

# Ions in a binary asymmetric dipolar mixture: Mole fraction dependent Born energy of solvation and partial solvent polarization structure

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Mean spherical approximation (MSA) for electrolyte solution has been extended to investigate the role of partial solvent polarization densities around an ion in a completely asymmetric binary dipolar mixture. The differences in solvent diameters, dipole moments, and ionic size are incorporated systematically within the MSA framework in the present theory for the first time. In addition to the contributions due to difference in dipole moments, the solvent-solvent and ion-solvent size ratios are found to significantly affect the nonideality in binary dipolar mixtures. Subsequently, the theory is used to investigate the role of ion-solvent and solvent-solvent size ratios in determining the nonideality in Born free energy of solvation of a unipositive rigid ion in alcohol-water and dimethyl sulfoxide-acetonitrile mixtures, where the solvent components are represented *only* by their molecular diameters and dipole moments. Nonideality in Born free energy of solvation in such simplified mixtures is found to be stronger for smaller ions. The slope of the nonideality for smaller alkali metal ions in methanol-water mixture is found to be opposite to that for larger ion, such as quaternary tertiary butyl ammonium ion. For ethanol-water mixtures, the slopes are in the same direction for all the ions studied here. These results are in qualitative agreement with experiments, which is surprising as the present MSA approach does not include the hydrogen bonding and hydrophobic interactions present in the real mixtures. The calculated partial polarization densities around a unipositive ion also show the characteristic deviation from ideality and reveal the microscopic origin of the ion and solvent size dependent preferential solvation. Also, the excess free energy of mixing (in the *absence* of any ion) for these binary mixtures has been calculated and a good agreement between theory and experiment has been found. © 2007 American Institute of Physics. [DOI: 10.1063/1.2792953]

## I. INTRODUCTION

Polarity of a medium is often found to have significant effects on the course and the outcome of a reaction in solution phase.<sup>1,2</sup> Mixed dipolar solvents are good reaction media because one can tune polarity, solubility, etc., by altering the composition of a mixture. The tunable polarity of a binary mixture is the key for selective dissolution and precipitation of reactants and/or products of a solution phase chemical reaction. Polar binary mixtures are therefore better reaction media than neat solvents. Size disparity in the constituent solvent molecules can have profound effects on both the equilibrium and dynamical properties of a solution. An increase in size of one of the species is likely to inhibit its ability to solvate an ion due to packing constraints. Therefore, relatively smaller molecules will be preferred giving rise to what is widely known as preferential solvation. Interestingly, the interdiffusion of these two types of molecules can make solvation considerably slower than that in a one-component solvent.<sup>3-5</sup> Moreover, simulation studies have in-

dicated that the slow exchange of one solvent species by the other in the adjacent solvent shells may not hold for mixtures with widely different effective volumes.<sup>6</sup>

Electrolyte solution in binary mixture is another important medium as many biologically relevant reactions occur in mixture in the presence of ions.<sup>7,8</sup> Addition of electrolytes not only enhances the average polarity of the medium but also takes part in altering the reaction equilibrium by inducing salting in or salting out effects. Moreover, interaction between ions and a dissolved solute (reactive or nonreactive polar molecule) competes with the preferential solvation and hence modifies the average solvation structure around the dissolved solute. The competition becomes even more interesting for a binary polar mixture where the relatively bigger (in size) solvent molecule possesses a larger dipole moment. Such competition is likely to affect the long-time dynamics of the solvent response. Naturally therefore, studies of structure and dynamics of the environment around an ionic or dipolar solute are essential for understanding the solvation processes and their effects on simple chemical events in such media.<sup>9,10</sup>

Several studies have already been carried out for determining the structure in binary polar mixtures.<sup>11-13</sup> For example, Adelman and Deutch<sup>12</sup> extended the Wertheim's so-

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lution for pure fluids<sup>11</sup> using the mean spherical approximation<sup>14</sup> (MSA) into the binary polar mixture, where solvent molecules of different species were characterized by equal hard sphere diameters ( $R_1=R_2$ ) with point dipoles of different magnitudes at the center ( $\mu_1 \neq \mu_2$ ) of these hard spheres. Isbister and Bearman solved the MSA for completely asymmetric binary fluid mixture<sup>13</sup> ( $R_1 \neq R_2$  and  $\mu_1 \neq \mu_2$ ). Subsequently, MSA was developed for electrolyte solution consisting of hard ions (charged hard spheres) in neat dipolar solvent and used to obtain the solvent structure around a dissolved ion.<sup>15</sup> Recently, MSA has been used to study the polarization structure around an ion in binary polar mixture composed of solvent molecules of equal size but different dipole moments ( $R_1=R_2 \neq R$ ,  $R$  is the diameter of ion and  $\mu_1 \neq \mu_2$ ).<sup>16</sup> All these studies have contributed significantly to the understanding of solvation structure in terms of ion-solvent and solvent-solvent interactions. However, solvent polarization structure around an ion in a mixture of dipolar solvents with arbitrary size and dipole moments (that is,  $R_1 \neq R_2 \neq R$  and  $\mu_1 \neq \mu_2$ ) has not been studied yet. Such a study is very important because many thermodynamic properties of electrolyte solutions in binary polar mixtures depend on the partial polarization densities of the constituent solvents around the dissolved ions.

In this paper we use MSA in order to obtain analytical expressions for partial solvent polarization densities and Born free energies of solvation in an electrolyte solution of a completely asymmetric binary polar mixture. We restrict our study for symmetric uniunivalent electrolyte in the limit of infinite dilution. One of our goals here is to investigate the effects of relative size of the constituent solvents on Born free energy of solvation for a dissolved ion in model binary polar mixtures and partial solvent polarization densities around a dissolved ion. The calculation of partial solvent polarization densities is crucial since it provides a microscopic explanation for the often observed nonideal composition dependence of Born free energies of solvation in mixtures. Subsequently, the calculation scheme is applied to obtain the partial solvent polarization densities around a unipositive rigid ion dissolved in room temperature binary mixtures of methanol-water, ethanol-water, and tertiary butyl alcohol (TBA)-water and dimethyl sulfoxide (DMSO)-acetonitrile solutions. Note here that in the present theory, the solvent components constituting the binary mixtures are characterized *only* by their molecular diameters and dipole moments. Specific interactions such as hydrogen bonding between solvent molecules of same species as well as between different species and hydrophobic interactions between alkyl groups of the alcohols have not been considered. Also, attempt has not been made in the present extension of the MSA to include any specific ion-solvent interaction that may be possible through the participation of lone pair of electrons on oxygen atom in water or alcohol molecules (for ion in alcohol-water mixtures) and in DMSO molecule (for ion in DMSO-acetonitrile mixtures). Therefore, these binary mixtures are much simplified versions of the real solutions, and the neglect of these specific and complex interactions may lead to predictions very different from experimental results. Therefore, explicit potentials<sup>17-20</sup> that are generally used in

simulation studies to represent the interactions more realistically in these systems have not been considered. This is because the present work focuses on, within the extended MSA framework, exploring the contributions to the nonideality in the Born free energy of solvation originating purely from the ion-solvent and solvent-solvent size ratios as well as from the differing dipole moments.

