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Dielectric Behavior of Aqueous Binary Mixtures of Hydrophobic Solutes[#]

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Synopsis. Dielectric constant data for aqueous binary mixtures of ethylene glycol (EG), 2-methoxyethanol (ME), and 1,2-dimethoxyethane (DME) at different mole fractions and at various temperatures are reported. A decrease in dielectric constant values has been observed with the increase in solvent content of the mixture as well as the temperature in case of all the three systems. The variations in Kirkwood's correlation factor (g_K) with respect to the solvent composition in the three types of mixtures have been attributed to the short-range dipolar interactions which lead to structural changes in respective solvent mixtures.

The molecular interactions and the consequent structural arrangements that occur at molecular level in the mixed solvent media can be better understood by the study of their physicochemical properties. Viscosity studies have been carried out by us[1,2] on the aqueous binary mixtures of ethylene glycol (EG), 2-methoxyethanol (ME), and 1,2-dimethoxyethane (DME). The structural changes that occur as a consequence of molecular interactions, in these solutions have been discussed in detail. Nevertheless, it would be of interest to see whether the information obtained from viscosity studies can be corroborated with that obtained from dielectric constant data. With this aim we have undertaken present studies on the dielectric behavior of afore-mentioned binary solutions.

In this paper, therefore, we report the dielectric constant data of aqueous binary mixtures of EG, ME, and DME over the entire solvent composition range and at five different temperatures, viz. 25, 30, 35, 40, and 45 °C. These data are interpreted in terms of structural changes that occur at molecular level in these solutions.

Experimental

Materials. The purification methods of the solvents ethylene glycol (B.D.H., Anala R), 2-methoxyethanol (A.R), and 1,2-dimethoxyethane (Riedel-de-Haenag) were described in our earlier publication.[1] Aqueous mixtures of these solvents were prepared with conductivity water (κ=0.2—0.5$\times$10^{-6} Ω^{-1}cm^{-1}) obtained by triple distillation of water in the presence of alkaline $KMnO_4$.

Apparatus. Dielectric constants were measured with a Wissenchaflich-Technische-Werkstatten (W.T.W) dipolemeter DM 01 using the dielectric cells MFL 3 and MFL 2. The dielectric cell was a cylindrical condenser and was used in connection with the dipolemeter for the dielectric constant measurements. Cell was provided with double jacket for connection to a circulating thermostatic bath for maintaining the constant temperature of the solvent under study. Measuring space of the cell was nickel-plated and space volume was 50 ml. Water was circulated at experimental temperature from Colora–Ultra thermostat with maximum fluctuation of ±0.01 °C. Initially the dielectric constant values of solvents such as water (78.54), propylene carbonate (64.9), methanol (32.63), and benzene (2.27) were measured at 25 °C whose values are available in literature[3,4] and a calibration plot was prepared. The dielectric constant values of test solvents and solvent mixtures were obtained from the calibration plot. The measured dielectric constant values of pure ethylene glycol, 2-methoxyethanol, and 1,2-dimethoxyethane were found to be 40.15, 16.59, and 7.2 which are in good agreement with the literature values 40.80,[5] 17.0,[6] and 7.07.[7] This substantiates the accuracy of our dielectric constant measurements of the test solvent mixtures.

Results and Discussion

The variations of dielectric constant as a function of solvent (EG, ME, or DME) composition at five different temperatures are depicted in Fig. 1. A gradual decrease in dielectric constant with the increase in solvent content showing negative deviation from ideal behavior can be observed in the three cases. But the magnitude of the decrease in dielectric constant at any particular composition is different for each solvent. These negative excesses in dielectric constants can be conveniently expressed in terms of the following relation,[8]

$$\Delta\varepsilon = \varepsilon_{\text{exptl}} - \varepsilon_{\text{ideal}}$$

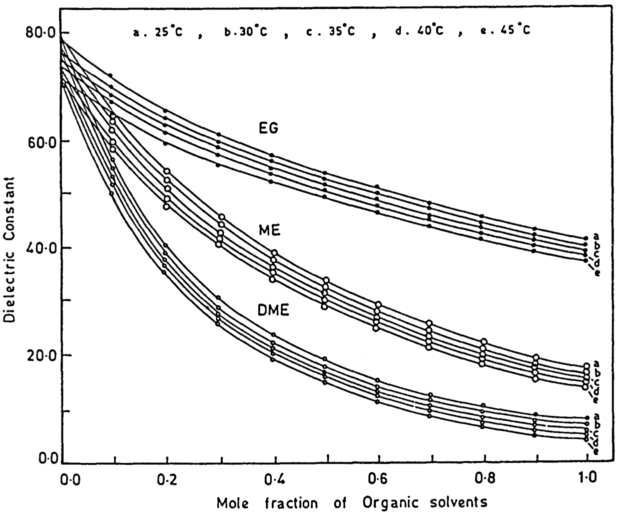

Fig. 1. Variation of dielectric constant with mole fraction of organic solvents (EG, ME, and DME) at different temperatures.

