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Dielectric characterization and molecular interaction behaviour in binary mixtures of amides with dimethylsulphoxide and 1,4-dioxane

R.J. Sengwa *, Sonu Sankhla, Vinita Khatri

Dielectric Research Laboratory, Department of Physics, J.N.V. University, Jodhpur – 342 005, Rajasthan, India

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ABSTRACT

Hydrogen bond molecular interactions and dipolar ordering in binary mixtures of amides (N-methylformamide (NMF), formamide (FA), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA)) with dimethylsulphoxide (DMSO) and 1,4-dioxane (Dx) have been investigated by dielectric measurements at 30 °C. The static dielectric constant, high frequency limit dielectric constant, excess dielectric constant, effective Kirkwood correlation factor, and corrective Kirkwood correlation factor of the binary mixtures over the entire concentration range were determined to explore the effect of substituted and unsubstituted amides on hetero-molecular interactions. Results confirm that the unlike molecule hydrogen bond interaction strength is comparatively 1.5 times stronger in amides–Dx mixtures as compared to the amides–DMSO mixtures, which vary linearly with the values of dielectric constant and Kirkwood correlation factor of pure amides. Dielectric studies inferred 2:1 complexation of NMF to DMSO/Dx, whereas other amides–DMSO and amides–Dx mixed solvents form most likely 1:1 complexes.

1. Introduction

Static dielectric constant (relative permittivity) is a fundamental property of dipolar liquids and characterization of their dielectric behaviour results in a highly interdisciplinary field of physics, chemistry, biochemistry, pharmaceutical, and materials science. The formation of intra- and intermolecular hydrogen bond (H-bond) has significant effects on the dielectric properties of polar liquids while their measurements provide the path to understand molecular structures and unlike molecule interactions in mixed solvents [1–8]. Investigation of dielectric constants of binary mixtures is important in the design of mixed solvents of required solvating power for the suitable solubility and chemical stability of the solute in the solution. Among the different polar solvents, amides are an important and interesting solvent class, which has large range liquid state properties with broad variation in their dielectric constant values on passing from an unsubstituted amide (formamide) to mono-substituted N-alkylamide (N-methylformamide) and then to the di-substituted N,N-dialkylamide (N,N-dimethylformamide and N,N-dimethylacetamide) [9–12]. They possess the donor–acceptor —CO–NH— peptide bond and most of them have H-bond self-association [13] due to which these polar solvents have been the subject of dielectric measurements [9–12,14–16]. The dielectric investigation of a series of amides molecules mixed with aprotic solvents draws interest to explore the effect of their molecular size on structural properties of mixed solvents [4,12,14–16].

Aprotic solvents generally share ion dissolving power with protic solvents. Dimethylsulphoxide (DMSO) is a dipolar aprotic, and hygroscopic solvent, which possesses large number of pharmacological properties, has the unique capability of penetrating living tissues without causing significant damage. One of the most interesting and significant properties of DMSO is its ability to act as a carrier for transferring drugs through the cell membrane [17]. The 1,4-dioxane (Dx) is a hetero cyclic diethyl ether with each of its two oxygen atoms forming an ether functional group. The molecular structure of Dx may be related to ethanediol and methoxyethanol, but is an almost apolar, aprotic and protophilic solvent [5]. It has very low dipole moment and there is no H-bond pair formation between two Dx molecules in pure liquid state [18,19], which is mainly due to the fact that in Dx molecule ether oxygens offer H-bond acceptor sites, but it cannot self-associate due to lack of H-bond donor positions [20].

In the present paper, dielectric properties of binary mixtures of unsubstituted, N-methylsubstituted and N,N-dimethylsubstituted amides with DMSO and Dx were carried out to confirm H-bond complexation behaviour of these mixed solvents for their solvating applications in biological, pharmaceutical and chemical laboratories. The main aim of the present work is to explore the nature of dipolar ordering, strength of H-bond complexation and stoichiometric ratio corresponding to the stable adduct in the amides–DMSO and amides–Dx mixtures over the entire composition range. Further, an attempt is made to find the correlation between unlike molecular H-bond interaction strength on pure amides dielectric constant and their Kirkwood correlation factor.