Alcohol-water mixtures are known to exhibit anomalous thermodynamic properties at low alcohol concentrations.<sup>21,22</sup> Extensive experimental<sup>23-43</sup> and simulation<sup>44-50</sup> studies have been carried out to investigate the liquid structure in alcohol-water mixtures. All these studies linked the deviation of a given property from its expected value with the modification of water structure in the presence of alcohol, the deviation being the maximum for TBA. Recently, Yoshida *et al.*<sup>49</sup> and Omelyan *et al.*<sup>50</sup> have extensively studied the TBA-water mixture by using the reference interaction site model (RISM) integral equation theory, where association of polar molecules is considered through an appropriate closure description. These authors have used the extended simple point charge model for water and the optimized potential for liquid simulation force field for TBA. These studies have indicated that the hydrogen bonding between all species becomes stronger with the increase in TBA, while the tetrahedral-like network of hydrogen bonding in dilute solution is gradually converted into a zigzaglike structure at concentrated TBA solution. Also, at low TBA concentration the TBA molecules have been found to form cluster through hydrophobic interactions among the methyl groups, whereas the TBA-hydroxyl groups are involved in hydrogen bonding with water molecules surrounding the cluster. However, the agreement between the calculated partial radial distribution functions and those from neutron diffraction experiments and molecular dynamics simulations has been found to be qualitative, even though realistic potentials with proper closer functions were used.<sup>49</sup> The globular tertiary butyl group is believed to be of perfect size that can suitably fit into the solvent cage made by several water molecules in a relatively strain-free manner.<sup>45-48</sup> Since this substantially modifies the water structure in the water-rich region, simple transport event such as ion diffusion shows interesting composition dependence.<sup>51</sup> For example, limiting ionic conductivity of alkali metal ions shows a nonmonotonic composition dependence in the water-rich region of TBA-water mixture, while a bigger ion such as tetrabutyl ammonium ion ( $\text{Bu}_4\text{N}^+$ ) exhibits a linear composition dependence.<sup>51</sup> Similar behavior in ion transport is also found for other binary polar mixtures, where hydrogen bonding interaction does not play a role in solvent association.<sup>52</sup> This difference in composition dependence may partly arise from the nature of solvation of these individual ions and partly from the modification of the solution dynamics. Therefore, solvation free energies can reflect the underlying solvent structure around these ions determined by a delicate balance of complex intermolecular interactions between the amphiphilic TBA and hydrophilic water molecules. The calculated excess Born free energy of solvation indicates that at low TBA concentration, ions with size larger than or equal to that of a water molecule (for example,  $\text{Cs}^+$  or  $\text{Bu}_4\text{N}^+$ ) show a composition dependence very differ-

ent from that for smaller ions such as  $\text{Li}^+$ . This is in sharp contrast to the more “regular” ion size dependence of excess Born free energy of solvation in methanol-water and ethanol-water mixtures.

As already discussed, the analytical expressions derived and calculations done here are within the MSA framework. This means that the dipolar solvent molecules are treated as hard spheres with point dipoles situated at the center.<sup>15</sup> The solvent dipoles are of different sizes and dipole moments. The ions are hard spheres of equal diameters with embedded point charges and are present at infinite dilution.<sup>15,16</sup> The electroneutrality is maintained, as usually done in MSA-type theories.<sup>15,16</sup> The present theory is neither able to distinguish the sign of the charge on hard sphere ions (cation or anion) nor can deal with any specific solvent-solvent and solute-solvent interactions. Although the MSA is known to be semi-quantitative for systems possessing complex interactions with dissimilar sizes and shapes, the possibility of deriving analytical and thus relatively simpler expressions for partial solvent polarization structures provides a further motivation for extending the MSA theory for such mixtures.

The rest of the paper is organized as follows. The derivation of analytical expressions for the Born free energy of solvation of a hard sphere ion and partial solvent polarization density around it are given in Sec. II. The numerical results and discussion are presented in Sec. III. Concluding remarks are provided in Sec. IV.

## II. THEORETICAL FORMULATION

Recently, Morillo *et al.* have extended the MSA theory to study the solvent structure around a hard sphere ion dissolved in a binary dipolar mixture.<sup>16</sup> These authors have modeled the binary mixture as a collection of dipolar hard spheres of equal size but with different dipole moments on different species and made use of the results of Adelman and Deutch<sup>12</sup> and those of Chan *et al.*<sup>15</sup> 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. We have, therefore, used the MSA frameworks provided by Isbister and Bearman,<sup>13</sup> Chan *et al.*,<sup>14</sup> and Blum and co-workers.<sup>53-57</sup>

### A. Ion-solvent and solvent-solvent correlations in binary dipolar mixtures

Let us now 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  $\mu_i$  and  $\mu_j$ , respectively. The solvent number densities are  $\rho_i$  and  $\rho_j$ . Here,  $R_i \neq R_j$  and  $\mu_i \neq \mu_j$ . The electroneutrality of such a solution is ensured by setting

$$\sum_{\alpha} \rho_{\alpha} z_{\alpha} = 0, \quad (1)$$

where  $\rho_{\alpha}$  denotes the number density of ionic species  $\alpha$  with charge  $z_{\alpha}$  and diameter  $R_{\alpha} = R$ . The interaction potentials consist of a hard core repulsive term and ion-ion, ion-dipole, and dipole-dipole components given by

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

$$u_{\alpha j}(\mathbf{r}, \boldsymbol{\omega}_2) = -z_{\alpha} e \mu_j E_2 / r^2, \quad r > R_{\alpha j} = (R + R_j) / 2, \quad (2b)$$

$$u_{i\beta}(\boldsymbol{\omega}_1, \mathbf{r}) = z_{\beta} e \mu_i E_1 / r^2, \quad r > R_{i\beta} = (R_i + R) / 2, \quad (2c)$$

$$u_{ij}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2) = -\mu_i \mu_j D_{12} / r^3, \quad r > R_{ij} = (R_i + R_j) / 2, \quad (2d)$$

where  $\alpha, \beta$  indices are for ions and  $i, j$  indices are for dipoles.  $E_i = \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_i) \cdot \hat{\mathbf{r}}$  and  $D_{12} = \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_1) \cdot (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{I}) \cdot \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_2)$  describe the angle dependent parts of the interaction potentials. In above equations,  $e$  represents the elementary charge,  $\mathbf{I}$  denotes a  $3 \times 3$  unit tensor, and  $\hat{\mathbf{r}}$  is the unit vector from the molecule denoted by the first index toward the one denoted by second index. The orientation of  $i$ th-type dipole is described by  $\boldsymbol{\omega}_i$ .

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.<sup>15</sup> The relevant OZ expressions along with the MSA closure relations are given in Appendix A. Subsequently, the algebra described in Chan *et al.*<sup>15</sup> leads to the following *ansatz*:

$$f_{\alpha\beta}(r) = f_{\alpha\beta}^{\text{HS}}(r) + z_{\alpha} z_{\beta} f_{\alpha\beta}^{\text{C}}(r), \quad (3a)$$

$$f_{\alpha j}(\mathbf{r}, \boldsymbol{\omega}_2) = f_{\alpha j}^{\text{HS}}(r) + z_{\alpha} f_{\alpha j}^{\text{E}}(r) E_2, \quad (3b)$$

$$f_{i\beta}(\boldsymbol{\omega}_1, \mathbf{r}) = f_{i\beta}^{\text{HS}}(r) - z_{\beta} f_{i\beta}^{\text{E}}(r) E_1, \quad (3c)$$

$$f_{ij}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2) = f_{ij}^{\text{HS}}(r) + f_{ij}^{\Delta}(r) \Delta_{12} + f_{ij}^{\text{D}}(r) D_{12}, \quad (3d)$$

where  $f^{\text{C}}$  represents the charge-charge correlations,  $f^{\text{E}}$  the charge-dipole correlations, and  $f^{\text{D}}$  and  $f^{\Delta}$  the dipole-dipole correlations. The relevant angle independent closure conditions are<sup>15</sup>

$$c_{\alpha\beta}^{\text{C}}(r) = -(k_B T)^{-1} e^2 / r, \quad r > R, \quad (4a)$$

$$c_{\alpha j}^{\text{E}}(r) = (k_B T)^{-1} e \mu_j / r^2, \quad r > R_{\alpha j}, \quad (4b)$$

$$c_{i\beta}^{\text{E}}(r) = (k_B T)^{-1} e \mu_i / r^2, \quad r > R_{i\beta}, \quad (4c)$$

$$c_{ij}^{\text{D}}(r) = (k_B T)^{-1} \mu_i \mu_j / r^3, \quad r > R_{ij}, \quad (4d)$$

where  $k_B T$  represents the Boltzmann constant times the absolute temperature. Using the following definition of three-dimensional Fourier transform:

$$\tilde{f}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_2) = \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} f(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2), \quad \tilde{f} = \tilde{h} \text{ or } \tilde{c}, \quad (5)$$

we obtain the OZ equations in the Fourier space as

$$\begin{aligned} \tilde{h}_{\alpha\beta}(\mathbf{k}) &= \tilde{c}_{\alpha\beta}(\mathbf{k}) + \sum_{\gamma} \rho_{\gamma} \tilde{c}_{\alpha\gamma}(\mathbf{k}) \tilde{h}_{\gamma\beta}(\mathbf{k}) \\ &\quad + \sum_k \rho_k \langle \tilde{c}_{\alpha k}(\mathbf{k}, \boldsymbol{\omega}_3) \tilde{h}_{k\beta}(\boldsymbol{\omega}_3, \mathbf{k}) \rangle_{\boldsymbol{\omega}_3}, \end{aligned} \quad (6a)$$

