increase of an effective number of dipoles aligned in the same direction due to the formation of the complex H-bonded heterogeneous structures. The (EG + Gly) + EA system shows negative ϵ_o^E values at all EG concentrations, but in case of the (EA + Gly) + EG system, the ϵ_o^E values change from positive to negative with the increase in the concentration of EG. Results also show that the heterogeneous H-bond interactions in the presence of Gly molecules in the binary and ternary mixtures of alcohols significantly increase the strength of electronic polarisation.

Keywords: ternary mixtures; dielectric constant; molecular interaction; excess dielectric parameter

1. Introduction

The formation of molecular clusters and network structures due to strong intermolecular interactions through H-bonds in alcohols results in their complicated molecular structures in liquid state. The broadband microwave dielectric measurement [1–7] has established that the homogeneous molecular structures of alcohols systematically changes with the increase in the number of carbon atoms and hydroxyl groups, and with their positions in the molecules. The complexities in the H-bonded alcohol structures at the molecular level changes significantly in binary mixtures of various characteristics of H-bonded liquids due

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to the breaking of their homogeneous structures and simultaneously the formation of H-bonded heterogeneous structures. In last two decades, the characterisation of heterogeneous interactions between associating polar liquids in binary mixtures over the entire concentration range using dielectric measurements has been the subject of several investigations [1–16]. The H-bond has a considerable effect on the dielectric parameters of the binary mixtures of the associating molecules. The evaluation of excess dielectric parameter properties over the entire concentration range [8–13,17] provides information about the formation of heterogeneous molecular interactions and their effect on the total number of aligned (same or opposite direction) dipoles, and also about the molar ratio corresponding to the formation of the strongest H-bonded interactions between the mixture constituents.

The heterogeneous structural complexities of the binary mixtures of associating liquids further increases when a third associating polar liquid is added at different concentration. The conformations of binary and ternary mixtures of industrial and biological useful H-bonded liquids, particularly alcohols, are the challenging problems in liquid state physics and chemistry. In the present work, dielectric measurements on the binary and ternary mixtures of mono-, di- and trihydric aliphatic alcohols were carried out, in order to get ideas about some of the universal rules in the structural variation and formation of the strongest H-bonded structure with increases in the number of hydroxyl group over the entire concentration variation of the mixture constituents.

2. Experimental

2.1. Materials

Grade reagent of ethyl alcohol (EA) and ethylene glycol (EG) were purchased from E. Merck, India. Glycerol (Gly) of spectroscopic grade was purchased from HiMedia Laboratories, India. Binary mixtures of the EA + EG, EA + Gly and EG + Gly systems were prepared at 21 volume percentage over the entire concentration range at room temperature. Using the equimolar EA + EG, EA + Gly and EG + Gly binary mixtures as one component, and Gly, EG and EA as a second component, respectively, ternary mixtures were prepared at 21 volume percentage compositions over the entire concentration range for their dielectric measurements. The mole fractions of the mixture constituents were determined using their individual volume concentration in the mixture, and density at room temperature and their molecular weight.

2.2. Measurements

The values of the static dielectric constant, ϵ_0 , of the aliphatic alcohols and their binary and ternary mixtures were determined by using ‘capacitive measurement method’ at 1 MHz. An Agilent 4284A Precision LCR Meter and a four terminal cell Agilent 16452A Liquid Test Fixture were used for the determination of the accurate ϵ_0 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 effect of stray capacitance for the determination of the ϵ_0 values. Further, a frequency of 1 MHz was used to avoid the effect of ionic conduction. The maximum error in the evaluated values is $\pm 0.1\%$. The high-frequency limiting dielectric constant ϵ_∞ was taken as being 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 using a Thermo-Haake DC10 controller.

3. Results

The values of static dielectric constant ε_0 , and high-frequency limiting dielectric constant ε_∞ , of the studied EA + EG, EA + Gly and EG + Gly binary mixtures with a mole fraction of one of the constituents of the mixture, and the ternary mixtures (the equimolar binary mixtures of two different alcohols as one component and the third alcohol as second component) (EA + EG) + Gly, (EA + Gly) + EG and (EG + Gly) + EA, with a mole fraction of a third constituent of the mixture, are depicted in Figures 1–6. The ε_0 and ε_∞ values of the binary and ternary alcohol mixtures are also recorded in Table 1, which can be applied in formulating adequate models of H-bonded liquid mixtures. The measured ε_0 values for alcohols at 1 MHz and 25°C are in good agreement with the ε_0 values reported earlier [4,18], which were determined by wide frequency measurements.