* Corresponding author. Tel.: +91 291 2720857; fax: +91 291 2649465.
E-mail address: rjsengwa@rediffmail.com (R.J. Sengwa).

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2. Experimental

2.1. Materials

Grade reagent N-methylformamide (NMF) was purchased from Sigma-Aldrich of USA. Formamide (FA), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA), dimethylsulphoxide (DMSO) and 1,4-dioxane (Dx) were obtained from Loba Chemie, Qualigens Fine Chemicals, and E. Merck of India. Binary mixtures of amides (NMF, FA, DMF, and DMA) with aprotic solvents (DMSO and Dx) were prepared over the entire composition range at room temperature and simultaneously mole fractions of the mixture constituents were determined by weight measurements.

2.2. Measurements

The values of static dielectric constant ε_0 of pure solvents and ε_{0m} of the amides–DMSO and amides–Dx binary mixtures were determined by using 'capacitive measurement method' with a short compensation at 1 MHz. Agilent 4284A precision LCR meter and Agilent 16452A liquid dielectric test fixture were used for the capacitance measurement without and with sample. The dielectric constant measurement accuracy of the fixture is $\pm 0.3\%$ which is estimated by the calibration of the cell with the standard liquids. The high frequency limit dielectric constant ε_∞ of pure solvents and $\varepsilon_{\infty m}$ of the binary mixtures were taken as the square of the refractive index n_D, which was measured with an Abbe refractometer at wavelength of sodium-D light. The maximum measurement error in ε_∞ values is $\pm 0.02\%$. All measurements were made at 30 °C and the temperature was controlled by Thermo-Haake DC10 controller.

3. Data analysis and results

The excess static dielectric constant ε_0^E of the binary mixture is evaluated by the mole-fraction mixture law Eq. (1)

$$\varepsilon_0^E = (\varepsilon_{0m} - \varepsilon_{\infty m}) - [(\varepsilon_{01} - \varepsilon_{\infty 1})X_1 + (\varepsilon_{02} - \varepsilon_{\infty 2})X_2] \quad (1)$$

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 evaluated values together with ε_{0m} and $\varepsilon_{\infty m}$ values of the amides–DMSO and amides–Dx binary mixtures with X_{DMSO} and X_{Dx} are plotted in Figs. 1 and 2, respectively. Fig. 3 shows the dependence of maximum excess dielectric constant values $\varepsilon_0{}^E{}_{(max)}$ of the amides–DMSO and amides–Dx mixtures on the values of static dielectric constant ε_0 and Kirkwood correlation factor g of pure amides.

The dielectric constant of liquid mixtures is commonly demonstrated by mole-fraction mixing law and volume-fraction mixing law. To overcome the controversy to choose one out of these mixing laws on the evaluation of mixture dielectric constant by simple additive formulae, the excess dielectric constant of amides–DMSO and amides–