[#] Dedicated in honour of Professor M. V. Ramanamurti, who passed away recently.

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where $\varepsilon_{\text{ideal}}=\varepsilon_1X_1+\varepsilon_2X_2$; ε_1 and ε_2 are the dielectric constants of water and solvent, X_1 and X_2 are the mole fractions respectively. The dependence of $-\Delta\varepsilon$ on mole fraction of solvent is plotted in Fig. 2. The negative deviations from ideal behavior in these three cases is very well projected and the remarkable difference in the magnitude of $-\Delta\varepsilon$ requires some reflection. The increase in magnitude of the minima in $\Delta\varepsilon$ is in accordance with the succinct addition of methyl groups in place of hydrogen atoms of the hydroxyl groups of ethylene glycol. The magnitude of minimum in $\Delta\varepsilon$ follows the order,

$$\text{EC}<\text{ME}<\text{DME}.$$

A more pronounced minimum is observed in the case of DME–water mixtures. The methyl groups are placed symmetrically in DME molecule and no hydrogen bonding is feasible in pure DME liquid. The dielectric behavior observed by adding DME to water can be rationalised, by assuming the formation of associated species (DME and water) of clusters in the mixtures. The variations in the dielectric constant indicate that such new species should be sufficiently long lived to be detected by static dielectric constant measurements and with space dislocation of dipoles such to modify the total polarizability of the system. Therefore, in the aqueous mixtures of DME the symmetrical orientation and favorable correlation of the dipoles of individual water and DME molecules in the aggregates renders the net dielectric constant of the system to decrease. This has resulted in a more pronounced minimum in $\Delta\varepsilon$.

In case of ME–water mixtures, water will participate in the dynamic association process with individual ME molecules (association through intermolecular hydrogen bonding is present in pure ME[9]) and forms the new associated species. However, the absence of one methyl group in ME molecule disrupts the symmetrical orientation of the dipoles of individual water and ME molecules in the associated species. This results in a relatively less decrease in the total polarizability (or overall dielectric constant) of the mixtures compared to that of DME–water system. A relatively less pronounced minimum in $\Delta\varepsilon$ for ME–water mixtures compared to that of DME–water mixtures can be observed from Fig. 2.

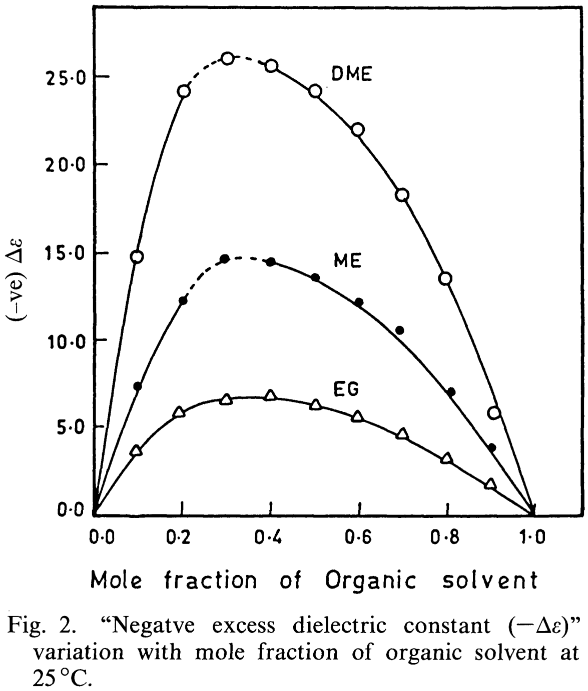

Fig. 2. "Negatve excess dielectric constant ($-\Delta\varepsilon$)" variation with mole fraction of organic solvent at 25 °C.

On the other hand, ethylene glycol–water mixtures show a different dielectric behavior exhibiting a very less decrease in overall dielectric constant of the mixtures. Ethylene glycol participating both in inter- and intramolecular hydrogen bonding will have cyclic association in its pure state which has been evidenced through spectroscopy.[10] The dipoles will be more or less antiparallel in these cyclic associates agree well with the moderate dielectric constant (40.15) of ethylene glycol. The dielectric behavior of these mixtures can be explained by assuming that a "break-up" of the cyclic associates in ethylene glycol occurs. Subsequently, a loose hydrogen-bonded network jumps into existence, between the ethylene glycol and water molecules. The parallel correlation and disordered orientation of dipoles in this network results in an overall less decrease in the dielectric constant of the mixtures.