The excess dielectric constant, ε_0^E , for binary mixture is defined as [8,17,19]:

$$\varepsilon_0^E = (\varepsilon_0 - \varepsilon_\infty)_m - [(\varepsilon_0 - \varepsilon_\infty)_1 X_1 + (\varepsilon_0 - \varepsilon_\infty)_2 X_2], \quad (1)$$

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

The excess dielectric constant, ε_0^E , for ternary mixture is determined by the relation [10]:

$$\varepsilon_0^E = (\varepsilon_0 - \varepsilon_\infty)_m - [(\varepsilon_0 - \varepsilon_\infty)_{12} X_{12} + (\varepsilon_0 - \varepsilon_\infty)_3 X_3], \quad (2)$$

where subscripts m, 12 and 3 represent the ternary mixture and components of the ternary mixture, i.e. equimolar binary mixture 12, and the third constituent of the ternary mixture 3, respectively. The evaluated ε_0^E values of the binary and ternary mixtures with X_{EA} , X_{EG} and X_{Gly} are plotted in Figures 1–6.

The value of Kirkwood correlation factor g gives information regarding the formation of multimers and ordering of dipoles in pure liquid. In pure liquid, g is related to other quantities by the expression [20]:

$$\frac{4\pi Nd}{9kTM} g\mu^2 = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}, \quad (3)$$

where μ is the dipole moment, d is the density of liquid at temperature T , M is the molecular weight, k is the Boltzmann constant and N is the Avagadro's number.

In binary mixtures of polar solvents, the effective averaged angular Kirkwood correlation factor g^{eff} between heterogeneous molecules can be evaluated by using the modified Kirkwood equation [21,22]:

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

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

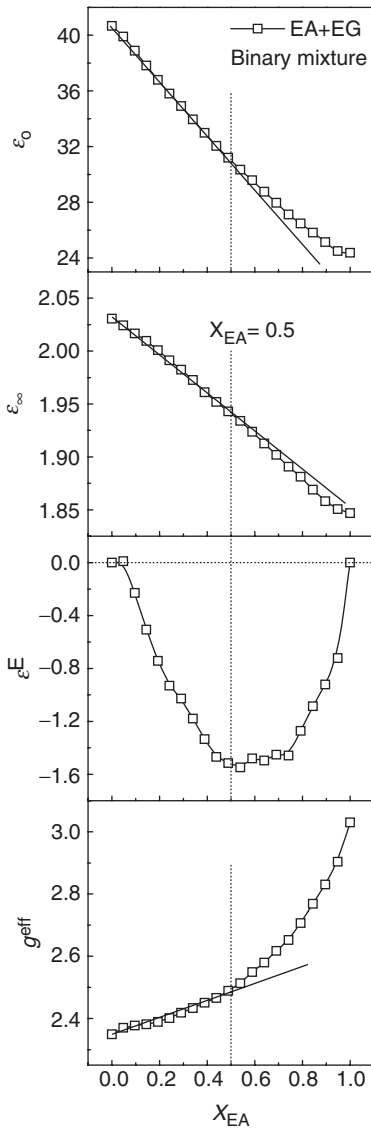


Figure 1. Plots of ϵ_0 , ϵ_∞ , ϵ_0^E and g^{eff} vs. X_{EA} of EA + EG binary mixtures.

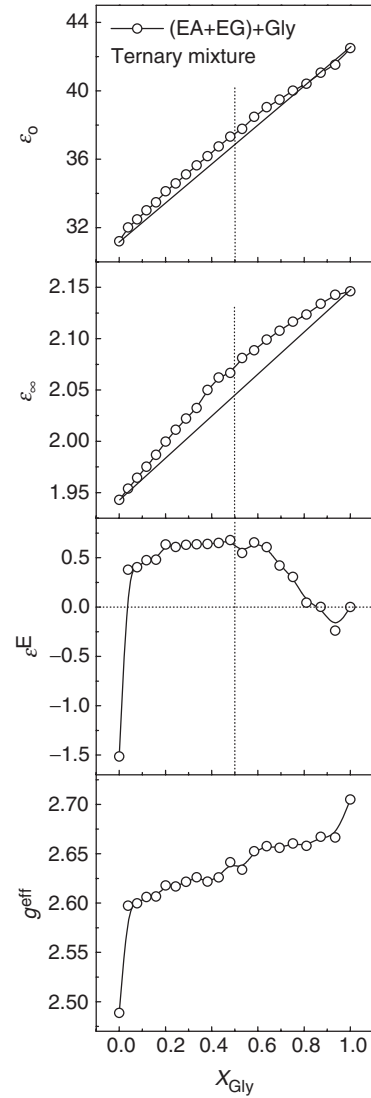


Figure 2. Plots of ϵ_0 , ϵ_∞ , ϵ_0^E and g^{eff} vs. X_{Gly} of (EA + EG) + Gly ternary mixtures.

