Molecular interactions in binary mixtures of 2-aminoethanol with 1,4-dioxane and dimethyl sulfoxide investigated by static permittivity measurements

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Received 20 May 2010; revised and accepted 15 November 2010

The relative static permittivity (dielectric constant) at 1 MHz and high frequency limit permittivity at wavelength of sodium-D line of the binary mixtures of 2-aminoethanol with 1,4-dioxane or dimethyl sulfoxide over the entire composition range have been investigated at 30 °C. The concentration dependent values of excess permittivity and Kirkwood correlation factor of the binary mixtures indicate the formation of hydrogen bonded molecular interactions between these unlike molecules, which modify the dipolar ordering of the self-associated structures of 2-aminoethanol molecules. 2-Aminoethanol forms 1:1 complexes with dimethyl sulfoxide with increase in number of effective parallel aligned dipoles, while with 1,4-dioxane it forms 2:1 stable adducts, which decrease in number of effective parallel aligned dipoles in their binary mixtures.

Keywords: Solution chemistry, Molecular interactions, Dielectric constants, Hydrogen bonded interactions, Aminoethanol, Dioxane, Dimethyl sulphoxide

The activity coefficient, ion interactions and solvation, drug solubility and chemical stability in the solutions are governed by the static permittivity (dielectric constant) of the solvents. Due to these facts, the study of static permittivity of the polar and non-polar solvents becomes the interdisciplinary field of condensed matter physics, analytical chemistry, pharmaceutical preparation, synthesis technology and soft material engineering. The relative static permittivity of dipolar liquids is a fundamental thermodynamical property and its value is significantly influenced by the strength of hydrogen bonded (H–bonded) molecular interactions, which provide the path to understand the inter and intra molecular H–bonded structures.1–14. The value of static permittivity of a dipolar liquid is a function of dipole moment, the Kirkwood correlation factor and the number of molecules per unit volume.15 The permittivity value is a main parameter used in design of mixed solvents of required solvating power to predict the solubility and chemical stability of the solute in solutions.

Among the different organic solvents, 2-aminoethanol (AE), 1,4-dioxane (Dx) and dimethyl sulphoxide (DMSO) are commonly used in biosciences, pharmaceutical and chemical technologies. The molecules of AE have the combined physical and chemical characteristics of both alcohol and amide in one molecule, due to which it finds extensive applications in pharmaceutical industries. DMSO is an aprotic solvent, has several pharmacological activities with large solventing strength to promote chemical reactions when used as a reaction medium in the organic synthesis. Dx is an almost apolar and aprotic solvent but the ether oxygens of its molecule offer H–bonding acceptor sites, which promotes the H–bonded molecular interactions with polar solvents.

The purpose of this study is to provide the precise static permittivity and high frequency limit permittivity values, and to explore the behaviour of H–bonded complexations in the binary mixtures of AE with Dx or DMSO over the entire mixing range to facilitate of their industrial and technological applications.

Experimental

Grade reagent 2-aminoethanol (ethanolamine) was purchased from Loba Chemie, India and 1,4-dioxane and dimethyl sulfoxide were purchased from E. Merck, India. The mass fraction purities of these samples as reported by the manufacturers are: AE > 0.99, Dx > 0.99 and DMSO > 0.995. The binary mixtures of AE with Dx and DMSO at eleven different concentrations over the entire composition range were prepared by volume percent using exact volume amounts of the pure liquids by syringing into stoppered bottles to prevent evaporation and environmental contamination at room temperature. Mole fractions of the mixture constituents were determined by weight measurements.

The static permittivity of pure solvents ε, and of the binary mixtures εm, were determined by capacitive measurement method at alternating current field frequency of 1 MHz. The evaluated ε and εm values
were free from ionic conduction and electrode polarization effects, which was confirmed by the measurements of $\varepsilon$ of the pure solvents over the frequency range 100 kHz to 1 MHz. Agilent 4284A precision LCR meter and Agilent 16452A liquid dielectric test fixture were used for the measurement of capacitance without and with sample. The static permittivity measurement accuracy was $\pm$ 0.3 %, which was estimated by the calibration of the dielectric test fixture using the standard dipolar liquids and their literature values of static permittivities. The high frequency limit permittivity of the pure solvents $\varepsilon_{\infty}$, and, of the binary mixtures $\varepsilon_{\infty m}$, were taken as the square of refractive index, $n^2$, which was measured with an Abbe refractometer at the wavelength of sodium-D line. The maximum measurement error in $\varepsilon_{\infty}$ values was $\pm$ 0.02 %. All measurements were made at a temperature of 30 $\pm$ 0.01 °C using a water circulatory bath mounted with a Thermo-Haake DC10 temperature controller. The measured $\varepsilon_m$ and $\varepsilon_{\infty m}$ values of the AE–Dx and AE–DMSO binary mixtures at various mole fraction of AE, $(X_{AE})$, are recorded in Table 1.