$$\begin{aligned} \tilde{h}_{\alpha j}(\mathbf{k}, \boldsymbol{\omega}_2) &= \tilde{c}_{\alpha j}(\mathbf{k}, \boldsymbol{\omega}_2) + \sum_{\gamma} \rho_{\gamma} \tilde{c}_{\alpha\gamma}(\mathbf{k}) \tilde{h}_{\gamma j}(\mathbf{k}, \boldsymbol{\omega}_2) \\ &\quad + \sum_k \rho_k \langle \tilde{c}_{\alpha k}(\mathbf{k}, \boldsymbol{\omega}_3) \tilde{h}_{kj}(\boldsymbol{\omega}_3, \mathbf{k}, \boldsymbol{\omega}_2) \rangle_{\boldsymbol{\omega}_3}, \end{aligned} \quad (6b)$$

$$\begin{aligned} \tilde{h}_{i\beta}(\boldsymbol{\omega}_1, \mathbf{k}) &= \tilde{c}_{i\beta}(\boldsymbol{\omega}_1, \mathbf{k}) + \sum_{\gamma} \rho_{\gamma} \tilde{c}_{i\gamma}(\boldsymbol{\omega}_1, \mathbf{k}) \tilde{h}_{\gamma\beta}(k) \\ &+ \sum_k \rho_k \langle \tilde{c}_{ik}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_3) \tilde{h}_{k\beta}(\boldsymbol{\omega}_3, \mathbf{k}) \rangle_{\boldsymbol{\omega}_3}, \end{aligned} \quad (6c)$$

$$\begin{aligned} \tilde{h}_{ij}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_2) &= \tilde{c}_{ij}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_2) + \sum_{\gamma} \rho_{\gamma} \tilde{c}_{i\gamma}(\boldsymbol{\omega}_1, \mathbf{k}) \tilde{h}_{\gamma j}(\mathbf{k}, \boldsymbol{\omega}_2) \\ &+ \sum_k \rho_k \langle \tilde{c}_{ik}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_3) \tilde{h}_{kj}(\boldsymbol{\omega}_3, \mathbf{k}, \boldsymbol{\omega}_2) \rangle_{\boldsymbol{\omega}_3}, \end{aligned} \quad (6d)$$

where,

$$\tilde{f}_{\alpha\beta}(k) = \tilde{f}_{\alpha\beta}^{\text{HS}}(k) + z_{\alpha} z_{\beta} \tilde{f}_{\alpha\beta}^{\text{C}}(k), \quad (7a)$$

$$\tilde{f}_{\alpha j}(\mathbf{k}, \boldsymbol{\omega}_2) = \tilde{f}_{\alpha j}^{\text{HS}}(k) + z_{\alpha} \tilde{f}_{\alpha j}^{\text{E}}(k) \tilde{E}_2, \quad (7b)$$

$$\tilde{f}_{i\beta}(\boldsymbol{\omega}_1, \mathbf{k}) = \tilde{f}_{i\beta}^{\text{HS}}(k) - z_{\beta} \tilde{f}_{i\beta}^{\text{E}}(k) \tilde{E}_1, \quad (7c)$$

$$\tilde{f}_{ij}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_2) = \tilde{f}_{ij}^{\text{HS}}(k) + \tilde{f}_{ij}^{\text{A}}(k) \Delta_{12} + \tilde{f}_{ij}^{\text{D}}(k) \tilde{D}_{12}, \quad (7d)$$

and

$$\tilde{E}_i = \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_i) \cdot \hat{\mathbf{k}}, \quad i = 1, 2$$

$$\tilde{D}_{12} = \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_1) \cdot (3\hat{\mathbf{k}}\hat{\mathbf{k}} - \mathbf{I}) \cdot \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_2). \quad (8)$$

Here each  $\tilde{f}(k)$  is related to corresponding  $f(r)$  by  $n$ th order Hankel transform<sup>15,16</sup> and the order of the transformation depends on the type of the correlation functions. Note that the last term in Eqs. (6a)–(6d) account for the angle averaged correlations between an ion and a dipole, and two dipoles of same and different types. Therefore, the summation runs over all solvent components present in the binary mixture. This term arises due to the difference in solvent size. Also, this term is absent in the works of Chan *et al.*<sup>15</sup> since it deals with electrolyte solution in one-component dipolar solvent. Further, these expressions reduce to those obtained by Morillo *et al.*<sup>16</sup> for binary mixtures in the limit of equal solvent size ( $R_i = R_j$ ) but different dipole moments ( $\mu_i \neq \mu_j$ ). We will come back to this point when we present numerical results. However, the first two terms are similar to those in Chan *et al.*<sup>15</sup> as these generalize the ion-ion, ion-dipole, and dipole-dipole correlations with summation over all ionic species in electrolyte solution of binary dipolar mixtures.

If we define two *orthogonal* angular functions using  $\Delta_{12}$  and  $\tilde{D}_{12}$  as<sup>15</sup>

$$J_{12}^+ = \frac{1}{3}(\Delta_{12} + \tilde{D}_{12}), \quad (9a)$$

$$J_{12}^- = \frac{1}{3}(2\Delta_{12} - \tilde{D}_{12}), \quad (9b)$$

with coefficients

$$\tilde{f}_{ij}^+ = \tilde{f}_{ij}^{\text{A}} + 2\tilde{f}_{ij}^{\text{D}}, \quad (10a)$$

$$\tilde{f}_{ij}^- = \tilde{f}_{ij}^{\text{A}} - \tilde{f}_{ij}^{\text{D}}, \quad (10b)$$

and substitute in Eq. (7d) we get

$$\tilde{f}_{ij}(\boldsymbol{\omega}_1, \mathbf{k}, \boldsymbol{\omega}_2) = \tilde{f}_{ij}^{\text{HS}}(k) + \tilde{f}_{ij}^+(k) J_{12}^+ + \tilde{f}_{ij}^-(k) J_{12}^-. \quad (11)$$

Carrying out the angular convolution in Eqs. (6a)–(6d) and using the charge neutrality condition, and setting

$$\rho_c = \sum_{\gamma} \rho_{\gamma} z_{\gamma}^2, \quad (12)$$

$$\rho_l = \sum_{\gamma} \rho_{\gamma}, \quad (13)$$

we obtain the following coupled set of equations for the correlation functions due to hard sphere interaction:

$$\tilde{h}_{\alpha\beta}^{\text{HS}}(k) = \tilde{c}_{\alpha\beta}^{\text{HS}}(k) + \rho_l \tilde{c}_{\alpha\gamma}^{\text{HS}}(k) \tilde{h}_{\gamma\beta}^{\text{HS}}(k) + \sum_k \rho_k \tilde{c}_{\alpha k}^{\text{HS}}(k) \tilde{h}_{k\beta}^{\text{HS}}(k), \quad (14a)$$

$$\tilde{h}_{\alpha j}^{\text{HS}}(k) = \tilde{c}_{\alpha j}^{\text{HS}}(k) + \rho_l \tilde{c}_{\alpha\gamma}^{\text{HS}}(k) \tilde{h}_{\gamma j}^{\text{HS}}(k) + \sum_k \rho_k \tilde{c}_{\alpha k}^{\text{HS}}(k) \tilde{h}_{kj}^{\text{HS}}(k), \quad (14b)$$

$$\tilde{h}_{i\beta}^{\text{HS}}(k) = \tilde{c}_{i\beta}^{\text{HS}}(k) + \rho_l \tilde{c}_{i\gamma}^{\text{HS}}(k) \tilde{h}_{\gamma\beta}^{\text{HS}}(k) + \sum_k \rho_k \tilde{c}_{ik}^{\text{HS}}(k) \tilde{h}_{k\beta}^{\text{HS}}(k), \quad (14c)$$

$$\tilde{h}_{ij}^{\text{HS}}(k) = \tilde{c}_{ij}^{\text{HS}}(k) + \rho_l \tilde{c}_{i\gamma}^{\text{HS}}(k) \tilde{h}_{\gamma j}^{\text{HS}}(k) + \sum_k \rho_k \tilde{c}_{ik}^{\text{HS}}(k) \tilde{h}_{kj}^{\text{HS}}(k). \quad (14d)$$