In case of ternary mixtures of polar solvents, the effective averaged angular Kirkwood correlation factor g^{eff} between mono-, di- and trihydric alcohol molecules can be evaluated by using the modified Kirkwood correlation equation [10,12]:

$$\frac{4\pi N}{9kT} \left(\frac{\mu_{12}^2 d_{12}}{M_{12}} \phi_{12} + \frac{\mu_3^2 d_3}{M_3} \phi_3 \right) g^{\text{eff}} = \frac{(\epsilon_{\text{om}} - \epsilon_{\infty\text{om}})(2\epsilon_{\text{om}} + \epsilon_{\infty\text{om}})}{\epsilon_{\text{om}}(\epsilon_{\infty\text{om}} + 2)^2}, \quad (5)$$

where ϕ_{12} and ϕ_3 are the volume fractions of the equimolar binary mixture, and third constituent of the ternary mixture, respectively, and μ_{12} , d_{12} and M_{12} are, respectively,

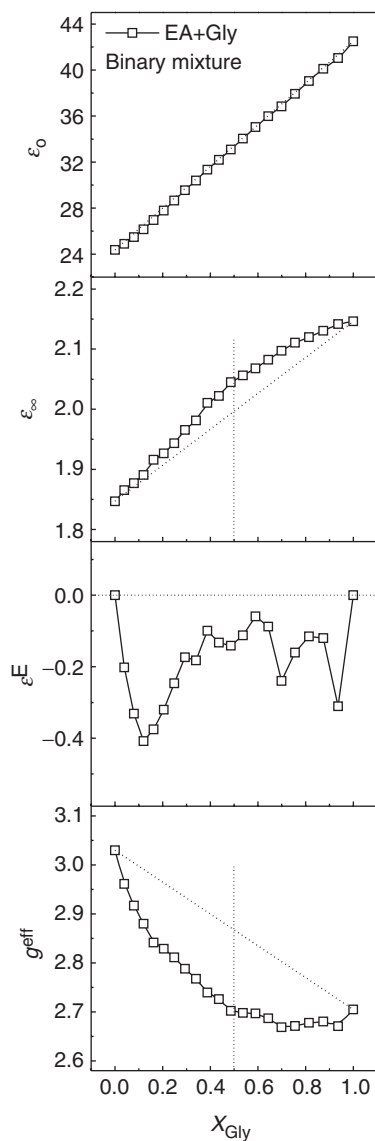


Figure 3. Plots of ϵ_0 , ϵ_∞ , ϵ_0^E and g^{eff} vs. X_{Gly} of EA + Gly binary mixtures.

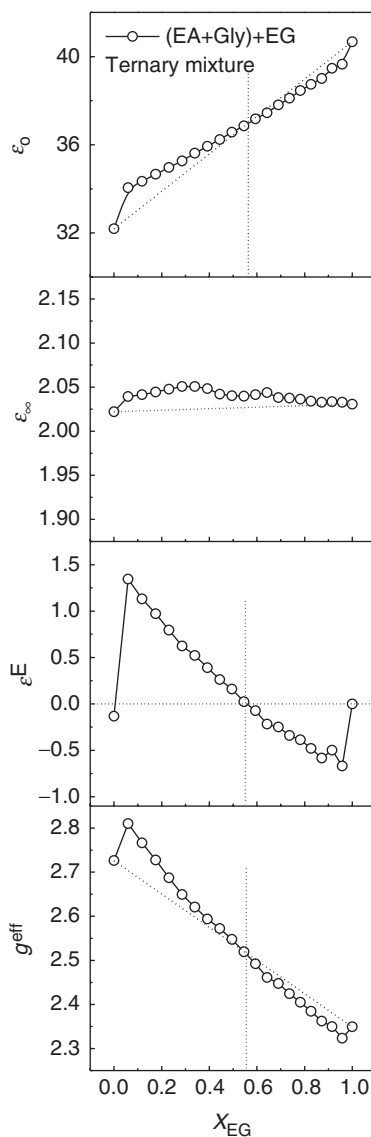


Figure 4. Plots of ϵ_0 , ϵ_∞ , ϵ_0^E and g^{eff} vs. X_{EG} of (EA + Gly) + EG ternary mixtures.

the average values of the dipole moment, density and molecular weight of the equimolar binary mixture.

