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Characterization of Heterogeneous Interaction in Binary Mixtures of Ethylene Glycol and Acetic Acid by Dielectric Analysis

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ABSTRACT

The associating behaviour of the binary mixture of ethylene glycol and acetic acid over the entire concentration range at 25 °C has been investigated through the measured values of dielectric constants. The static dielectric constant ε_0, high frequency limiting dielectric constant ε_∞, excess dielectric parameters ε_0^E and ε_∞^E, the effective Kirkwood correlation factor g^{eff} and corrective correlation factor g_f for the above binary mixture were determined to obtain the qualitative and quantitative information about the complex formation.

1. Introduction

Dielectric studies are of great help in the assignment of the molecular structures or configurations, particularly those of organic compounds. Relative permittivity measurement is popular and effective technique for characterizing molecular structure and intermolecular or intramolecular interactions in solutions [1-3]. The precise permittivity data of binary liquid mixtures are necessary for understanding of the nature and strength of intermolecular interactions and the consequent structural rearrangement of molecules in solution. Measured values of dielectric permittivity can be used to calculate Kirkwood correlation factor and excess permittivity, which can give information about the structural properties of polar liquids [4]. Many researchers have attempted to get insight into the nature and degree of interactions that are present in polar liquid mixtures using excess properties [5-10]. Ethylene glycol is recognized as the non-aqueous aprotic solvent having dielectric constant 37.7 at 25 °C, dipole moment 2.28D at 25 °C and boiling point 115 °C. Ethylene glycol is used as a precursor to agrochemicals pharmaceuticals and is also an important solvent and reagent. Ethylene glycol has also been used as the major constituents of binary mixtures of required characteristics. R.J. Sengwa et al [11] have studied the dielectric behavior of ethylene glycol and its mixture with water, glycerol etc. Ethylene glycol, on the other hand is associative liquid and useful in variety of industrial fields like oil industry, refrigeration, air conditioning and others. Dielectric parameters for alcohol-acid binary mixtures have been reported earlier by Chaudhari et al [12]. They observed at systematic change in the dielectric parameters with concentration and chain length of alcohols. Molecular aspect of ethylene glycol and acetic acid is the motivation behind the present study for understanding the molecular interaction in their binary mixture. In the present paper, measured values of static permittivity and permittivity at optical frequency of ethylene glycol, acetic acid and their binary mixtures at 25 °C are reported. The excess static permittivity and Kirkwood correlation factor have also been calculated from measured data. The excess properties provide valuable information for qualitatively analyzing the molecular interaction among molecules.

2. Experimental Methods

Ethylene glycol (AR grade) and acetic acid (AR grade) were commercially obtained from SD Fine-chem Limited (India) and used without further purification. Binary mixtures of ethylene glycol and acetic acid were prepared at nine concentrations by volume fraction. Assuming ideal mixing behavior the concentration was converted into the mole fraction [13]. The dielectric constant was measured at 1 KHz using a Systronix Digital LCR meter 925. The scale of the instrument was calibrated using standard liquids like carbon tetrachloride, benzene, toluene and chlorobenzene. The temperature was maintained at 298±1 K using Sigma constant temperature bath. The refractive indices were measured using Abbe's refractometer. Densities were determined using a 10 mL specific gravity bottle and a K-Roy microbalance. Ethylene glycol was purified by standard methods. The uncertainties in the measurement of dielectric constants, refractive indices and densities were ± 0.0001, ±0.0002 and ± 0.0001 g/cc respectively.

From the experimental values of static permittivity and permittivity at optical frequency, the excess static permittivity (ε_0^E) for binary mixtures was calculated using relation [14],

$$\varepsilon^E = (\varepsilon_0 - \varepsilon_\infty)_m - \left[(\varepsilon_0 - \varepsilon_\infty)_A X_A + (\varepsilon_0 - \varepsilon_\infty)_B X_B\right] \quad \text{.....(1)}$$

where m, A and B are mixture, ethylene glycol and acetic acid respectively.