These equations define a mixture of hard spheres with diameter  $R_{\alpha} = R$  at number density  $\rho_l$  and diameter  $R_i$  at density  $\rho_i$  with Percus-Yevick closure.<sup>14</sup> Simultaneously, the correlations due to the electrostatic interactions between ions, ion-dipole, and dipoles are described by the following set of coupled equations:

$$\tilde{h}_{\alpha\beta}^{\text{C}}(k) = \tilde{c}_{\alpha\beta}^{\text{C}}(k) + \rho_c \tilde{c}_{\alpha\gamma}^{\text{C}}(k) \tilde{h}_{\gamma\beta}^{\text{C}}(k) - \frac{1}{3} \sum_k \rho_k \tilde{c}_{\alpha k}^{\text{E}}(k) \tilde{h}_{k\beta}^{\text{E}}(k), \quad (15a)$$

$$\tilde{h}_{\alpha j}^{\text{E}}(k) = \tilde{c}_{\alpha j}^{\text{E}}(k) + \rho_c \tilde{c}_{\alpha\gamma}^{\text{C}}(k) \tilde{h}_{\gamma j}^{\text{E}}(k) + \frac{1}{3} \sum_k \rho_k \tilde{c}_{\alpha k}^{\text{E}}(k) \tilde{h}_{kj}^{\text{E}}(k), \quad (15b)$$

$$\tilde{h}_{i\beta}^{\text{E}}(k) = \tilde{c}_{i\beta}^{\text{E}}(k) + \rho_c \tilde{c}_{i\gamma}^{\text{E}}(k) \tilde{h}_{\gamma\beta}^{\text{E}}(k) + \frac{1}{3} \sum_k \rho_k \tilde{c}_{ik}^{\text{E}}(k) \tilde{h}_{k\beta}^{\text{E}}(k), \quad (15c)$$

$$\tilde{h}_{ij}^+(k) = \tilde{c}_{ij}^+(k) - \rho_c \tilde{c}_{i\gamma}^E(k) \tilde{h}_{j\gamma}^E(k) + \frac{1}{3} \sum_k \rho_k \tilde{c}_{ik}^+(k) \tilde{h}_{kj}^+(k). \quad (15d)$$

Since the electrostatic Coulomb potential is longitudinal field and couples with  $J_{12}^+$  function alone, the addition of ions therefore affects only the longitudinal response ( $\tilde{h}_{ij}^+$ ).<sup>15</sup> Hence,  $J_{12}$  function is decoupled from the rest, and we obtain the following equation:<sup>11-16</sup>

$$\tilde{h}_{ij}^-(k) = \tilde{c}_{ij}^-(k) + \frac{1}{3} \sum_k \rho_k \tilde{c}_{ik}^-(k) \tilde{h}_{kj}^-(k). \quad (16)$$

### B. Born free energy of solvation of an ion in a binary dipolar mixture

The Born free energy of solvation for an ion of charge  $z_\alpha e$  can be obtained from Eqs. (15a)–(15d) with the condition  $\rho_c = 0$ . Since the functions  $\tilde{f}_{\alpha\beta}^C(k)$ ,  $\tilde{f}_{\alpha j}^E(k)$ ,  $\tilde{f}_{i\beta}^\Delta(k)$ , and  $\tilde{f}_{ij}^D(k)$ , which describe electrostatic interactions, depend only on  $k = |\mathbf{k}|$ , and therefore these quantities can be transformed back to  $r$  space by using the following one-dimensional Fourier inverse transform:

$$F(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk e^{-ikx} \tilde{f}(k), \quad (17)$$

where  $F$  can be  $F_{\alpha\beta}^C$ ,  $F_{\alpha j}^E$ ,  $F_{i\beta}^\Delta$ , or  $F_{ij}^D$ , and  $\tilde{f}$  can be  $\tilde{f}_{\alpha\beta}^C$ ,  $\tilde{f}_{\alpha j}^E$ ,  $\tilde{f}_{i\beta}^\Delta$ , or  $\tilde{f}_{ij}^D$ . The relation between all  $f$ 's and  $F$ 's are given in Appendix B.

The Born energy of a single ion of charge  $z_\alpha e$  dissolved in a dipolar mixture is given by<sup>16</sup>

$$\begin{aligned} E_{\text{Born}} &= \sum_k \rho_k \int d\mathbf{r} \langle u_{\alpha k}(\mathbf{r}, \boldsymbol{\omega}) g_{\alpha k}(\mathbf{r}, \boldsymbol{\omega}) \rangle_{\boldsymbol{\omega}} \\ &= -\frac{4\pi z_\alpha^2 e^2}{3} \sum_k \rho_k \mu_k \int_{R_{\alpha k}}^{\infty} dr h_{\alpha k}^E(r), \end{aligned} \quad (18)$$

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  $E_{\text{Born}}$ . This is calculated from the ion-dipole correlation function as follows:<sup>15,16</sup>

$$\begin{aligned} H_{\alpha j}^E(x) &= 2\pi \int_x^{\infty} dr P_1(x/r) r h_{\alpha j}^E(r) \\ &= 2\pi x \int_{R_{\alpha j}}^{\infty} dr h_{\alpha j}^E(r) \\ &= x H 1_{\alpha j}^E \quad \text{for } x \leq R_{\alpha j}, \end{aligned} \quad (19)$$

where  $H 1_{\alpha j}^E = 2\pi \int_{R_{\alpha j}}^{\infty} dr h_{\alpha j}^E(r)$  is a constant that needs to be determined. Equation (18) and the above discussion now provide the following expression of Born energy ( $E_{\text{Born}}$ ) for an ion dissolved in binary mixture of dipolar solvents with unequal size and different dipole moments:

$$E_{\text{Born}} = -\frac{2z_\alpha^2 e^2}{3} \sum_k \rho_k \mu_k H 1_{\alpha k}^E = -\frac{2z_\alpha^2 e^2}{3} \sum_k \rho_k \mu_k H 1_{k\alpha}^E. \quad (20)$$

Now we need to calculate  $H 1_{k\alpha}^E (= H 1_{\alpha k}^E)$ . Baxter factorization<sup>57</sup> gives for  $x > S_{j\alpha} = (R_j - R_\alpha)/2$

$$H_{j\alpha}^E(x) = -Q_{j\alpha}^E(x) + \frac{1}{3} \sum_k \rho_k \int_{S_{jk}}^{R_{jk}} dy Q_{jk}^+(y) H_{k\alpha}^E(x-y), \quad (21)$$

From Eq. (19) when  $S_{j\alpha} < x \leq R_{j\alpha}$ ,

$$x H 1_{j\alpha}^E = -Q_{j\alpha}^E(x) + \frac{1}{3} \sum_k \rho_k H 1_{k\alpha}^E \int_{S_{jk}}^{R_{jk}} dy Q_{jk}^+(y) (x-y), \quad (22)$$

where  $Q_{jk}^+(x)$  depends solely on the dipolar mixture properties and is given by<sup>15,54</sup>

$$Q_{ij}^+(x) = 3 \left[ \frac{1}{2} a_{ij} (x - R_{ij})(x - S_{ij}) + b_{ij} (x - R_{ij}) \right], \quad (23)$$

where the values of  $a_{ij}$  and  $b_{ij}$  are given in Appendix C.

Equation (22) consists of two coupled simultaneous equations in  $H 1_{j\alpha}^E$  when  $j=1,2$  and  $\alpha$  is fixed (a given ionic species). Using Baxter's method we obtain the following expression for  $C_{j\alpha}^E(x)$ :

$$\begin{aligned} C_{j\alpha}^E(x) &= -Q_{j\alpha}^E(x) + \frac{1}{3} \sum_k \rho_k \int_{S_{kj}}^{R_{kj}} dy Q_{kj}^+(y) Q_{k\alpha}^E(x+y), \\ &x \geq R_{j\alpha}, \end{aligned} \quad (24)$$

with closure relation,

$$C_{j\alpha}^E(x) = 2\pi e \beta \mu_j, \quad x \geq R_{j\alpha}. \quad (25)$$

Therefore, from Eqs. (24) and (25), we obtain

$$\begin{aligned} 2\pi e \beta \mu_j &= -Q_{j\alpha}^E(x) + \frac{1}{3} \sum_k \rho_k \int_{S_{kj}}^{R_{kj}} dy Q_{kj}^+(y) Q_{k\alpha}^E(x+y), \\ &x \geq R_{j\alpha}. \end{aligned} \quad (26)$$