The dipole moment values [4] 1.73D, 2.38D and 2.56D of the EA, EG and Gly respectively, and 2.055D, 2.145D and 2.47D of the equimolar EA + EG, EA + Gly and EG + Gly mixtures, respectively, were used in the Equations (3)–(5), for the evaluation of g and g^{eff} values of these systems. The evaluated g^{eff} values of binary and ternary mixtures are also plotted in Figures 1–6.

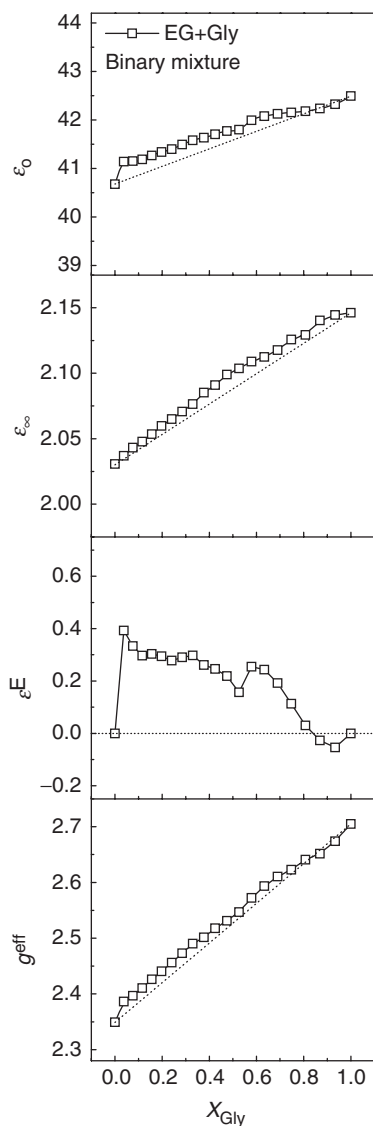


Figure 5. Plots of ϵ_0 , ϵ_∞ , ϵ_0^E and g^{eff} vs. X_{Gly} of EG+Gly binary mixtures.

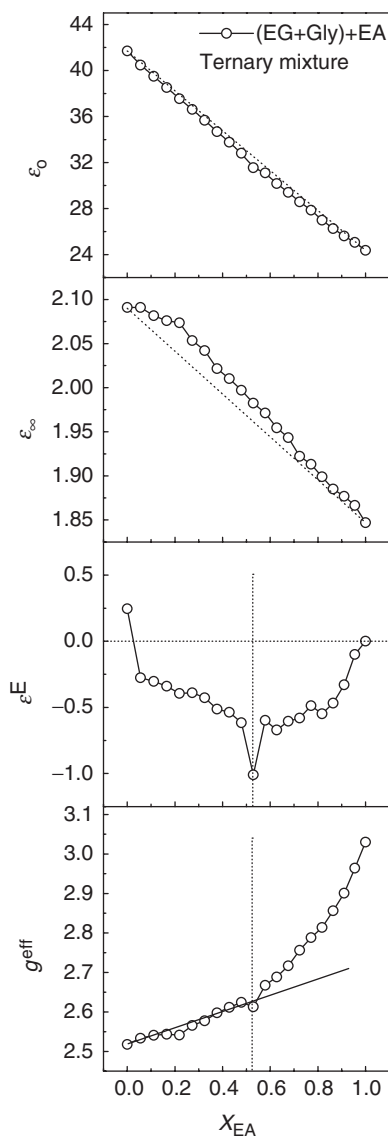


Figure 6. Plots of ϵ_0 , ϵ_∞ , ϵ_0^E and g^{eff} vs. X_{EA} of (EG+Gly)+EA ternary mixtures.

