Non-ideality in Born-free energy of solvation in alcohol–water and dimethylsulfoxide–acetonitrile mixtures: Solvent size ratio and ion size dependence

HEMANT K KASHYAP and RANJIT BISWAS*

Department of Chemical, Biological and Macromolecular Sciences, and Unit for Nanoscience and Technology, S.N. Bose National Centre for Basic Sciences, JD Block, Sector III, Salt Lake City, Kolkata 700 098
e-mail: ranjit@bose.res.in

Abstract.   Recent extension of mean spherical approximation (MSA) for electrolyte solution has been employed to investigate the non-ideality in Born-free energy of solvation of a rigid, mono-positive ion in binary dipolar mixtures of associating (ethanol–water) and non-associating (dimethylsulfoxide–acetonitrile) solvents. In addition to the dipole moments, the solvent size ratio and ion size have been treated in a consistent manner in this extended MSA theory for the first time. The solvent–solvent size ratio is found to play an important role in determining the non-ideality in these binary mixtures. Smaller ions such as Li^+ and Na^+ show stronger non-ideality in such mixtures compared to bigger ions (for example, Cs^+ and Bu_4N^+). The partial solvent polarization densities around smaller ions in tertiary butanol (TBA)–water mixture is found to be very different from that in other alcohol–water mixtures as well as to that for larger ions in aqueous solutions of TBA. Non-ideality is weaker in mixtures consisting of solvent species possessing nearly equal diameters and dipole moments and is reflected in the mole fraction dependent partial solvent polarization densities.

Keywords.   Non-ideality; Born-energy; dipolar-mixtures; unequal size; MSA.

1.   Introduction

Solvent mixtures are important reaction media as one can tune the polarity, solubility, etc. of a solution by altering the composition. In the traditional barrier crossing model where an activation barrier separates the reactant and product, the reaction time scale is given by the rate at which the reactant crosses the barrier frequency.[1–22] Solvation environment around a reactant affects the barrier-crossing rate both via solvent arrangement and time-dependent re-arrangement of solvent particles.[1–22] As inter-diffusion and preferential solvation significantly slows down the dynamics in binary mixtures than in pure solvents,[23–40] solvent effects on chemical reactions are expected to be different in binary liquid mixtures. In addition to simple chemical reactions, transport property such as ion mobility is also significantly modified in binary mixtures. For example, limiting ionic conductivity of uni-positive alkali metal ions tertiary butanol (TBA)–

water exhibits a non-monotonic alcohol mole fraction dependence.[41] Moreover, bigger ion such as tetrabutyl ammonium ion (Bu_4N^+) shows a linear mole fraction dependence in the same mixture.[41] This different composition dependence originates partly from the nature of solvation of these individual ions and partly from the modification of the solution dynamics. In order to understand solvent effects on these simple events in binary mixtures, one therefore needs to investigate the solution structure in terms of intra- and inter-molecular liquid correlations and modifications of solution dynamics.

Anomalous physical properties of alcohol–water mixtures at room temperature have been studied extensively over the years.[42–69] Different structures and mechanism for formation of those structures in alcohol–water solutions at low to high alcohol concentrations have been proposed.[42–69] Several experimental studies indicate that at low alcohol content water structure is stronger than that in pure water.[70–72] This is then used to explain the anomalous decrease in entropy,[42,43] anomalous increase in sound

*For correspondence

attenuation coefficient[44] and emergence of an endo-thermic peak in the partial heat of solution of several crystalline salts in aqueous alcohol solutions.[70,71] Further experimental support[72] to this idea came from the fact that partial molal heat of solution showed an even larger endothermic peak when the relevant experiments were carried out at ~ 277 K. At higher alcohol concentration, however, the water structure breaks down and the characteristic chain-like structure of pure alcohol predominates.[50–72] At high water content, an infinitely dilute third component (an ion or a neutral solute) competes with the alcohol molecules to be properly 'surrounded' by water structure.[70–72] This is dictated by the relative interaction strengths between the solute and the solvent molecules of different species. As a result, the structure forming or breaking ability of alcohol in water is modified in presence of an ion or a solute.[70–72] Moreover, specific interactions among these components may favour enriching of one component over the other in the first few solvation shells giving rise to what is known as preferential solvation. In such a situation one would like to ask the following questions. First, will there be any preferential solvation and thus non-ideality in the absence of any solute–solvent and solvent–solvent specific interactions? This can indeed be a situation as evidenced by the recent simulation studies of non-ideality in viscosity for model binary mixtures.[73,74] Second, how solvent size disparity would affect the preferential solvation and thus the non-ideality? Third, what are the effects of solute size on the non-ideality? Fourth, can one develop a theoretical formalism which will be simple and analytically tractable yet capable of describing the liquid structure in these complex mixtures, at least, qualitatively?