Equation (26) contains two coupled simultaneous equations in  $Q_{j\alpha}^E(x)$  when  $j=1,2$  for a fixed  $\alpha$ . By solving these two equations for  $j=1$  and  $2$  and applying the condition that  $Q_{j\alpha}^E(x) = Q_{j\alpha}^E(x+y)$  for  $x \geq R_{j\alpha}$ , we obtain the following expressions for  $Q_{j\alpha}^E(x)$ :

$$Q_{1\alpha}^E(x) = \frac{\left[ 2\pi\beta e \mu_1 - \frac{2\pi\beta e \mu_2}{-1 + I_{22}} I_{21} \right]}{\left[ -1 + I_{11} \right] - \frac{I_{21} I_{12}}{[-1 + I_{22}]}}, \quad x \geq R_{1\alpha}, \quad (27)$$

$$Q_{2\alpha}^E(x) = \frac{\left[ 2\pi\beta e \mu_2 - \frac{2\pi\beta e \mu_1}{-1 + I_{11}} I_{12} \right]}{\left[ -1 + I_{22} \right] - \frac{I_{12} I_{21}}{[-1 + I_{11}]}}, \quad x \geq R_{2\alpha}, \quad (28)$$

with

$$I_{ij} = \int_{S_{ij}}^{R_{ij}} \frac{1}{3} \rho_i Q_{ij}^+(y) dy = \rho_i \left[ -\frac{1}{12} a_{ij} R_j^3 - \frac{1}{2} b_{ij} R_j^2 \right], \quad i = 1, 2. \quad (29)$$

Solution of Eq. (22) at  $x=R_{j\alpha}$  provides the following expressions of  $H1_{1\alpha}^E$  and  $H1_{2\alpha}^E$ :

$$H1_{1\alpha}^E = \frac{-Q_{1\alpha}^E(R_{1\alpha})[R_{2\alpha} - R_{2\alpha}I_{22} + \tilde{I}_{22}] - Q_{2\alpha}^E(R_{2\alpha})[R_{1\alpha}\tilde{I}_{12} - \tilde{I}_{12}]}{[R_{1\alpha} - R_{1\alpha}I_{11} + \tilde{I}_{11}][R_{2\alpha} - R_{2\alpha}I_{22} + \tilde{I}_{22}] - [R_{1\alpha}\tilde{I}_{12} - \tilde{I}_{12}][R_{1\alpha}\tilde{I}_{21} - \tilde{I}_{21}]}, \quad (30)$$

$$H1_{2\alpha}^E = \frac{-Q_{2\alpha}^E(R_{2\alpha})[R_{1\alpha} - R_{1\alpha}I_{11} + \tilde{I}_{11}] - Q_{1\alpha}^E(R_{1\alpha})[R_{2\alpha}\tilde{I}_{21} - \tilde{I}_{21}]}{[R_{1\alpha} - R_{1\alpha}I_{11} + \tilde{I}_{11}][R_{2\alpha} - R_{2\alpha}I_{22} + \tilde{I}_{22}] - [R_{1\alpha}\tilde{I}_{12} - \tilde{I}_{12}][R_{1\alpha}\tilde{I}_{21} - \tilde{I}_{21}]}, \quad (31)$$

where

$$\tilde{I}_{ij} = \int_{S_{ij}}^{R_{ij}} \frac{1}{3} \rho_j Q_{ij}^+(y) dy = \rho_j \left[ -\frac{1}{12} a_{ij} R_j^3 - \frac{1}{2} b_{ij} R_j^2 \right], \quad (32)$$

$$i = 1, 2,$$

$$\tilde{I}_{ij} = \int_{S_{ij}}^{R_{ij}} \frac{1}{3} \rho_i Q_{ij}^+(y) y dy = \rho_i \left[ \frac{1}{12} b_{ij} R_j^3 - \frac{1}{24} R_i a_{ij} R_j^3 - \frac{1}{4} R_i b_{ij} R_j^2 \right], \quad i = 1, 2. \quad (33)$$

Substitution of  $H1_{j\alpha}^E$  [from Eqs. (30) and (31)] into Eq. (20) provides the required expression for  $E_{\text{Born}}$ . Born free energy ( $F_{\text{Born}}$ ) of solvation is then calculated from the following relation:<sup>15</sup>

$$F_{\text{Born}} = \int_0^e de(E_{\text{Born}}/e). \quad (34)$$

### C. Solvent polarization densities around an ion at infinite dilution in a binary dipolar mixture

In this section we give the expressions for partial polarization densities of constituent solvents around an ion with charge  $z_\alpha e$  at infinite dilution. The total polarization density about an ion with charge  $z_\alpha e$  is defined as<sup>15,16</sup>

$$P_\alpha(r) = \sum_k P_{\alpha k}(r) = \frac{1}{4\pi} \sum_k \rho_k \mu_k \int d\omega g_{\alpha k}(r, \omega) \times (\hat{\mu}_k(\omega) \cdot \hat{r}), \quad (35)$$

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

$$P_\alpha(r) = \frac{1}{3} \sum_k \rho_k \mu_k h_{\alpha k}^E(r) = \frac{1}{3} \sum_k \rho_k \mu_k h_{k\alpha}^E(r) = \frac{1}{3} \sum_k \rho_k \mu_k \left[ \frac{1}{2\pi r} \left\{ \frac{1}{r} H_{k\alpha}^E(r) - \frac{d}{dr} H_{k\alpha}^E(r) \right\} \right], \quad (36)$$

where  $H_{k\alpha}^E(r)$  is given by<sup>15</sup>

$$H_{j\alpha}^E(r) = r H1_{j\alpha}^E, \quad r \leq R_{j\alpha}, \quad (37a)$$

$$H_{j\alpha}^E(r) = -Q_{j\alpha}^E(r) + \frac{1}{3} \sum_k \rho_k \int_{S_{jk}}^{R_{jk}} ds Q_{jk}^+(s) H_{k\alpha}^E(r-s), \quad r > R_{j\alpha}. \quad (37b)$$

Since  $Q_{jk}^+(r)$  is known,  $H_{j\alpha}^E(r)$  can easily be obtained numerically and hence  $P_\alpha(r)$ .

### III. RESULTS AND DISCUSSION

This section consists of two parts. In the first part we present numerical results for the Born free energy of solvation and excess Born free energy of solvation of a dissolved ion in a model binary polar mixture. Here we show the effects of relative size of constituent solvent components on the nonideality of these quantities for a given ion. We then present numerical results for systems consisting of unipositive ions in binary polar mixtures where the diameters and dipole moments of the solvent components used in the calculations are those of water, methanol, ethanol, tertiary butanol, DMSO, and acetonitrile. Ion size dependence of Born free energy of solvation in a model binary mixture is also discussed here. The calculated results for the mole fraction dependent partial solvent polarization densities around an ion in these mixtures are presented in the second part where the microscopic origin for the observed nonideality is discussed. All the numerical results presented here are calculated at temperature  $T=298.15$  K.

#### A. Born free energy of solvation

In Fig. 1 we show the Born free energy of solvation of an ion,  $F_{\text{Born}}$ , and excess Born free energy of solvation,  $\Delta F_{\text{Born}}$ , as a function of mole fraction of the second component ( $x_2$ ) whose dipole moment is larger than the other one. The parameters necessary for the calculation are given in Table I. We have presented four sets of calculations for different solvent-solvent size ratios, while the dipole moments ( $\mu_1$  and  $\mu_2$ ), ion diameter ( $R$ ), and total packing fraction are kept fixed. The squares, inverted triangles, triangles, and circles indicate calculations at  $R_2=0.5R_1$ ,  $0.8R_1$ ,  $R_1$ , and  $1.2R_1$ , respectively. It is clear from the above figure (*upper panel*) that Born free energy of solvation ( $F_{\text{Born}}$ ) increases nonlinearly as one increases the mole fraction of the component which possesses larger dipole moment. Born free energy