4. Discussion

The g values of EA, EG, Gly are 3.05, 2.35 and 2.70, respectively, which are greater than unity and confirm that these molecules exist in self-associated structures through H-bonds with parallel (same direction) dipole alignment in their pure liquid state [20]. The higher magnitude of g value indicates the large range self-association in these alcohol molecules. The order of the g values are ethyl alcohol > glycerol > ethylene glycol, which does not show the monotonous increase in g values with the increase in number of hydroxyl groups in these molecules. This suggests that the ordering of

Table 1. The ϵ_0 and ϵ_∞ values of binary and ternary mixtures of alcohols at 25°C.

| Binary mixtures | | | | | | | | |
|-----------------|--------------|-------------------|-----------|--------------|-------------------|-----------|--------------|-------------------|
| EA + EG | | | EA + Gly | | | EG + Gly | | |
| X_{EA} | ϵ_0 | ϵ_∞ | X_{Gly} | ϵ_0 | ϵ_∞ | X_{Gly} | ϵ_0 | ϵ_∞ |
| 0.00 | 40.68 | 2.03 | 0.00 | 24.38 | 1.85 | 0.00 | 40.68 | 2.03 |
| 0.05 | 39.91 | 2.02 | 0.04 | 24.89 | 1.87 | 0.04 | 41.14 | 2.04 |
| 0.10 | 38.89 | 2.02 | 0.08 | 25.48 | 1.88 | 0.08 | 41.15 | 2.04 |
| 0.14 | 37.82 | 2.01 | 0.12 | 26.15 | 1.89 | 0.12 | 41.19 | 2.05 |
| 0.19 | 36.80 | 2.00 | 0.16 | 26.96 | 1.92 | 0.16 | 41.27 | 2.05 |
| 0.24 | 35.81 | 1.99 | 0.21 | 27.79 | 1.93 | 0.20 | 41.34 | 2.06 |
| 0.29 | 34.92 | 1.98 | 0.25 | 28.66 | 1.94 | 0.24 | 41.40 | 2.06 |
| 0.34 | 33.96 | 1.97 | 0.29 | 29.56 | 1.97 | 0.28 | 41.49 | 2.07 |
| 0.39 | 33.00 | 1.96 | 0.34 | 30.39 | 1.98 | 0.33 | 41.58 | 2.08 |
| 0.44 | 32.06 | 1.95 | 0.39 | 31.35 | 2.01 | 0.38 | 41.63 | 2.09 |
| 0.49 | 31.20 | 1.94 | 0.44 | 32.19 | 2.02 | 0.43 | 41.71 | 2.09 |
| 0.54 | 30.35 | 1.93 | 0.49 | 33.09 | 2.04 | 0.47 | 41.77 | 2.10 |
| 0.59 | 29.60 | 1.92 | 0.54 | 34.04 | 2.06 | 0.53 | 41.80 | 2.10 |
| 0.64 | 28.75 | 1.91 | 0.59 | 35.04 | 2.07 | 0.58 | 41.99 | 2.11 |
| 0.69 | 27.97 | 1.90 | 0.64 | 35.99 | 2.08 | 0.63 | 42.08 | 2.11 |
| 0.74 | 27.13 | 1.89 | 0.70 | 36.84 | 2.10 | 0.69 | 42.13 | 2.12 |
| 0.79 | 26.48 | 1.88 | 0.76 | 37.94 | 2.11 | 0.75 | 42.16 | 2.13 |
| 0.84 | 25.82 | 1.87 | 0.81 | 39.04 | 2.12 | 0.81 | 42.18 | 2.13 |
| 0.90 | 25.14 | 1.86 | 0.87 | 40.12 | 2.13 | 0.87 | 42.24 | 2.14 |
| 0.95 | 24.50 | 1.85 | 0.94 | 41.04 | 2.14 | 0.93 | 42.32 | 2.14 |
| 1.00 | 24.38 | 1.85 | 1.00 | 42.49 | 2.15 | 1.00 | 42.49 | 2.15 |