Recently, we have extended the mean spherical approximation[75] (MSA) framework in order to investigate answers to these questions. The extended MSA incorporates the difference in solvent diameters and dipole moments as well as ion size systematically for the first time.[76] In this article, we apply this extended MSA formalism to study the solvent size ratio dependence of non-ideality in Born-free energy of solvation of an infinitely dilute ion in two different types of binary mixtures at different mole fraction of the solvent components: mixtures containing associating (that is, H-bonding) solvents and those made up of non-associating solvents. We consider mono-hydroxy alcohol such as ethanol and water in the first category, and dimethyl sulfoxide (DMSO) mix-ture and acetonitrile in the second. The DMSO–acetonitrile is interesting because the larger component (DMSO) possesses higher dipole moment.[5,77] This leads to a competition in packing around a dissolved ion in DMSO–acetonitrile mixture. More-over, the molecular diameters of these solvents are similar[5,77] and hence the non-ideality in polarization structure (and hence in Born-free energy of solvation) is expected to be weaker. In contrast, the dipole moment of water is slightly larger than the alcohol studied here but the size is considerably smaller. This assists water molecules to be preferably chosen in the first solvation shell and hence the non-ideality is likely to be stronger. Therefore, larger ions would be able to accommodate the larger solvent components leading to a more 'homogeneous' solvation structure. This, in turn, will render the non-ideality weaker. It is to be noted here that the preferential solvation in model binary mixtures have been studied earlier.[78,79] In these studies either the size disparity of all the species was not treated systematically or the solvent size ratio was not incorporated. However, these studies indicated that specific interactions among the components are not crucial for giving rise to non-ideality.[78]

In the present, work we are studying solvent structure around an ion in a binary mixture of fluids made up of dipolar hard spheres with unequal radii and dipole moments.[80–87] We have, therefore, used the MSA frameworks provided by Isbister and Bearman,[82] Chan *et al*[80] and Blum *et al*[84–87]. Here we model the solvent molecules of different species as dipolar hard spheres with single point dipoles located at the centers.[80] Ions are considered as hard spheres carrying point charges of one unit at the respective centers.[80] The ions are present at infinite dilution. The electroneutrality is maintained, as usually done in the MSA. The molecular diameters of solvent molecules have been calculated from the van der Waals' space filling model.[77] Experimental values of dipole moments are used to specify different solvent components.[5] Experimental crystallographic ionic radii are used to denote the sizes of the ions studied.[5] Mole fraction dependent densities are taken from relevant experiments[44,88–89] and used to calculate the mole fraction dependent properties of these binary mixtures. As we use the MSA framework in our formalism, the analytical tractability of the former is retained. This makes the present theory simple to use in cases where intra and inter-molecular correlations are required as inputs. However, the correlations obtained

by the present theory would be at best semi-quantitative as MSA is known to work rather poorly for strongly dipolar systems.[80]

The organization of the rest of the paper is as follows. We describe the theoretical formulation in the next section. This will be brief as the details have been given elsewhere. Numerical results and discussions are given in §III. Concluding remarks are provided in §IV.

2. Theoretical formulation

We shall present here briefly the relevant theory as details have been discussed in ref. 76. Let us consider a solution of an electrolyte of equal-sized ions in a binary dipolar mixture. Let R_i and R_j be the hard sphere diameters of the two types of solvent molecules with dipole moments μ_i and μ_j, respectively. The solvent number densities are ρ_i and ρ_j. Here, $R_i \neq R_j$, and $\mu_i \neq \mu_j$. The electro-neutrality is maintained by setting

$$\sum_\alpha \rho_\alpha z_\alpha = 0, \tag{1}$$

where ρ_α denotes the number density of ionic species α with charge z_α and diameter $R_\alpha = R$. The interaction potentials are given by[79–80]

$$u_{\alpha\beta}(r) = z_\alpha z_\beta e^2 / r, \quad r > R_{\alpha\beta} = R, \tag{2a}$$

$$u_{\alpha j}(\mathbf{r}, \omega_2) = -z_\alpha e \mu_j E_2 / r^2,$$
$$r > R_{\alpha j} = (R + R_j)/2 \tag{2b}$$

$$u_{i\beta}(\omega_1, \mathbf{r}) = z_\beta e \mu_i E_1 / r^2,$$
$$r > R_{i\beta} = (R_i + R)/2 \tag{2c}$$

$$u_{ij}(\omega_1, \mathbf{r}, \omega_2) = -\mu_i \mu_j D_{12} / r^3,$$
$$r > R_{ij} = (R_i + R_j)/2, \tag{2d}$$

where α, β indices are for ions and i, j indices are for dipoles. $D_{12} = \hat{\mu}(\omega_1) \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \hat{\mu}(\omega_2)$, which arises due to the angle dependent parts of the interaction potentials. $E_i = \hat{\mu}(\omega_i) \cdot \hat{\mathbf{r}}$. In above equations, e represents the elementary charge, $\mathbf{I}$ denotes a 3×3 unit tensor, and $\hat{\mathbf{r}}$ is the unit vector from the molecule denoted by the first index towards the one denoted by second index. The orientation of ith type dipole is described by ω_i.