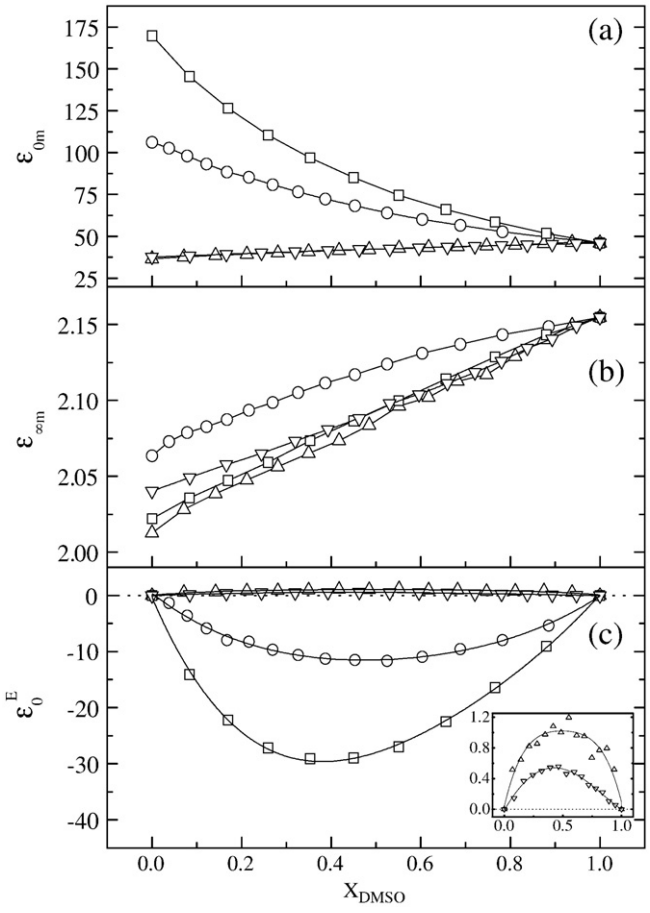

Fig. 1. Plots of ε_{0m}, $\varepsilon_{\infty m}$ and ε_0^E against mole fraction of DMSO, X_{DMSO} for amides–DMSO binary mixtures at 30 °C: (□) NMF–DMSO; (○) FA–DMSO; (Δ) DMF–DMSO; and (▽) DMA–DMSO binary mixtures. In (a) and (b) lines are smooth joining through the data points, whereas in (c) lines are non-linear fits. For clarity, error bars are not indicated. Error bars are smaller than the size of the symbols.

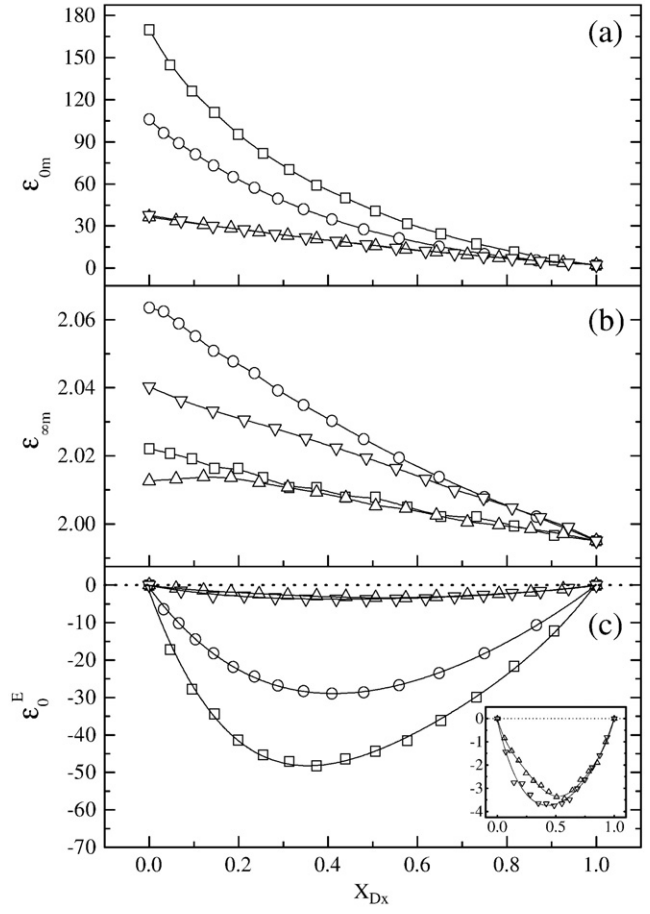

Fig. 2. Plots of ε_{0m}, $\varepsilon_{\infty m}$ and ε_0^E against mole fraction of Dx, X_{Dx} for amides–Dx binary mixtures at 30 °C: (□) NMF–Dx; (○) FA–Dx; (Δ) DMF–Dx; and (▽) DMA–Dx binary mixtures. In (a) and (b) lines are smooth joining through the data points, whereas in (c) lines are non-linear fits. For clarity, error bars are not indicated. Error bars are smaller than the size of the symbols.