| Ternary mixtures | | | | | | | | |
|---------------------------|--------------|-------------------|---------------------------|--------------|-------------------|---------------------------|--------------|-------------------|
| (Equimolar EA + EG) + Gly | | | (Equimolar EA + Gly) + EG | | | (Equimolar EG + Gly) + EA | | |
| X_{Gly} | ϵ_0 | ϵ_∞ | X_{EG} | ϵ_0 | ϵ_∞ | X_{EA} | ϵ_0 | ϵ_∞ |
| 0.00 | 31.20 | 1.94 | 0.00 | 32.19 | 2.02 | 0.00 | 41.71 | 2.09 |
| 0.04 | 32.01 | 1.95 | 0.06 | 34.06 | 2.04 | 0.06 | 40.48 | 2.09 |
| 0.08 | 32.48 | 1.96 | 0.12 | 34.34 | 2.04 | 0.11 | 39.50 | 2.08 |
| 0.12 | 33.01 | 1.98 | 0.17 | 34.67 | 2.04 | 0.17 | 38.52 | 2.08 |
| 0.16 | 33.48 | 1.99 | 0.23 | 34.97 | 2.05 | 0.22 | 37.55 | 2.07 |
| 0.20 | 34.12 | 2.00 | 0.29 | 35.26 | 2.05 | 0.27 | 36.62 | 2.05 |
| 0.24 | 34.59 | 2.01 | 0.34 | 35.62 | 2.05 | 0.33 | 35.68 | 2.04 |
| 0.29 | 35.12 | 2.02 | 0.39 | 35.93 | 2.05 | 0.38 | 34.68 | 2.02 |
| 0.34 | 35.64 | 2.03 | 0.44 | 36.24 | 2.04 | 0.43 | 33.77 | 2.01 |
| 0.38 | 36.18 | 2.05 | 0.50 | 36.57 | 2.04 | 0.48 | 32.81 | 2.00 |
| 0.43 | 36.74 | 2.06 | 0.55 | 36.85 | 2.04 | 0.53 | 31.55 | 1.98 |
| 0.48 | 37.33 | 2.07 | 0.59 | 37.18 | 2.04 | 0.58 | 31.10 | 1.97 |
| 0.53 | 37.78 | 2.08 | 0.64 | 37.44 | 2.04 | 0.63 | 30.17 | 1.95 |
| 0.58 | 38.48 | 2.09 | 0.69 | 37.81 | 2.04 | 0.68 | 29.40 | 1.94 |
| 0.64 | 39.04 | 2.10 | 0.74 | 38.11 | 2.04 | 0.72 | 28.59 | 1.92 |
| 0.69 | 39.48 | 2.11 | 0.78 | 38.45 | 2.04 | 0.77 | 27.86 | 1.91 |
| 0.75 | 40.01 | 2.12 | 0.83 | 38.74 | 2.03 | 0.82 | 26.99 | 1.90 |
| 0.81 | 40.42 | 2.12 | 0.87 | 39.01 | 2.03 | 0.86 | 26.26 | 1.89 |
| 0.87 | 41.06 | 2.13 | 0.92 | 39.46 | 2.03 | 0.91 | 25.61 | 1.88 |
| 0.93 | 41.53 | 2.14 | 0.96 | 39.65 | 2.03 | 0.96 | 25.06 | 1.87 |
| 1.00 | 42.49 | 2.15 | 1.00 | 40.68 | 2.03 | 1.00 | 24.38 | 1.85 |

self-association depends not only on the steric arrangement of the respective groups, but is also sensitive to the size and shape of the polar molecule. The ethyl alcohol molecule has one –OH group but forms higher order self-associated structures, which results the linear polymeric structures with a switch-over type of molecular reorientation throughout their homogeneous structures [18,23]. The molecules of ethylene glycol have at both ends hydroxyl groups with a gauche conformation, which results in intramolecular H-bonding, and hence probably only one –OH group of the EG molecule can interact with neighbouring molecules through an H-bond [17,24,25]. The glycerol molecule contains two primary alcohol groups and one secondary alcohol group. The primary alcohol groups are more reactive than the secondary alcohol group, but the H-bond formation through the secondary alcohol group results in the cross linkage H-bonded structures (three-dimensional structures) in the pure liquid state of glycerol [6].

The ϵ_0 value of the H-bonded liquid is mainly dependent on: (i) the dipole moment; (ii) the number of molecules per unit volume; and (iii) Kirkwood's correlation factor. In the case of binary or ternary mixtures of H-bonded alcohols, the ϵ_0 value is set by the balance of all the three factors of the mixture constituents described above. The ϵ_0 values of EA, EG and Gly are 24.38, 40.68 and 42.49, respectively, at 25°C. Comparative ϵ_0 values confirm that the increase in number of hydroxyl groups in the alcohol molecule increases the ϵ_0 value. Nearly equal ϵ_0 values of EG and Gly suggests that the contribution in the enhancement of ϵ_0 value by the increase in one hydroxyl group is compensated by an increase in one carbon atom in Gly molecule. However, the ϵ_∞ values of EA, EG and Gly (1.85, 2.03 and 2.15, respectively) increases almost linearly with the increase in number of hydroxyl groups in these molecules.

4.1. Binary mixture

The plots (Figures 1, 3 and 5) of ϵ_0 , ϵ_∞ and g^{eff} with the mole fraction of one of the mixture constituents of the EA + EG, EA + Gly and EG + Gly mixtures show the deviation from their linear behaviour, which suggests the formation of the heterogeneous structures through the H-bond with the breaking of their homogeneous structures over the entire concentration range.