Now the Ornstein–Zernike (OZ) relation can be used to obtain the MSA solution for the correlation functions in an electrolyte solution of binary dipolar mixture.[80] The relevant OZ expressions along with the MSA closure relations are discussed in ref. 80. Subsequently, the algebra described in Chan *et al*[80] leads to the following expressions for the wave number (k) and orientation dependent static correlation functions

$$\tilde{h}_{\alpha\beta}(k) = \tilde{c}_{\alpha\beta}(k) + \sum_\gamma \rho_\gamma \tilde{c}_{\alpha\beta}(k)\tilde{h}_{\gamma\beta}(k) +,$$
$$\sum_k \rho_k \langle \tilde{c}_{\alpha k}(\mathbf{k}, \omega_3)\tilde{h}_{k\beta}(\omega_3, \mathbf{k})\rangle_{\omega_3} \tag{3a}$$

$$\tilde{h}_{\alpha j}(\mathbf{k}, \omega_2) = \tilde{c}_{\alpha j}(\mathbf{k}, \omega_2) + \sum_\gamma \rho_\gamma \tilde{c}_{\alpha\gamma}(k)\tilde{h}_{\gamma j}(\mathbf{k}, \omega_2) +$$
$$\sum_k \rho_k \langle \tilde{c}_{\alpha k}(\mathbf{k}, \omega_3)\tilde{h}_{kj}(\omega_3, \mathbf{k}, \omega_2)\rangle_{\omega_3} \tag{3b}$$

$$\tilde{h}_{i\beta}(\omega_1, \mathbf{k}) = \tilde{c}_{i\beta}(\omega_1, \mathbf{k}) + \sum_\gamma \rho_\gamma \tilde{c}_{i\gamma}(\omega_1, \mathbf{k})\tilde{h}_{\gamma\beta}(k) +$$
$$\sum_k \rho_k \langle \tilde{c}_{ik}(\omega_1, \mathbf{k}, \omega_3)\tilde{h}_{k\beta}(\omega_3, \mathbf{k})\rangle_{\omega_3}, \tag{3c}$$

$$\tilde{h}_{ij}(\omega_1, \mathbf{k}, \omega_2) = \tilde{c}_{ij}(\omega_1, \mathbf{k}, \omega_2) +$$
$$\sum_\gamma \rho_\gamma \tilde{c}_{i\gamma}(\omega_1, \mathbf{k})\tilde{h}_{\gamma j}(\mathbf{k}, \omega_2) +$$
$$\sum_k \rho_k \langle \tilde{c}_{ik}(\omega_1, \mathbf{k}, \omega_3)\tilde{h}_{kj}(\omega_3, \mathbf{k}, \omega_2)\rangle_{\omega_3}. \tag{3d}$$

Carrying out the angular convolution in (3a–d) and using the charge neutrality condition, and setting

$$\rho_c = \sum_\gamma \rho_\gamma z_\gamma^2, \tag{4}$$

$$\rho_I = \sum_\gamma \rho_\gamma, \tag{5}$$

we obtain the following coupled set of equations for the correlation functions due to the electrostatic interactions between ions, ion-dipole and dipoles[76]

$$\tilde{h}_{\alpha\beta}^C(k) = \tilde{c}_{\alpha\beta}^C(k) + \rho_c \tilde{c}_{\alpha\gamma}^C(k)\tilde{h}_{\gamma\beta}^C(k)$$
$$-\frac{1}{3}\sum_k \rho_k \tilde{c}_{\alpha k}^E(k)\tilde{h}_{k\beta}^E(k) \tag{6a}$$

$$\tilde{h}_{\alpha j}^{E}(k) = \tilde{c}_{\alpha j}^{E}(k) + \rho_c \tilde{c}_{\alpha \gamma}^{C}(k) \tilde{h}_{\gamma j}^{E}(k)$$

$$+ \frac{1}{3} \sum_k \rho_k \tilde{c}_{\alpha k}^{E}(k) \tilde{h}_{kj}^{+}(k) \tag{6b}$$

$$\tilde{h}_{i\beta}^{E}(k) = \tilde{c}_{i\beta}^{E}(k) + \rho_c \tilde{c}_{i\gamma}^{E}(k) \tilde{h}_{\gamma \beta}^{C}(k)$$

$$+ \frac{1}{3} \sum_k \rho_k \tilde{c}_{ik}^{+}(k) \tilde{h}_{k\beta}^{E}(k) \tag{6c}$$

$$\tilde{h}_{ij}^{+}(k) = \tilde{c}_{ij}^{+}(k) - \rho_c \tilde{c}_{i\gamma}^{E}(k) \tilde{h}_{\gamma j}^{E}(k)$$

$$+ \frac{1}{3} \sum_k \rho_k \tilde{c}_{ik}^{+}(k) \tilde{h}_{kj}^{+}(k). \tag{6d}$$