The excess static permittivity, $\varepsilon^E$, also known as permittivity increment, $\Delta \varepsilon$, of the binary mixture is defined by mole-fraction additive law (Eq. 1),

$$\varepsilon^E = \varepsilon_m - (\varepsilon_1 X_1 + \varepsilon_2 X_2)$$

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 evaluated $\varepsilon^E$ values along with $\varepsilon_m$ and $\varepsilon_{\infty m}$ values of the AE–Dx and AE–DMSO binary mixtures are plotted against $X_{AE}$ in Fig. 1.

The Kirkwood correlation factor, $g$, which is a measure of H–bonded dipolar ordering of the molecules in pure liquid state is determined by Eq. (2),

$$\frac{4 \pi N d}{9 k T M} g \mu^2 = \frac{(\varepsilon - \varepsilon_{\infty})(2 \varepsilon + \varepsilon_{\infty})}{\varepsilon (\varepsilon_{\infty} + 2)^2}$$

where $\mu$ is the dipole moment, $d$ is the density of the liquid at temperature $T$, $M$ is the molecular weight, $k$ is the Boltzmann constant, and $N$ is the Avogadro’s number. The $\mu$ values used in Eq. (2) for AE, Dx and DMSO are 2.30, 0.45 and 4.34 D, respectively. The evaluated $g$ values of AE, Dx and DMSO in their pure liquid state are 2.06, 1.01 and 0.99, respectively.

The average angular effective Kirkwood correlation factor, $g_{eff}$, of a binary mixture is determined by the volume-fraction additive mixture law (Eq. 3).

$$\frac{4 \pi N}{9 k T} \left( \frac{\mu_1^2 d_1}{M_1} \phi_1 + \frac{\mu_2^2 d_2}{M_2} \phi_2 \right) g_{eff} = \frac{(\varepsilon_m - \varepsilon_{\infty m})(2 \varepsilon_m + \varepsilon_{\infty m})}{\varepsilon_m (\varepsilon_{\infty m} + 2)^2}$$

For volume fractions $\phi_1 = 1$ and $\phi_2 = 0$, Eq. (3) reduces to Eq. (2) of the $g$ value of pure liquid 1, and vice-versa. The evaluated $g_{eff}$ values (Table 1) of the AE–Dx and AE–DMSO binary mixtures are plotted against the volume fraction of AE, $\phi_{AE}$ in Fig. 2a.

#### Table 1 — Values of the relative static permittivity ($\varepsilon_m$), high frequency limit permittivity ($\varepsilon_{\infty m}$), effective Kirkwood correlation factor ($g_{eff}$) and corrective Kirkwood correlation factor ($g_t$) of the binary mixtures of AE–Dx and AE–DMSO at different mole fraction of AE at 30 °C