From the dielectric parameters, the information about the liquid structure as well as orientation of electric dipoles in polar liquids could be obtained using the Kirkwood correlation parameter g [15].

$$\frac{4\pi N\mu^2\rho}{9kTM} g = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} + \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2} \quad \text{.....(2)}$$

where ρ is the density of liquid, M the molecular weight, k the Boltzmann constant, N the Avogadro's number and μ the dipole moment of polar molecule in gas phase, ε_∞ is taken as square of the refractive index. For the mixtures of two polar liquids, the effective averaged angular Kirkwood correlation factor (g^{eff}) of two different molecules is evaluated from the modified Kirkwood equation [16] for the binary mixture.

$$\frac{4\pi N_A}{9kT}\left(\frac{\mu_A^2\rho_A}{M_A}X_A + \frac{\mu_B^2\rho_B}{M_B}X_B\right) g^{eff} = \frac{(\varepsilon_{om} - \varepsilon_{\infty m})(2\varepsilon_{om} + \varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m} + 2)^2} \quad \text{.....(3)}$$

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$$\frac{4\pi N_A}{9kT}\left(\frac{\mu_A^2\rho_A g_A}{M_A}X_A+\frac{\mu_B^2\rho_B g_B}{M_B}X_B\right)g_f=\frac{(\varepsilon_{om}-\varepsilon_{\infty m})(2\varepsilon_{om}+\varepsilon_{\infty m})}{\varepsilon_{om}(\varepsilon_{\infty m}+2)^2} \quad \text{.....(4)}$$

3. Results and Discussion

Measured values of static permittivity and refractive index of ethylene glycol and acetic acid along with their literature values and are found to be in good agreement. The measured values ε_{0m} and $\varepsilon_{\infty m}$ for binary mixtures are presented in Table 1. Fig. 1 shows the variation of static permittivity with variation in concentration of ethylene glycol at 298 K and Fig. 2 shows the variation of permittivity at optical frequency with variation in concentration of ethylene glycol at 298 K.

Table 1 Experimental values of static permittivity and permittivity at optical frequency of mixtures of ethylene glycol+acetic acid at 298 K

Mol fraction of ethylene glycol	Static permittivity at 298 K	Permittivity at optical frequency at 298 K
1	37.7	2.046
0.9	34.5	2.029
0.8	31.4	2.012
0.7	28.2	1.995
0.6	25.1	1.978
0.5	21.9	1.962
0.4	18.8	1.945
0.3	15.6	1.928
0.2	12.5	1.912
0.1	9.35	1.896
0	6.2	1.879

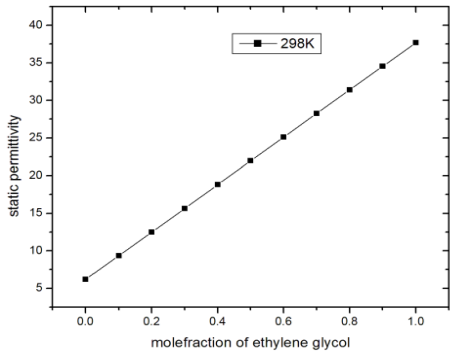

Fig. 1 Plot of static permittivity vs molefraction of ethylene glycol

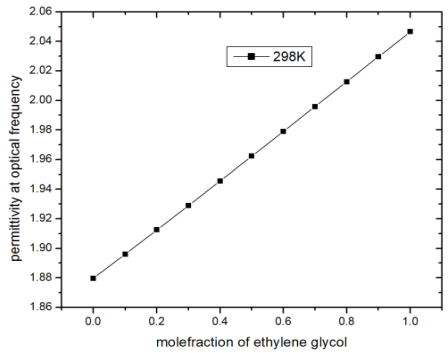

Fig. 2 Plot of permittivity at optical frequency vs molefraction of ethylene glycol

Static permittivity is found to increase linearly with the concentration of ethylene glycol. This indicates interaction between the components of the mixture. Mehrotra et al [17] have reported that elevation of static permittivity with the concentration of the solute in a binary liquid mixture is due to the transition of spherical molecular aggregates to more correlated elongated aggregates, implying that when solute is added it modifies the packing density condition of the dipoles in the solvent. Rana et al [18] have reported that non-linear variation of static permittivity with the concentration of one of the components in the mixture is an indication for the interaction between unlike molecules. Hence, it may be concluded that in this system hetero interaction exists.

3.1 Kirkwood Correlation Factor

Kirkwood correlation factor g is a parameter for obtaining information regarding orientation of electric dipoles in polar liquids [19]. Many researchers have interpreted the fluid structure using the Kirkwood correlation factor. The departure of g value from unity is a measure of degree of short range dipolar alignment due to H-bond interactions. For a liquid in which molecules tend to orient themselves with the parallel dipole alignments in the same direction results in g value greater than unity. When the polar liquid molecules prefer an ordering with antiparallel dipoles, the g value becomes smaller than unity. Table 2 presents the evaluated g^{eff} values of the investigated Ethylene glycol-acetic acid mixtures.