Now using the algebra described in ref. 76 we obtain the following expression for the Born-free energy of solvation for an ion

$$E_{\text{Born}} = \sum_k \rho_k \int d\mathbf{r} \langle \Omega_{\alpha k}(\mathbf{r}, \omega) g_{\alpha k}(\mathbf{r}, \omega) \rangle_\omega$$

$$= -\frac{4\pi z_\alpha^2 e}{3} \sum_k \rho_k \Omega_k \int_{R_{\alpha k}}^{\infty} dr h_{\alpha k}^{E}(r), \tag{7}$$

where the second equality follows because $h_{\alpha k}^{E}(r) = 0$ for $r < R_{\alpha k}$. We now need to find

$$\int_{R_{\alpha k}}^{\infty} dr h_{\alpha k}^{E}(r)$$

for evaluating E_{Born}. This is calculated from the ion-dipole correlation function as follows[79,80]

$$H_{\alpha j}^{E}(x) = 2\pi \int_{x}^{\infty} dr P_1(x/r) r h_{\alpha j}^{E}(r),$$

$$= 2\pi x \int_{R_{\alpha j}}^{\infty} dr h_{\alpha j}^{E}(r) = x H1_{\alpha j}^{E} \text{ for } x \le R_{\alpha j}, \tag{8}$$

where

$$H1_{\alpha j}^{E} = 2\pi \int_{R_{\alpha j}}^{\infty} dr h_{\alpha j}^{E}(r),$$

is a constant that needs to be determined. Equation (7) and the above discussion now provide the fol-

lowing expression of Born-energy (E_{Born}) for an ion dissolved in binary mixture of dipolar solvents with unequal size and different dipole moments

$$E_{\text{Born}} = -\frac{2z_\alpha^2 e}{3} \sum_k \rho_k \mu_k H1_{\alpha k}^{E}$$

$$= -\frac{2z_\alpha^2 e}{3} \sum_k \rho_k \mu_k H1_{k\alpha}^{E}. \tag{9}$$

Now we need to calculate $H1_{k\alpha}^{E}(= H1_{\alpha k}^{E})$. Baxter factorization[80,90] gives for $x > S_{j\alpha} = (R_j - R_\alpha)/2$

$$H_{j\alpha}^{E}(x) = -Q_{j\alpha}^{E}(x)$$

$$+ \frac{1}{3} \sum_k \rho_k \int_{S_{jk}}^{R_{jk}} dy Q_{jk}^{+}(y) H_{k\alpha}^{E}(x - y). \tag{10}$$

From (8) when $S_{j\alpha} < x \le R_{j\alpha}$

$$x H1_{j\alpha}^{E} = -Q_{j\alpha}^{E}(x)$$

$$+ \frac{1}{3} \sum_k \rho_k H1_{k\alpha}^{E} \int_{S_{jk}}^{R_{jk}} dy Q_{jk}^{+}(y)(x - y), \tag{11}$$

where $Q_{jk}^{+}(x)$ depends solely on the dipolar mixture properties and is given by,[76,79,80]

$$Q_{ij}^{+}(x) = 3 \left[\frac{1}{2} a_{ij}(x - R_{ij})(x - S_{ij}) + b_{ij}(x - R_{ij}) \right], \tag{12}$$

where the values of a_{ij} and b_{ij} are described in ref. 76.

Equation (11) consists of two coupled simultaneous equations in $H1_{j\alpha}^{E}$ when $j = 1, 2$ and α is fixed (a given ionic species). Using Baxter's method[90] we obtain the following expression for $C_{j\alpha}^{E}(x)$

$$C_{j\alpha}^{E}(x) = -Q_{j\alpha}^{E}(x), \quad x R_{j\alpha}$$

$$+ \frac{1}{3} \sum_k \rho_k \int_{S_{kj}}^{R_{kj}} dy Q_{kj}^{+}(y) Q_{k\alpha}^{E}(x + y), \quad x R_{j\alpha} \tag{13}$$

with closure relation

$$C_{j\alpha}^{E}(x) = 2\pi e \beta \mu_j, \quad x \ge R_{j\alpha}. \tag{14}$$

Therefore, from (13) and (14), we obtain

$$2\pi e\beta\mu_j = -Q_{j\alpha}^E(x)$$

$$+\frac{1}{3}\sum_k \rho_k \int_{S_{kj}}^{R_{kj}} dy Q_{kj}^+(y) Q_{k\alpha}^E(x+y) , \ x \geq R_{j\alpha}$$