<table>
<thead>
<tr>
<th>$X_{AE}$</th>
<th>$\varepsilon_m$</th>
<th>$\varepsilon_{\infty m}$</th>
<th>$g_{eff}$</th>
<th>$g_t$</th>
<th>$X_{AE}$</th>
<th>$\varepsilon_m$</th>
<th>$\varepsilon_{\infty m}$</th>
<th>$g_{eff}$</th>
<th>$g_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>2.26</td>
<td>1.9951</td>
<td>1.01</td>
<td>1.000</td>
<td>0.000</td>
<td>46.05</td>
<td>2.1547</td>
<td>0.99</td>
<td>1.000</td>
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<tr>
<td>0.136</td>
<td>4.65</td>
<td>2.0093</td>
<td>1.42</td>
<td>0.745</td>
<td>0.117</td>
<td>44.91</td>
<td>2.1521</td>
<td>1.05</td>
<td>1.012</td>
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<tr>
<td>0.262</td>
<td>7.34</td>
<td>2.0164</td>
<td>1.51</td>
<td>0.761</td>
<td>0.229</td>
<td>43.94</td>
<td>2.1462</td>
<td>1.12</td>
<td>1.028</td>
</tr>
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<td>0.378</td>
<td>10.15</td>
<td>2.0306</td>
<td>1.58</td>
<td>0.784</td>
<td>0.380</td>
<td>42.64</td>
<td>2.1374</td>
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<tr>
<td>0.486</td>
<td>12.58</td>
<td>2.0420</td>
<td>1.58</td>
<td>0.779</td>
<td>0.443</td>
<td>41.21</td>
<td>2.1316</td>
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<td>1.042</td>
</tr>
<tr>
<td>0.587</td>
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<td>1.64</td>
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<td>0.544</td>
<td>39.67</td>
<td>2.1258</td>
<td>1.35</td>
<td>1.041</td>
</tr>
<tr>
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<td>0.641</td>
<td>38.09</td>
<td>2.1199</td>
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</tr>
<tr>
<td>0.768</td>
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<td>2.0707</td>
<td>1.79</td>
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<td>36.50</td>
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<tr>
<td>0.850</td>
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<td>0.827</td>
<td>34.89</td>
<td>2.1068</td>
<td>1.69</td>
<td>1.027</td>
</tr>
<tr>
<td>0.927</td>
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<td>1.95</td>
<td>0.949</td>
<td>0.915</td>
<td>33.31</td>
<td>2.0996</td>
<td>1.89</td>
<td>1.018</td>
</tr>
<tr>
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<td>31.46</td>
<td>2.0903</td>
<td>2.06</td>
<td>1.000</td>
<td>1.000</td>
<td>31.46</td>
<td>2.0903</td>
<td>2.06</td>
<td>1.000</td>
</tr>
</tbody>
</table>
Defining the Kirkwood correlation factor $g$ as $g_1$ and $g_2$ in pure liquid state for the molecules of liquids 1 and 2 of the binary mixture, respectively, Eq. (3) can be written as the following Eq. (4),

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

where $g_f$ is the corrective Kirkwood correlation factor for a binary mixture. The evaluated $g_f$ values (Table 1) of the AE–Dx and AE–DMSO are plotted against $\phi_{AE}$ in Fig. 2b.

**Results and discussion**

The $\varepsilon$ values of AE, DMSO and Dx in their pure liquid state (Table 1) are found to be in good agreement with the literature values\(^{11,16,17}\). Generally, for ideal binary mixtures of non-interacting molecules, $\varepsilon_m$ varies linearly with mole fraction concentration of the mixture constituents. The $\varepsilon_m$ versus $X_{AE}$ plots of AE–Dx and AE–DMSO mixtures are non-linear (Fig. 1a), which suggests the formation of H–bonded complexes in these mixtures over the entire concentration range. The almost linear behaviour of plots of $\varepsilon_{\infty m}$ versus $X_{AE}$ (Fig. 1b), reflects that the electronic polarization of the molecules of these mixtures, unaffected by their H–bonded hetero-molecular interactions.

Investigations on concentration dependent excess permittivity, $\varepsilon^E$, values of the mixed dipolar solvents provide information regarding the change in number of parallel aligned dipoles contributed to the dielectric polarization, the strength of H–bonded interactions and the molar ratio of stable adduct\(^4,8,11–14\). Figure 1c shows that the AE–Dx mixtures have negative values of $\varepsilon^E$, which confirms the formation of heterogeneous molecular pairs with decrease in the total number of effective parallel aligned dipoles contributing to the molecular dielectric polarization. However, in the case of AE–DMSO mixtures, the positive $\varepsilon^E$ values reveal the formation of H–bonded molecular interactions between AE and DMSO molecules with increase in number of effective parallel aligned dipoles.