The excess dielectric constant [10–13,19,21,24], ϵ_0^E , of the liquid mixtures provides experimental evidence for the formation of solvent–cosolvent complexes through heterogeneous H-bonds, which is as follows:

- (i) $\epsilon_0^E = 0$ indicates that mixture constituents do not interact or there is no change in the net dipole alignments due to heterogeneous interactions.
- (ii) $\epsilon_0^E < 0$ indicates that mixture constituent interactions arrange some of the neighbouring dipoles in the opposite direction, which results in a reduction in the total number of effective dipoles contributed in electric polarisation.
- (iii) $\epsilon_0^E > 0$ indicates that the constituents of the binary mixture align a greater number of the neighbouring dipoles in the same direction, i.e. the number of effective dipoles contributed in ϵ_0 values increases.

In the present case, we can identify at least three effects which contribute to the ϵ_0^E values: (i) the breaking of liquid order on mixing; (ii) favourable interactions between polar groups of unlike molecules; and (iii) favourable hydrophobic interactions. All of

these effects should be responsible for the orientation of molecular dipole moments of like and/or unlike neighbouring molecules.

Figures 1 and 3 show that the ϵ_0^E values of EA + EG and EA + Gly mixtures are always negative over the entire concentration range. This behaviour may be interpreted at the molecular level, because negative ϵ_0^E values can arise either from dipolar association between the components in the mixture or from dipolar self-association of the more polar component to form species of lower dipole moment [17]. The minimum in the ϵ_0^E values of EA + EG mixtures is a reliable indication of the presence of maximum solvent–cosolvent complex units at a molar ratio of around 1:1, which extends up to the range 3:1 molar ratio of EA to EG in the mixture. But in case of EA + Gly mixture, there is anomalous variation in the observed negative values of ϵ_0^E with the mole fraction of Gly. Further, the ϵ_0^E values of EA + Gly are much smaller than the ϵ_0^E values of EA + EG. From these comparative results, it is inferred that the H-bond heterogeneous interaction connectivity of EA + EG mixture is stronger, when compared to the EA + Gly mixture. These results also confirm that there is a larger change in the homogeneous structures of the mixture constituents in EA + EG mixtures when compared to the EA + Gly mixtures, although the H-bond interactions sites are higher in EA + Gly mixtures.

In case of EG + Gly mixtures, the positive ϵ_0^E values (Figure 5) indicate the formation of H-bond heterogeneous interactions with the increase in total number of effective dipoles aligned in same direction. Further, a large increase in the total number of aligned dipoles is found at the lowest concentration of Gly in the EG + Gly mixture, which further decreases anomalously with the increase in the X_{Gly} . From ϵ_0^E values it seems that the addition of the smallest fraction of Gly in EG breaks a large number of homogeneous structures of EG molecules before they undergo the formation of the heterogeneous H-bonded structures, which are due to the presence of three –OH groups in Gly molecules.

4.2. Ternary mixture

Figures 2, 4 and 6 show the plots of ϵ_0 , ϵ_∞ and ϵ_0^E values of the ternary mixtures of the equimolar EA + EG with Gly [(EA + EG) + Gly], the equimolar EA + Gly with EG [(EA + Gly) + EG], and the equimolar EG + Gly with EA [(EG + Gly) + EA] over the entire concentration range of X_{Gly} , X_{EG} and X_{EA} , respectively. The non-linear behaviour of ϵ_0 against mole fraction X of the third constituent in the ternary mixture confirms the alteration in equimolar system H-bonded heterogeneous structures in the presence of the mixture's third constituent.

The comparative study of the ϵ_0^E values of these mixtures (Figures 2, 4 and 6) also shows that the total number of dipoles aligned (same or opposite direction) due to the heterogeneous H-bond interactions varies from system to system. In the case of the (EA + EG) + Gly system, the equimolar EA + EG mixture has negative ϵ_0^E values, which change abruptly to positive with the addition of the smallest concentration of Gly, and finally at the concentrations near pure Gly, it again changes from positive to negative (Figure 2). Similarly, in the case of the (EA + Gly) + EG mixture, by addition of a small concentration of EG in EA + Gly, the ϵ_0^E value abruptly changes from negative to positive, which also confirms the large number of dipole orientations in the H-bonded heterogeneous structures of equimolar binary mixture in the presence of the third alcohol molecules. Further increase of EG concentration in the ternary mixture (EA + Gly) + EG and the ϵ_0^E values decrease almost linearly from positive values, and at $X_{\text{Gly}} \approx 0.55$