$$(15)$$

Equation (15) contains two coupled simultaneous equations in $Q_{j\alpha}^E(x)$ when $j = 1, 2$ for a fixed α. Using the expressions of $Q_{j\alpha}^E(x)$ given in ref. 76 and carrying out the relevant algebra, from (11) we obtain the following expressions for as,

$$H1_{1\alpha}^E = \frac{\begin{aligned}-Q_{1\alpha}^E(R_{1\alpha})[R_{2\alpha}-R_{2\alpha}I_{22}+\tilde{I}_{22}]-\\Q_{2\alpha}^E(R_{2\alpha})[R_{1\alpha}\overline{I}_{12}-\tilde{I}_{12}]\end{aligned}}{\begin{aligned}[R_{1\alpha}-R_{1\alpha}I_{11}+\tilde{I}_{11}][R_{2\alpha}-R_{2\alpha}I_{22}+\tilde{I}_{22}]-\\ [R_{1\alpha}\overline{I}_{12}-\tilde{I}_{12}][R_{1\alpha}\overline{I}_{21}-\tilde{I}_{21}]\end{aligned}} , \quad (16)$$

$$H1_{2\alpha}^E = \frac{\begin{aligned}-Q_{2\alpha}^E(R_{2\alpha})[R_{1\alpha}-R_{1\alpha}I_{11}+\tilde{I}_{11}]-\\Q_{1\alpha}^E(R_{1\alpha})[R_{2\alpha}\overline{I}_{21}-\tilde{I}_{21}]\end{aligned}}{\begin{aligned}[R_{1\alpha}-R_{1\alpha}I_{11}+\tilde{I}_{11}][R_{2\alpha}-R_{2\alpha}I_{22}+\tilde{I}_{22}]-\\ [R_{1\alpha}\overline{I}_{12}-\tilde{I}_{12}][R_{1\alpha}\overline{I}_{21}-\tilde{I}_{21}]\end{aligned}} , \quad (17)$$

where I_{ij}, $\overline{I}_{ij}$ and $\tilde{I}_{ij}$ are given in ref. 76.

Substitution of $H1_{j\alpha}^E$ (from (16) and (17)) into (9) provides the required expression for E_{Born}. Born free energy (F_{Born}) of solvation is then calculated from the following relation[80]

$$F_{\text{Born}} = \int_0^e de(E_{\text{Born}}/2) . \tag{18}$$

The expressions for partial polarization densities of constituent solvents around an ion with charge $z_\alpha e$ at infinite dilution has been shown to be given by[79,80]

$$P_\alpha(r) = \sum_k P_{\alpha k}(r)$$

$$= \frac{1}{4\pi}\sum_k \rho_k \Omega_k \int d\omega g_{\alpha k}(r,\omega)(\Omega_k(\omega)\cdot\hat{\mathbf{r}}) \tag{19}$$

where $P_{\alpha k}(r)$ is partial polarization density of kth species. Since $h_{\alpha k}^E = h_{k\alpha}^E$ one can write the above equation as

$$P_\alpha(r) = \frac{1}{3}\sum_k \rho_k \mu_k h_{\alpha k}^E(r) = \frac{1}{3}\sum_k \rho_k \mu_k h_{k\alpha}^E(r)$$

$$= \frac{1}{3}\sum_k \rho_k \mu_k \left[\frac{1}{2\pi r}\left\{\frac{1}{r}H_{k\alpha}^E(r) - \frac{d}{dr}H_{k\alpha}^E(r)\right\}\right],$$

$$(20)$$

where $H_{k\alpha}^E(r)$ is given by[79,80]

$$H_{j\alpha}^E(r) = rH1_{j\alpha}^E , \ r \leq R_{j\alpha}, \tag{21a}$$

$$H_{j\alpha}^E(r) = -Q_{j\alpha}^E(r) + \frac{1}{3}\sum_k \rho_k \int_{S_{jk}}^{R_{jk}} ds Q_{jk}^+(s)H_{k\alpha}^E(r-s),$$

$$r > R_{j\alpha}. \ r > R_{j\alpha} . \tag{21b}$$

3. Numerical results and discussion

As discussed in the Introduction, we would now present numerical results of two different mixtures, namely; ethanol–water and DMSO–acetonitrile mixtures. The relevant parameters required for calculations are summarized in table 1. All the calculations done here are at 298·15 K. The non-ideality in mole fraction (x_2) dependent Born free energy of solvation of an ion is expressed as follows[76,78,79]

$$\Delta F_{\text{Born}}(x_2) = F_{\text{Born}}(x_2) - F_{\text{Born}}(x_2 = 0)$$

$$-x_2[F_{\text{Born}}(x_2 = 1) - F_{\text{Born}}(x_2 = 0)]$$

$$= F_{\text{Born}}(x_2) - [(1-x_2)F_{\text{Born}}(x_2 = 0) + x_2 F_{\text{Born}}(x_2 = 1)]$$

$$(22)$$

The second equality of (22) indicates that the excess Born-free energy of solvation is the deviation in Born-free energy of solvation for an ion at a mole fraction (x_2) in a binary mixture from the sum of the mole fraction weighted Born-free energies in the pure

Table 1. Solvent parameters used in the calculation.