The pronounced maximum in $\varepsilon^E$ values at around $X_{AE} \sim 0.5$ for the AE–DMSO mixtures confirms the formation of a stable adduct of 1:1 molar ratio. In the case of AE–Dx mixtures, the maximum magnitude of $\varepsilon^E$ at $X_{AE} \sim 0.63$ suggests the formation of 2:1 complexes of AE and Dx molecules. DMSO forms the H–bonded complexes through its sulphoxide group with the hydroxyl or amide groups of AE molecules. In the Dx molecules, the presence of ether oxygens offers H–bonding acceptor sites, which promote the complexation between AE and Dx molecules. The 2:1 complexes of AE–Dx indicate that both the oxygen atoms of Dx molecules participate in complexation between two neighbouring AE molecules. Comparative values of $\varepsilon^E$ of AE–Dx and AE–DMSO mixtures suggest that the H–bonded interactions between AE and Dx molecules are comparatively stronger than the AE and DMSO molecular interactions.
The Kirkwood correlation factor $g = 1$ confirms the absence of H–bonded dipolar interactions in pure liquid state, whereas $g$ values greater than unity and less than unity are evidence of H–bonded parallel dipolar ordering and antiparallel dipolar ordering, respectively. The experimental $g$ value of AE is 2.06, which confirms its linear polymeric chain type self-associated H–bonded molecular structures with parallel dipolar alignments. The presence of hydroxyl and amide group in the AE molecule results in the formation of H–bonded molecular structures. The $g = 1$ value of both Dx and DMSO reveals their non-associative H–bonded molecular behaviour in pure liquid state.

The $g_{\text{eff}}$ values of the binary mixtures provide qualitative information on the change in dipolar orientation ordering due to the formation of H–bonded complexes. The $g_{\text{eff}}$ values of these mixtures vary non-linearly from the $g$ value of one constituent to that of the other (Fig. 2a). The non-linear behaviour of $g_{\text{eff}}$ values with volume-fraction concentration dependence of the AE–Dx and AE–DMSO binary mixtures suggests the change in dipolar ordering due to heterogeneous H–bonded molecular interactions in these binary mixtures. Figure 2a shows that the $g_{\text{eff}}$ values of the AE–Dx binary mixtures are higher than in ideal behaviour. It may arise due to formation of 2AE:Dx complexes, which enhances the heterogeneous molecular dipolar ordering with the breaking of the self-associated H–bonded structures of AE molecules. The $g_{\text{eff}}$ values less than that in ideal behaviour of the AE–DMSO mixtures reveals that the coalescence of DMSO molecules into H–bonded AE structures results in decrease in unlike molecules dipolar ordering, which may arise due to the formation of 1:1 complexes of AE and DMSO molecules. The corrective Kirkwood correlation factor $g_t$ of the AE–Dx and AE–DMSO mixtures have significant deviation from unity (Fig. 2b), further confirming the change in net dipolar ordering due to unlike molecules dipolar ordering, which may arise due to the formation of 1:1 complexes of AE and DMSO molecules. The corrective Kirkwood correlation factor $g_t$ of the AE–Dx and AE–DMSO mixtures have significant deviation from unity (Fig. 2b), further confirming the change in net dipolar ordering due to unlike molecules dipolar ordering, which may arise due to the formation of 1:1 complexes of AE and DMSO molecules. For AE–DMSO, the $\varepsilon^E$ values are positive, which is also supported by the $g_t$ values greater than unity, whereas for AE–Dx binary mixture the negative $\varepsilon^E$ values are favoured by the $g_t$ values lower than unity.

In the above study, the precise static permittivity and high frequency limit permittivity values of AE–Dx and AE–DMSO binary mixtures are studied over the entire composition range at 30 °C. The excess static permittivity values indicate that these mixtures have non-ideal mixing behaviour. The AE–DMSO mixtures form stable adducts of 1:1 molar ratio. The 2AE:Dx complexes in AE–Dx mixtures confirm that both the ether oxygens of Dx molecule participate in complexation with the two neighbouring AE molecules. The above study indicates that the Dx molecules are built-in via H–bonding into the self-associated AE structures, with a large breaking of H–bonded AE linear chain structures, whereas DMSO molecules H–bond interactions with AE acts as structure–maker for self-associated AE molecules.

**Acknowledgement**

The authors thank the University Grants Commission, New Delhi, for a project grant (No. 33–15/2007 (SR)) under which the work was carried out. The Department of Science and
Technology, Government of India, New Delhi, is kindly acknowledged for providing experimental facilities through the research project (No. SR/S2/CMP-09/2002). One of the authors (SC) is grateful to the UGC, New Delhi, for the award of RFSMS fellowship.

References