Further, the displacement of the minimum $\Delta\varepsilon$ toward water rich region (shown by dashed lines in Fig. 2) with the addition of methyl groups supports the postulation of interstitial solvation of water in the ME and DME. With the increase in water content of the mixture the methyl groups are more and more exposed to water and a denser packing of the water molecules around the hydrocarbon moieties occurs. Insulated water molecules possess a lower dielectric constant than the hydrogen-bonded water molecules present in the bulk. The more dense liquid structures in the case of aqueous mixtures of ME and DME are supported by the viscosity increase.[1] The postulation of interstitial solvation of water molecules is also supported by our viscosity studies.[1]

Static dielectric constant measurements provide information[11–14] about the internal structure through the Kirkwood theory.[15] The change of Kirkwood's correlation factor (g_K) as a function of solvent mole fraction for the aqueous mixtures of EG, ME, and DME was evaluated from the experimental values of the dielectric constant using the cole equation,[16]

$$g_K=g\cdot k\cdot T(M_1N_1/d_1+M_2N_2/d_2)/4\pi N(\mu_1N_1+\mu_2N_2)^2 \times(\varepsilon_{12}-\varepsilon_\infty)(2\varepsilon_{12}+\varepsilon_\infty)/\varepsilon_{12}(\varepsilon_\infty+2)^2 \quad (2)$$

where M_1 is the molecular weight of water, N_1 is its mole fraction, d_1 is its density, M_2, M_2, and d_2 are the corresponding quantities for the solvent (EG, ME, and DME), μ_1 and μ_2 are the dipole moment of water and solvent respectively. ε_{12} is the static dielectric constant of the mixtures, ε_∞ is the high frequency dielectric constant (set, as suggested by Dannhauser,[17] equal to 1.1 times the refractive index at sodium light), N is Avogadro's number and k the Boltzmann constant. Literature[3,4] data were used for the dipole moments of water and solvents. The refractive indices of pure liquids were taken in the calculation of ε_∞, since there is not much of a difference in the refractive index value of a

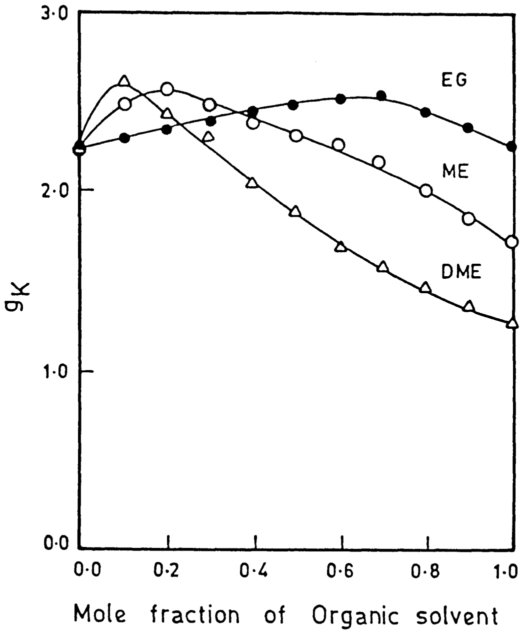

Fig. 3. Variation of Kirkwood's correlation factor with mole fraction of organic solvent at 25 °C.

pure liquid and its mixtures. Also, the calculated g_K values do not involve any error because of this approximation.

The variations of Kirkwood's correlation factor with mole fraction of solvent EG, ME, and DME in water are represented in Fig. 3. In case of EG–water mixtures a continuous increase in the correlation factor upto 0.70 mole fraction of EG and thereafter a decrease with further increase in EG content could be observed. The increase in correlation factor is because of the linear association of EG and water molecules, which results in a roughly parallel alignment of neighboring dipoles in a chain. In EG rich region, the predominant cyclic association (due to excess presence of EG) results in a gradual favorable correlation of the neighboring dipoles decreasing the g_K value gradually as observed in Fig. 3.

In water rich region for aqueous mixtures of ME and DME an increase in correlation factor is observed. Later with the increase in ME and DME content the value of g_K has decreased substantially. The slight maximum observed for g_K in water rich region of aqueous mixtures of ME and DME is an indication of the presence of associated species in the mixtures and the efficient parallel alignment of neighboring dipoles in the species resulted in a greater g_K value. The gradual decrease of correlation factor in aqueous mixtures of ME (or DME) with increase of ME (or DME) content in the mixture (in both the cases) is because of the disruption of the parallel alignment of the individual dipoles of ME (or DME) and water. In other words, excess presence of ME or DME in the mixtures will lead to a rather symmetrical orientation of the antiparallel dipoles (g_K value tending towards unity) of individual water and ME (or DME) molecules, decreasing the correlation factor substantially.

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