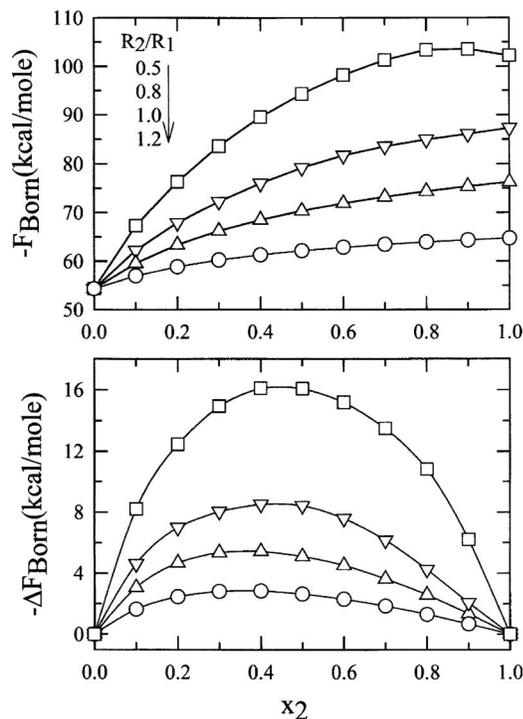


FIG. 1. Born free energy of solvation,  $F_{\text{Born}}$  (upper panel) and excess Born free energy of solvation,  $\Delta F_{\text{Born}}$  (lower panel) of a unipositive, rigid ion as a function of mole fraction of second component ( $x_2$ ) with higher dipole moment at different solvent-solvent size ratios ( $R_2/R_1$ ). The circles, triangles, inverted triangles, and squares are for solvent-solvent size ratios equal to 1.2, 1.0, 0.8, and 0.5, respectively. The line going through the points for each  $R_2/R_1$  is a guide to the bare eye. The dipole moments of two solvent components ( $\mu_1$  and  $\mu_2$ ) and diameter of the ion ( $R$ ) are kept fixed for all the solvent-solvent size ratios (Table I).

of solvation calculated for  $R_1=R_2$  matches *exactly* with available results of Morillo *et al.*<sup>16</sup> This indicates that the theory is correctly predicting the equal radii case. Note also that the reduction in size of the solvent component possessing larger dipole moment enhances the Born free energy of solvation. As a result, the nonlinearity is most pronounced for  $R_2=0.5R_1$ . The extent of nonlinearity, which is a measure of nonideality, is better understood in terms of the excess Born free energy of solvation,  $\Delta F_{\text{Born}}$ , calculated as follows:<sup>16,58</sup>

$$\begin{aligned} \Delta F_{\text{Born}}(x_2) &= F_{\text{Born}}(x_2) - F_{\text{Born}}(x_2=0) \\ &\quad - x_2[F_{\text{Born}}(x_2=1) - F_{\text{Born}}(x_2=0)] \\ &= F_{\text{Born}}(x_2) - [(1-x_2)F_{\text{Born}}(x_2=0) \\ &\quad + x_2F_{\text{Born}}(x_2=1)]. \end{aligned} \quad (38)$$

TABLE I. Parameters used in the calculation for model binary dipolar mixture.  $\mu_1$  and  $\mu_2$  are dipole moment of solvents 1 and 2, respectively.  $\varsigma$  is packing fraction,  $R$ ,  $R_1$ , and  $R_2$  are diameters of ion and solvent components 1 and 2, respectively. D stands for Debye.

| $\mu_1$ (D) | $\mu_2$ (D) | $\varsigma$ | $R$ ( $10^{-8}$ cm) | $R_1$ ( $10^{-8}$ cm) | $R_2$ ( $10^{-8}$ cm)  |
|-------------|-------------|-------------|---------------------|-----------------------|--|
| 0.816       | 1.632       | 0.42        | 2.88                | 2.88                  | (i) $0.5R_1$<br>(ii) $0.8R_1$<br>(iii) $1.0R_1$<br>(iv) $1.2R_1$ |

TABLE II. Solvent parameters used in the calculation for alcohol-water mixtures. Diameters of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ , and  $\text{C}_4$  ions are taken as 1.24, 1.96, 3.52, and  $10 \text{ \AA}$ , respectively (Ref. 2).

| Solvent      | Dipole moment (D) | Diameter ( $10^{-8}$ cm) |
|--------------|-------------------|--------------------------|
| Water        | 1.85              | 2.80                     |
| Methanol     | 1.70              | 4.24                     |
| Ethanol      | 1.69              | 4.78                     |
| Tert-butanol | 1.66              | 5.58                     |

The second equality of Eq. (38) indicates that the excess Born free energy of solvation is the deviation in Born free energy of solvation for an ion at a given mole fraction ( $x_2$ ) in a binary mixture from the *sum* of the mole fraction weighted Born free energies of solvation in the pure components. The excess Born free energy of solvation thus obtained is shown as a function of  $x_2$  in the *lower panel* of Fig. 1. It is clear that the magnitude of nonideality increases as the size of the solvent having higher dipole moment is decreased. However, the peak positions of  $\Delta F_{\text{Born}}$  on the mole fraction axis do not change substantially as one alters the solvent-solvent size ratio. This is because the ion size is kept fixed. All these observations indicate that the degree of nonideality in a completely asymmetric binary mixture depends not only on the relative dipole moments but also on the relative sizes of the constituent solvent species. The solvent size ratio dependence of nonideality in the excess Born free energy of solvation of an ion in a binary mixture is one of the main results of the present work and is demonstrated here for the first time to the best of our knowledge.

We next apply the present scheme for calculating the Born free energy of solvation ( $F_{\text{Born}}$ ) and excess Born free energy ( $\Delta F_{\text{Born}}$ ) of unipositive ions in alcohol-water binary mixtures. We have studied methanol-water, ethanol-water, and tertiary butanol (TBA)-water mixtures. The essential parameters<sup>2,59</sup> used in the calculation are summarized in Table II. The results obtained for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ , and  $\text{C}_4$  (quaternary tertiary butyl ammonium ion) in methanol-water mixture are shown in Fig. 2. Several interesting features are to be noted from the upper panel of Fig. 2. First,  $F_{\text{Born}}$  for  $\text{Li}^+$  at all methanol compositions is the largest of all the ions studied here. This is also the prediction of earlier works in pure solvents<sup>15</sup> and equal-sized dipolar mixtures.<sup>16</sup> Also,  $F_{\text{Born}}$  calculated here for all ions in pure liquid (water or alcohol) matches exactly with those from Chan *et al.*<sup>15</sup> Second, the nonideality in  $F_{\text{Born}}$  decreases as the size of the ion is increased. Note the peak ratio in  $\Delta F_{\text{Born}}$  between  $\text{Li}^+$  and  $\text{C}_4 \sim 4$ . This indicates that the larger solvent species is in-

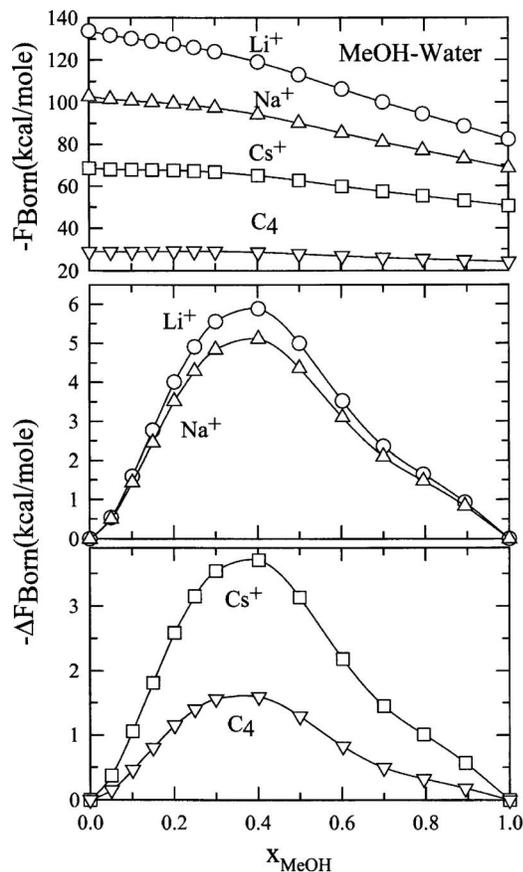


FIG. 2. Upper panel. Comparison of Born free energy of solvation  $F_{\text{Born}}$  for  $\text{Li}^+$  (circles),  $\text{Na}^+$  (triangles),  $\text{Cs}^+$  (squares), and  $\text{C}_4$  (inverted triangles) ions as a function of mole fraction of methanol ( $x_{\text{MeOH}}$ ) in methanol-water mixture. Middle panel. Comparison of excess Born free energies of solvation  $\Delta F_{\text{Born}}$  for  $\text{Li}^+$  (circles) and  $\text{Na}^+$  (triangles) ions as a function of mole fraction of methanol ( $x_{\text{MeOH}}$ ) in methanol-water mixture. Lower panel. Comparison of excess Born free energy of solvation  $\Delta F_{\text{Born}}$  for  $\text{Cs}^+$  (squares) and  $\text{C}_4$  (inverted triangles) ions as a function of mole fraction of methanol ( $x_{\text{MeOH}}$ ) in methanol-water mixture. Other representations remain the same as in the Fig. 1.