Solvent	Dipole moment (D)	Diameter* $(10^{-8}$ cm)
Water	1·85	2·80
Ethanol	1·69	4·78
Acetonitrile (ACN)	3·5	4·5
Dimethylsulfoxide (DMSO)	4·1	5·3

*The diameters of Li$^+$ and C$_4$ ions used in the calculations are 1·24 and 10 Å, respectively

components. We would use (22) to investigate the mole fraction dependent non-ideality in ΔF_{Born} in ethanol–water and DMSO–acetonitrile mixtures.

Figure 1 shows the mole fraction dependence of Born-free energy of solvation, F_{Born} and excess Born-free energy of solvation, ΔF_{Born} in these mixtures for two ions of very different diameters, Li^+ and tetrabutyl ammonium ion (C$_4$). The Born-free energy of solvation, F_{Born} (upper panel) indicate different mole fraction dependence in ethanol–water and DMSO–acetonitrile mixtures. The insensitivity (or very weak dependence) of F_{Born} on DMSO mole fraction in DMSO–acetonitrile mixture (filled symbols) is a manifestation of competition between packing and electrostatic interactions. The dipole moment of DMSO is little larger than that of acetonitrile and hence ion–dipole interaction would favor DMSO more in number in the first solvation shell of an ion. However, packing constraint (repulsion) would not favour disfavor DMSO as its size is slightly larger than acetonitrile. Therefore, a delicate balance between these two interactions renders the mole fraction depend-

ence of F_{Born} a very weak one. Note also that even in ethanol–water mixture (open symbols), the mole fraction dependence in F_{Born} for C$_4$ (triangles) is very weak. This indicates that C$_4$ being large in size can accommodate larger solvent molecules more favourably than smaller ions, resulting much less concentration fluctuations in the nearest neighbour solvent arrangements. As expected, the values of F_{Born} for these ions in pure solvents match exactly with predictions from the works of Chan *et al*[80].

The lower panel of figure 1 shows the mole fraction dependence of the excess Born-free energy of solvation, ΔF_{Born} for Li^+ and C$_4$ in ethanol–water and DMSO–acetonitrile mixtures. Note that the slope of ΔF_{Born} for DMSO–acetonitrile mixture is opposite to that found in ethanol–water mixtures. Similar results have also been found for smaller ions in TBA–water mixtures when we studied aqueous solutions of methanol and TBA.[76] The positive values of ΔF_{Born} clearly indicates that DMSO molecules around a small ion such as Li^+ is increasingly disfavored due to
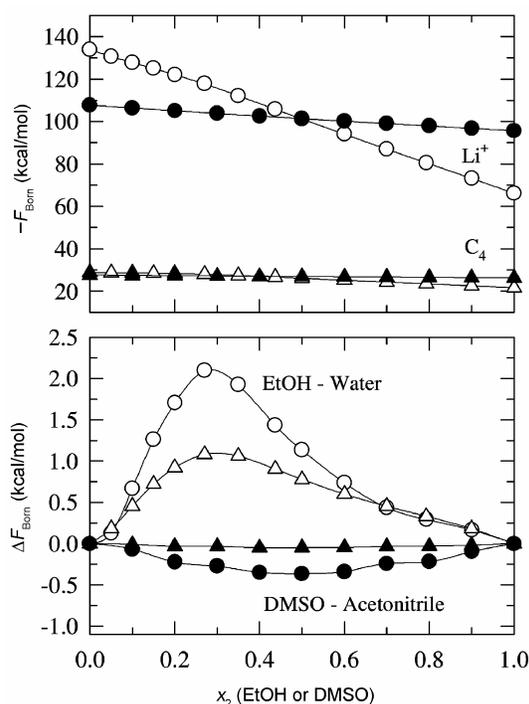