Table 2 Experimental values of Kirkwood correlation factor (g^{eff}) and corrective correlation factor (g_f) of ethylene glycol + acetic acid at 298 K

Mol fraction of ethylene glycol	Kirkwood correlation factor at 298 K	Corrective correlation factor at 298 K
1	2.353	1
0.9	2.267	1.007
0.8	2.169	1.015
0.7	2.058	1.022
0.6	1.93	1.029
0.5	1.784	1.036
0.4	1.616	1.041
0.3	1.422	1.045
0.2	1.196	1.046
0.1	0.93	1.037
0	0.611	1

The effective correlation factor g^{eff} of the binary mixtures are plotted against mole fraction of ethylene glycol at 298 K in Fig. 3. The value of g^{eff} for ethylene glycol is close to unity, or less than unity, indicating antiparallel ordering of dipoles, whereas higher values of g^{eff} for ethylene glycol indicate parallel alignment of the electric dipoles. The plot shows nonlinear variation of g^{eff} over the entire concentration range at 298 K. This confirms the net increase in dipolar ordering due to H-bond complexation.

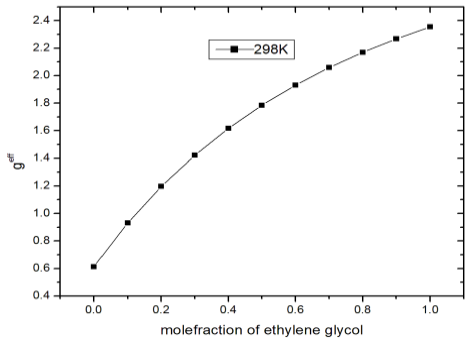

Fig. 3 Plot of Geff vs molefraction of ethylene glycol

3.2 Excess Permittivity

From the excess permittivity values of the liquid binary mixtures, following information can be extracted. (a) $\varepsilon^E=0$ indicates that the mixture constitutes do not interact or there is no change in the net dipole alignments and thus polar liquids have ideal mixing behavior. (b) $\varepsilon^E<0$ indicates that one of the mixture constitutes act as structure breaker for other constituent H-bonded structure with orientation of some of the neighboring dipoles in opposite direction (anti-parallel). Hence, there is decrease in total number of parallel aligned effective dipoles that contributes to the mixture dielectric polarization. (c) $\varepsilon^E>0$ indicates that the constituent of the binary mixture interact in such a way that act as H-bonded structure makers with parallel dipolar alignments in the same direction, which results in increase in total number of parallel align effective dipoles that contributes to the mixture dielectric polarization. The magnitude of ε^E values is the evidence of the strength of unlike molecular H-bond interactions. i.e. the higher the values, the stronger the H-bond molecular connectivity and vice versa (Table 3).

Plot of excess permittivity versus mole fraction of ethylene glycol at 298 K is shown in Fig. 4. The excess permittivity values show mixed behavior with change in concentrations of ethylene glycol in the mixture. Excess permittivity is found to be negative, this indicates dipolar alignment is antiparallel and the effective dipole moment decreases. While in this region, the excess permittivity at optical frequency is positive, and this indicates that both unlike molecules interact in such a way that the dipolar alignment is parallel and the effective dipole moment increases.

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Table 3 Experimental values of excess permittivity (ε_0^E) and excess permittivity at optical frequency (ε_∞^E) of ethylene glycol + acetic acid at 298 K

Mol fraction of ethylene glycol	Excess permittivity(ε_0^E) at 298 K	Excess permittivity at optical freq (ε_∞^E) at 298 K
1	-0.97	0.176
0.9	-1.10	0.148
0.8	-1.00	0.065
0.7	-1.15	0.062
0.6	-1.01	0.019
0.5	-1.50	0.013
0.4	-1.59	0.010
0.3	-1.50	0.005
0.2	-2.00	0.003
0.1	-3.00	0.003
0	-3.08	0.001