creasingly accommodated as the ion size is increased. The situation becomes even more interesting for TBA-water mixtures, shown in Fig. 3. Here, the nonideality in  $F_{\text{Born}}$  for  $\text{Li}^+$  to  $\text{Na}^+$  shows a slope opposite to that found in aqueous methanol solutions. The positive values of  $\Delta F_{\text{Born}}$  for  $\text{Li}^+$  to  $\text{Na}^+$  in TBA-water mixture indicate that due to larger size TBA molecules cannot be packed around these smaller ions as efficiently as methanol or ethanol. This constraint is, however, partially lifted when the ion becomes larger. Consequently,  $\Delta F_{\text{Born}}$  for  $\text{Cs}^+$  and  $\text{C}_4$  show the similar mole fraction dependence as found in methanol-water and ethanol-water mixtures. This completes the nonideal behavior on both sides of the ideal curve. It is interesting to note that even though TBA is larger in size than methanol,  $\Delta F_{\text{Born}}$  for  $\text{Cs}^+$  and  $\text{C}_4$  is smaller in TBA-water mixture than that in methanol-water mixture. This is a manifestation of the role of ion-solvent size ratio in determining the extent of nonideality. As we would see later, the solvent structure in asymmetric binary polar mixture around larger ions is relatively more “homogeneous” than around smaller ions. Since dipole moments of these alcohols are almost the same,<sup>2</sup> this result

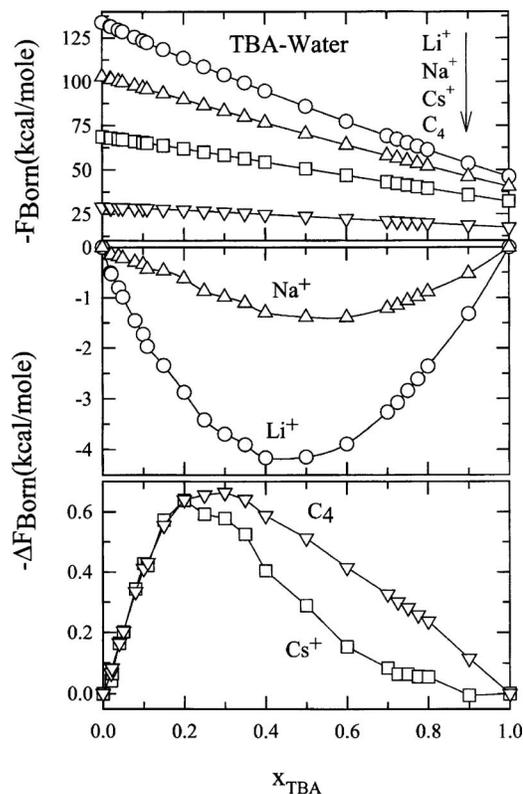


FIG. 3. Upper panel: Comparison of Born free energy of solvation  $F_{\text{Born}}$  for  $\text{Li}^+$  (circles),  $\text{Na}^+$  (triangles),  $\text{Cs}^+$  (squares), and  $\text{C}_4$  (inverted triangles) ions as a function of mole fraction of tertiary butanol ( $x_{\text{TBA}}$ ) in tertiary butanol-water (TBA-water) mixture. Middle panel. Comparison of excess Born free energy of solvation  $\Delta F_{\text{Born}}$  for  $\text{Li}^+$  (circles) and  $\text{Na}^+$  (triangles) ions as a function of mole fraction of TBA ( $x_{\text{TBA}}$ ) in TBA-water mixture. Bottom panel: Comparison of excess Born free energy of solvation  $\Delta F_{\text{Born}}$  for  $\text{Cs}^+$  (squares) and  $\text{C}_4$  (inverted triangles) ions as a function of mole fraction of TBA ( $x_{\text{TBA}}$ ) in TBA-water mixture.

indicates the important roles being played by ion-solvent and solvent-solvent size ratios in governing the solvent structure around an ion in binary mixtures.

The solvent size ratio dependences of  $F_{\text{Born}}$  and  $\Delta F_{\text{Born}}$  are shown in Fig. 4, where Born free energy of solvation and excess Born free energy of solvation are calculated for  $\text{C}_4$  in aqueous methanol, ethanol, and TBA solutions. As expected, the Born free energy of solvation ( $F_{\text{Born}}$ , upper panel) is the largest in aqueous methanol solutions at all compositions. Also, the peak in excess Born free energy ( $\Delta F_{\text{Born}}$ , lower panel) is the highest in aqueous methanol solution. Note that the peak in  $\Delta F_{\text{Born}}$  is shifting toward lower alcohol mole fraction as the chain length of the alcohol increases. It is believed that because the perturbation on water structure becomes stronger as the alkyl chain length increases, leading to an appreciable modification in water structure at lower alcohol concentration for TBA than for methanol.<sup>60–62</sup> The fact that the solvent-solvent size ratio plays an important role in these complex mixtures is indeed manifested in Fig. 4. Moreover, these peaks are occurring between 0.3 and 0.2 mole fractions of alcohols studied here. In addition, the peak size depends on the size of the alcohol as well as that of the ion dissolved (see Fig. 2 also). All these observations are similar to what have been observed earlier when partial molal heat of solution for several crystalline salts were measured in

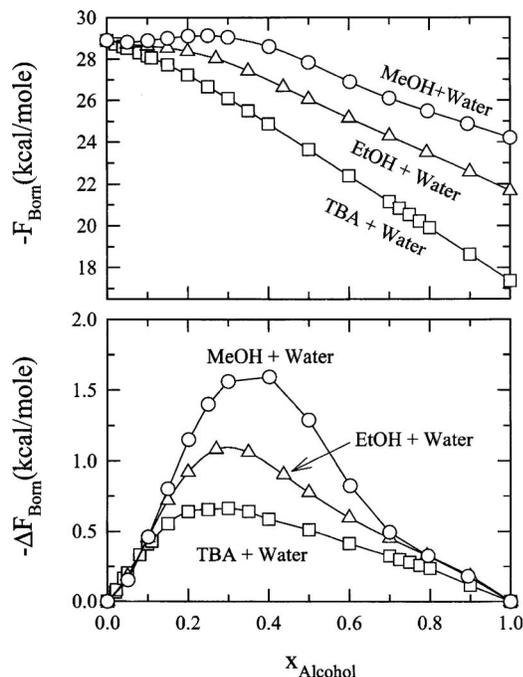


FIG. 4. Comparison of Born free energy of solvation  $F_{\text{Born}}$  (upper panel) and excess Born free energy of solvation  $\Delta F_{\text{Born}}$  (lower panel) for  $C_4$  ion in methanol-water (circles), ethanol-water (triangles), and TBA-water mixture (squares). For further discussion, see text.

alcohol-water mixtures.<sup>60–62</sup> Studies of these systems using techniques such as sound velocity measurements,<sup>23–25</sup> Fourier transform near-infrared spectroscopy,<sup>26</sup> light<sup>34,35</sup> and x-ray scattering,<sup>36,37</sup> neutron scattering and diffraction,<sup>29–32,38–41</sup> dielectric relaxation,<sup>27,43</sup> and computer simulation<sup>44–49</sup> also revealed similar nonmonotonic alcohol mole fraction dependence in the respective properties which was subsequently explained in terms of modification of the three-dimensional hydrogen-bonded network structure of water by successive addition of alcohols. Since specific interaction such as hydrogen bonding between water and alcohol molecules is absent in the present theory, the emergence of these peaks and tuning of them with alcohol size are purely originating from the interactions between the ion and solvents of different types and also between solvent molecules of the same and different types. These interactions are essentially size mediated electrostatic attraction or repulsion giving rise to solvent structural rearrangement. Therefore, the size mediated structural rearrangement is an inherent property of an asymmetric binary mixture, the magnitude of which is accentuated or attenuated by the presence of specific interactions.