Figure 1. Born-free energy of solvation F_{Born} (upper panel) and excess Born-free of solvation ΔF_{Born} (lower panel) for Li^+ (circles) and C$_4$ (triangles) ions as a function of mole fraction of second (larger) component (x_2) in ethanol–water (open symbols) and dimethylsulfoxide–acetonitrile (solid symbols) mixtures.
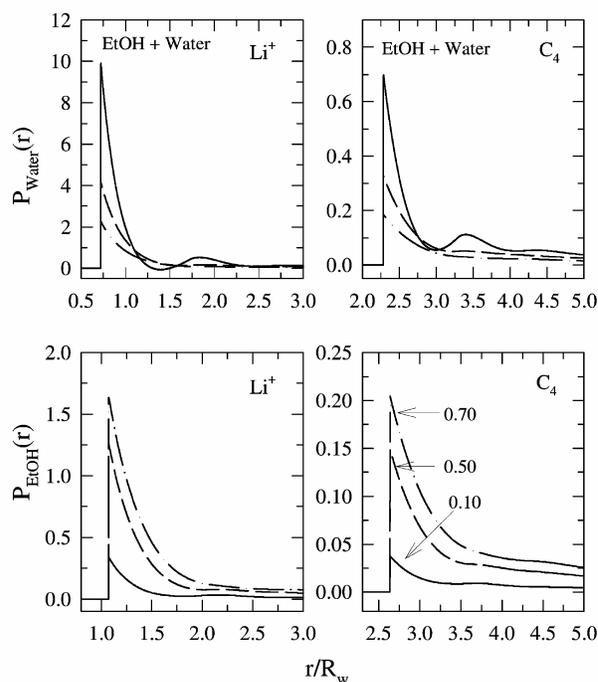
Figure 2. Partial polarization densities of water $P_{\text{water}}(r)$ and ethanol $P_{\text{EtOH}}(r)$ (both scaled by $\sqrt{k_B T / R_w^3}$) around Li^+ and C$_4$ ions as a function of distance r (scaled by water diameter R_w) from the centre of the ion at 0·10 (solid line), 0·50 (short dashed line) and 0·70 (dotted dashed line) mole fractions of ethanol in ethanol–water mixtures. For discussion, see text.

larger size. This is indeed a manifestation of dominance of repulsive interactions in determining the solvation structure around a solvated ion. Another important aspect of this figure (lower panel) is that the absolute magnitude of ΔF_{Born} is 4 times less for Li^+ in DMSO–acetonitrile mixture than that in ethanol–water solution. This indicates that the solvent size ratio indeed plays a crucial role in determining the extent of non-ideality in binary mixtures. This is one of the new results of the present scheme described here. Also, the position of the extremum of DMSO–acetonitrile curve occurs at almost 50:50 composition whereas that for ethanol–water occurs at ~ 0·3 mol fraction of ethanol. This further proves that the solvent size ratio not only determines the extent of non-ideality in Born-free energy of solvation in binary mixtures, but determines also the location of the extremum on the mole fraction axis.

We next present the numerical results on the partial solvent polarization densities around Li^+ and C_4 in these mixtures at three different mole fractions of either ethanol or DMSO. Figure 2 shows the partial solvent polarization densities in ethanol–water mixtures. While the upper panels describe the partial polarization densities of water around Li^+ and C_4, those of ethanol are shown in the lower panels. Note that at the lowest ethanol mole fraction (0·10), both the first and second solvation shells are clearly visible whereas the second solvation shell disappears with the increase in alcohol mole fraction in the mixture. As expected, the peak value of the water polarization density decreases with the increase in ethanol concentration and *vice-versa*. The results for DMSO–acetonitrile mixtures are shown in figure 3. As observed in the ethanol–water mixture (figure 2), the polarization peak also decreases here as one increases the DMSO (larger component) concentration. However, the second solvation shell is well formed for most of the cases in this mixture. This is in contrast to what has been observed in ethanol–water mixtures (figure 2). This is again due to the larger size of the solvent components constituting the binary mixtures.

We show in figure 4 the mole fraction dependence of partial polarization peaks for these two mixtures. The decrease or increase of partial solvent polarization peak is non-linear for ethanol–water mixtures,
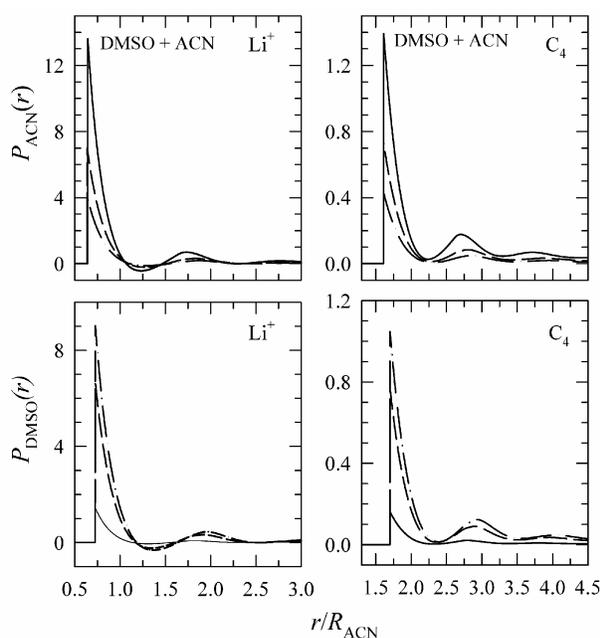