(Figure 4) it again becomes negative, which confirms the systematic variation in the dipolar alignment in the H-bonded heterogeneous structures of equimolar binary mixture of EA + Gly in the presence of EG molecules. The ϵ_0^E values of the (EA + Gly) + EG mixture suggest that the phase shifting in the effective associating dipoles from the same direction alignment to the opposite direction alignment takes place around the 1:1 mole fraction ratio of equimolar concentration of (EA + Gly) and EG. The equimolar EG + Gly mixture has positive ϵ_0^E values, but by addition of a small amount of EA to this system, the ϵ_0^E value abruptly changes from positive to negative and remains negative over the entire concentration range of EA in the (EG + Gly) + EA mixture. This also confirms the orientation of a large number of dipoles which make the complex heterogeneous structures.

Comparative results confirm that in ternary mixtures of mono-, di- and trihydric alcohols, at the equimolar concentration of the equimolar binary mixture (one system) and the third constituent (second system) of the ternary mixtures, there are phase inversions of the dipoles' alignment. Furthermore, the comparative dielectric study of the studied alcohols confirms that the heterogeneous structures of the equimolar monohydric + trihydric alcohols changes more systematically with the variation of the dihydric alcohol concentration in their ternary mixture, as evident from the almost linear change in the values of ϵ_0^E and g^{eff} (Figure 4).

4.3. H-bond interaction effect on electronic polarisation

The changes in the electronic polarisation caused by heterogeneous H-bond formation in the mixtures can be detected by the refractive index measurements [24,26], but it is difficult to detect in solution the separate changes produced in the orientation and the atomic polarisation. The non-linear behaviour of ϵ_∞ values with the mixture constituent concentrations of the studied alcohol mixtures show that the electronic polarisation is significantly affected by the heterogeneous H-bond interactions. Further, in the alcohol mixtures the increase in ϵ_∞ values from linear behaviour (Figures 1–6) confirms the increase in magnitude of electronic polarisation, except in the EA-rich region of the EA + EG mixture. Furthermore, the comparative ϵ_∞ values show that the heterogeneous H-bond formation by Gly molecules affects comparatively more the electronic polarisation.

4.4. Kirkwood correlation factor

To confirm the effect of heterogeneous H-bond interactions on the orientation of the dipoles, the values of the effective Kirkwood correlation factor g^{eff} were evaluated over the entire concentration range of the mixtures, which are shown in Figures 1–6. The deviation from linearity of the g^{eff} versus concentration plots of the alcohol mixtures confirms the orientation of the dipoles required for the formation of heterogeneous interactions. From these results it can be concluded that a larger number of dipole orientations in monohydric alcohol are required, as compared to the dipole orientation of dihydric and trihydric alcohols in their binary mixtures, to form heterogeneous H-bonded complex structures. Further, it is difficult to detect the effect of H-bond formation on the dipole orientation of the individual alcohol, but results show that the dipole orientation in the studied ternary mixtures significantly varies with the change in the composition of the alcohols in the mixture. Further, in case of (EA + EG) + Gly and (EA + Gly) + EG ternary mixtures,

the g^{eff} values abruptly changes at the extreme concentrations of the mixtures but in the middle concentration range it varies almost linearly, which is not observed in the case of the (EG + Gly) + EA mixture.

5. Conclusions

The self-association through H-bonds in EA, EG and Gly vary anomalously with increase in the number of hydroxyl groups in the alcohol molecules. The enhances in value of static dielectric constants with the increase in one hydroxyl group in the alcohol molecule is compensated by the simultaneous increase of one carbon atom. The presence of EA in the binary mixtures with EG and Gly forms heterogeneous interactions with some opposite alignment of effective dipoles, but in the EG + Gly mixture, H-bond interactions align the effective dipoles in the same direction. In ternary mixtures of different aliphatic alcohols, an abrupt reorientation in the number of effective dipoles takes place due to heterogeneous interactions in the presence of a third alcohol constituent of the mixture. Further, in all the studied alcohol mixtures, the H-bond interactions influence the electronic polarisation. The values of the dielectric constant of the alcohol mixtures reported in the article can be applied for the formulation of adequate dielectric models of similar types of heterogeneous H-bonded liquid mixtures.

Acknowledgement

The authors (RJS & SS) gratefully acknowledge the financial support from the Department of Science and Technology DST, New Delhi, India, through the Research Project No. SR/S2/CMP-9/2002.

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