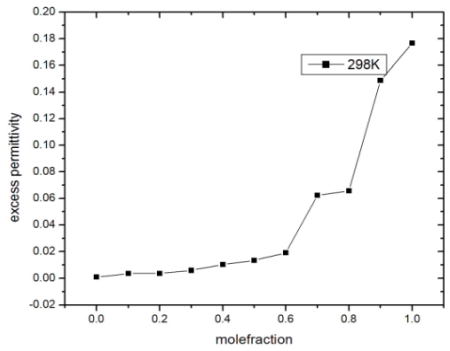

Fig. 4 Curve of excess permittivity vs molefraction

3.3 Estimation Models of Refractive Index

Measured experimental refractive index values of the ethylene glycol + acetic acid binary mixtures were compared to those estimated by four mixing rules which are shown in Table 3 were proposed by Eyring-John (E-J).

$$n = n_A\phi^2{}_A + n_B\phi^2{}_B + 2(\mathrm{n_A n_B})^{1/2} \quad (5)$$

Table 4 Comparison of the experimental refractive index values with those from estimated by the mixing rules proposed by Eyring-John (E-J), Gladstone-Dale (G-D), Newton (NW), Heller (H) for binary mixture of ethylene glycol and acetic acid at the temperature 298 K

Molefraction of Ethylene glycol	Eyring-John (E-J) 298 K	Gladstone-Dale(G-D) 298 K	Newton(NW) 298 K	Heller(H) 298 K
1	4.231	1.430	1.430	1.430
0.9	3.973	1.424	1.424	1.424
0.8	3.771	1.418	1.418	1.412
0.7	3.625	1.412	1.412	1.412
0.6	3.535	1.406	1.407	1.406
0.5	3.501	1.400	1.401	1.400
0.4	3.523	1.394	1.395	1.394
0.3	3.601	1.388	1.389	1.388
0.2	3.735	1.382	1.383	1.382
0.1	3.925	1.376	1.377	1.376
0	4.171	1.371	1.371	1.370

Gladstone-Dale (G-D),

$$n-1 = (\mathrm{n_A}-1)\phi_\mathrm{A} + (\mathrm{n_B}-1)\phi_\mathrm{B} \quad (6)$$

Newton (Nw),

$$n^2-1 = (\mathrm{n^2{}_A}-1)\phi_\mathrm{A} + (\mathrm{n^2{}_B}-1)\phi_\mathrm{B} \quad (7)$$

Heller (H),

$$\frac{n-n_A}{n_A} = \frac{3}{2}\times\frac{\left[\left(\frac{n_B}{n_A}\right)-1\right]}{\left[\left(\frac{n_B}{n_A}\right)+1\right]}\phi_B \quad (8)$$

$$R.M.S.D = \left(\frac{1}{m\sum\left(n_{\exp}-n_{cal}\right)^2}\right)^{1/2} \quad (9)$$

where m is the number of experimental data points.

Table 5 Values of RMSD against various mixing rules

Mixing rule	RMSD Refractive Index
E-J (298 K)	0.0484
G-D (298 K)	0.2637
NW (298 K)	0.3087
H (298 K)	0.1666

The Root Mean Square Deviation (RMSD) values for the Eyring-Johns (E-J), Gladstone-Dale (G-D), Newton (NW) and Heller (H) are presented in Table 5. As RMSD values indicate, refractive index for mixtures are predicted with high accuracy for all the mixtures under consideration. A close similarity is observed between the E-J, G-D and Nw relations. The RMSD values for E-J, G-D and relations are found to be identical when volume additivity is assumed. The best predictions are observed for the E-J followed by H while the RMSD values predicted by G-D and Nw are relatively higher. Since the liquid mixtures of different nature and significantly different molecular sizes are considered, a particular relation provides good agreement at one place and deviates at others. This study indicates that all the theoretical mixing rules are interrelated in a simple quantitative manner and perform well within the limits of experimental error. The applicability of these semi-empirical relations for predicting refractive indices has also been emphasized by others [15-19].

4. Conclusion

This paper reports experimental data for static permittivity, refractive index, density and related properties of binary mixtures of ethylene glycol and acetic acid at 298 K. The investigation of binary mixture showed a systematic change in static permittivity and permittivity at optical frequency with change in concentration of ethylene glycol in acetic acid. Excess permittivity values are found to be positive in ethylene glycol rich region; this indicates both unlike molecules interact in such a way that the dipolar alignment is parallel and the effective dipole moment increases. While in acetic acid rich region excess permittivity value is negative, this indicates that the mixture constitutes interact so as to reduce total effective dipoles. The value of g^{eff} for ethylene glycol is greater than unity indicates parallel alignment of dipoles. Binary mixture data of refractive index are compared with the predicted values using various mixing rules. For refractive index the E-J rule provides the best possible values close to the observed values.

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About the Conference…

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