Figure 3. Partial polarization densities of acetonitrile $P_{ACN}(r)$ and dimethylsulfoxide $P_{DMSO}(r)$ (both scaled by $\sqrt{k_B T / R_{ACN}^3}$) around Li^+ and C_4 ions as a function of distance r (scaled by water diameter R_{ACN}) from the centre of the ion at 0·10 (solid line), 0·50 (short dashed line) and 0·70 (dotted dashed line) mole fractions of DMSO in DMSO–ACN mixtures. For discussion, see text.
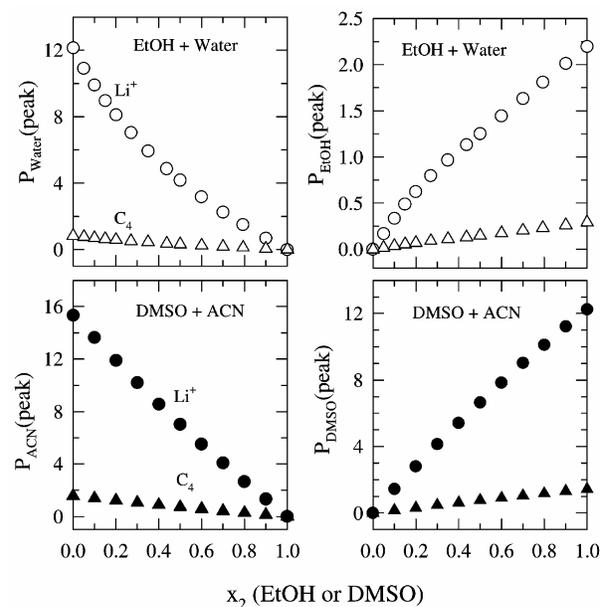
Figure 4. Upper panels: Comparison of peak values of partial polarization of water P_{water} (peak) and ethanol P_{EtOH} (peak) for Li^+ (open circles) and C_4 (open triangles) ions as a function of mole fraction x_2 of ethanol in ethanol–water mixture. Lower panel: Comparison of peak values partial polarization of acetonitrile P_{ACN} (peak) and dimethylsulfoxide P_{DMSO} (peak) for Li^+ (solid circles) and C_4 (solid triangles) ions as a function of mole fraction x_2 of DMSO in CAN–DMSO mixture.

the extent of non-linearity being very weak for C_4. As discussed earlier here and elsewhere,[76] the non-linearity is a manifestation of preferential solvation and hence this explains the microscopic origin of the strong non-ideality observed for smaller ions in ethanol–water and other alcohol–water mixtures. In DMSO–acetonitrile mixture, however, the peaks of the partial solvent polarization densities decrease or increase almost linearly for both the ions showing a very weak preferential solvation. This is again due to the comparable sizes and dipole moments of DMSO and acetonitrile molecules.

4. Conclusion

Let us first summarize the main results of the paper. We have used the recently extended MSA formalism[76] to study the Born-free energy of solvation and non-ideality associated with it in associating (alcohol–water) and non-associating (DMSO–acetonitrile) solvent mixtures. The solvent dipoles are treated as dipolar hard spheres and ions as hard spheres with unit charge at centers. The electrolyte concentration has been infinitely dilute. The sizes of every species in the solution and the dipole moments of the different components have been systematically incorporated. The ethanol–water mixtures show greater non-ideality than DMSO–acetonitrile mixtures. The slope of the excess Born-free energy of solvation is found to be opposite in DMSO–acetonitrile mixture than that in ethanol–water solutions. The extremum positions of the excess Born-free energy of solvation versus mole fraction (of bigger component) curves have been found to be affected significantly by the solvent size ratio. Also, the larger ion exhibits smaller non-ideality.

Since we treat these binary mixtures within the MSA framework, the present approach can neither distinguish between ions of different signs (cation or anion) nor can deal with any specific interactions and shape (say, spherical or ellipsoid) asymmetry that are present in real mixtures. Also, MSA is a linear theory which is known to fail for strongly polar systems. Therefore, the intra and inter-molecular correlations derived in this present work can be at best semi-quantitative in nature. For an accurate description of these quantities one should use a better and non-linear theories that are likely to be more numerically involved. The present approach, in contrast, is simple and analytically tractable yet captures the physics qualitatively correctly. This is definitely a positive aspect of the present work given the complexity of real solution mixtures.

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