## B. Partial solvent polarization densities

Since the Born free energy of solvation ( $F_{\text{Born}}$ ) is obtained from the partial solvent polarization densities [see Eqs. (18), (34), and (35)], one needs to look at these quantities for molecular level understanding of the nonideality shown by  $F_{\text{Born}}$  in these alcohol-water mixtures. Figure 5 shows the partial solvent polarization for  $\text{Li}^+$  and  $C_4$  dissolved in TBA-water mixture at three different alcohol mole fractions. Note that the peak height in all cases is larger for

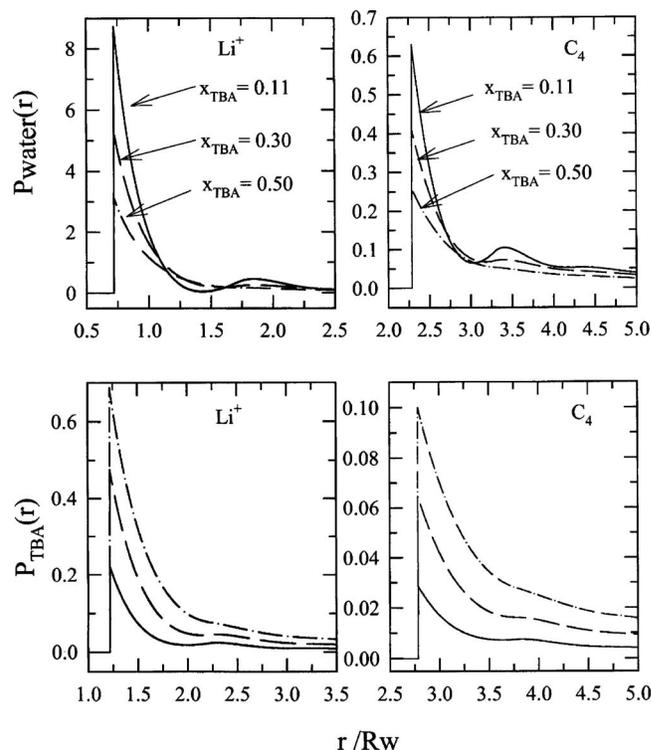


FIG. 5. Partial polarization of water  $P_{\text{water}}(r)$  and TBA  $P_{\text{TBA}}(r)$  (both scaled by  $\sqrt{k_B T / R_w^3}$ ) around  $\text{Li}^+$  and  $C_4$  ions as a function of distance  $r$  (scaled by water diameter  $R_w$ ) from the center of the ion at three different TBA mole fractions. In all the panels calculated data for TBA mole fractions 0.11, 0.30, and 0.50 are represented by solid, dashed, and dotted-dash lines, respectively. For discussion, see text.

smaller ions. This is consistent with the findings of Chan *et al.*<sup>15</sup> in pure solvents. It is evident from this figure that the polarization density due to water around these ions is greater at all compositions than that due to TBA. Also, the water polarization density is decreased as the mole fraction of the alcohol is gradually increased. Interestingly, even in 50:50 alcohol-water mixture, the peak in polarization density due to water is approximately three times larger than that due to TBA. This means that water is preferred over TBA molecules in the first solvation shells around these ions. This is the molecular origin of the nonideality in Born energy of solvation, discussed already in connection with Figs. 2–4. In fact, as shown in Fig. 6, the excess partial polarization densities [ $\Delta P$  (peak)] calculated from the mole fraction dependent peak values in TBA-water mixtures also show nonideality similar to what has been observed for the excess Born free energy of solvation (see Figs. 2–4). Also,  $\Delta P$  (peak) and  $\Delta F_{\text{Born}}$  exhibit similar ion size dependence.

## C. Comparison with experiments

As already discussed, the present theory treats the binary solvent components as dipoles embedded on hard spheres which is very different from the real situation. For example, alcohol-water solutions are known to exhibit anomalous behavior due to hydrophobic interaction and specific interaction (H bonding) between the alcohol and water molecules. In such solutions where an intricate balance between hydrophobic hydration and H-bonding interaction dictates the so-

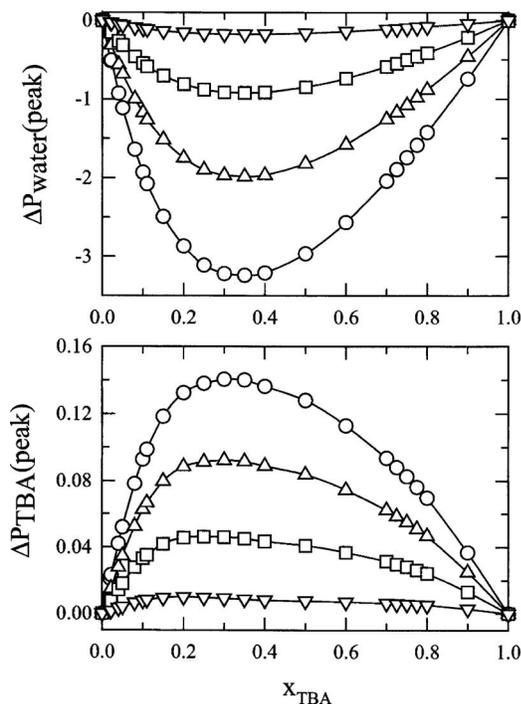


FIG. 6. Excess partial polarization of water (upper panel)  $\Delta P_{\text{water}}(\text{peak})$  and TBA  $\Delta P_{\text{TBA}}(\text{peak})$  calculated from the peak values of respective partial polarizations for  $\text{Li}^+$  (circles),  $\text{Na}^+$  (triangles),  $\text{Cs}^+$  (squares), and  $\text{C}_4$  (inverted triangles) ions as a function of mole fraction of TBA ( $x_{\text{TBA}}$ ) in TBA-water mixture. The following expression has been used to calculate  $\Delta P_i(\text{peak})$  ( $i = \text{water}$  or TBA):  $\Delta P_i(\text{peak}, x_2) = P_i(\text{peak}, x_2) - P_i(\text{peak}, x_2 = 0) - x_2 [P_i(\text{peak}, x_2 = 1) - P_i(\text{peak}, x_2 = 0)]$ .

lution property, the success of a simple theory such as MSA in predicting the experimental behavior is somewhat fraught with danger. However, nonspecific interactions such as size mediated and Coulomb (ion-dipole and dipole-dipole) interactions could still play a significant role in determining the solvent structure around an ion in these complex mixtures. Therefore, there is always a possibility that for some ion-solvent and solvent-solvent combinations, the nonspecific interactions would dominate the preferential solvation. For those cases, one would expect a qualitative agreement between the present theory and the relevant experimental results. We will now discuss several of those cases.

Figure 7 depicts the comparison of nonideality in Born free energy of solvation in three different binary mixtures, namely, methanol-water, ethanol-water, and DMSO-acetonitrile solutions. While the excess free energy of solvation obtained from experiments<sup>63</sup> for different ions in these solvent mixtures is shown in the left panels of Fig. 7, the theoretical results are presented in the right panels. We would like to mention here that one should not directly compare the experimental results with the theory as the present theory calculates only the electrostatic part of the free energy of solvation. It is also known that for alkali metal ions, the entropic contribution to the solvation free energy is negligible.<sup>64</sup> Several aspects are to be noted in this figure. First, for a large ion such as tetra-alkyl quaternary ammonium ion ( $\text{C}_4$ ) in methanol-water mixture, the calculated excess Born free energy of solvation ( $-\Delta F_{\text{Born}}$ ) shows a slope

qualitatively similar to that in experimentally observed mole fraction dependent excess free energy of solvation ( $-\Delta G$ ). For alkali metal ions, however, the slope is opposite to that found in experiments. This is probably because the solution structure in the presence of a big organic ion is more homogeneous, where the specific and hydrophobic interactions play a secondary role. Recent neutron diffraction studies of ternary mixtures composed of cyclohexene, TBA, and water in 2:6:1 ratio suggest that the microscopic heterogeneity is much weaker in ternary solutions than in binary mixtures<sup>40</sup> and hence the solution is less biphasic where microclustering of water molecules is not supported. Similar modifications may also take place in methanol-water mixtures in the presence of tetra-alkyl ammonium ion ( $\text{C}_4$ ). Since the solvent structure around a dissolved ion in such cases is likely to be governed by the size mediated and electrostatic interactions, the MSA may be able to predict the qualitative behavior of the experimentally observed mole fraction dependence of free energy of solvation. However, the microscopic heterogeneity in solution structure is likely to remain unchanged in the presence of smaller ions, and hence the theory is in poor agreement with experiments in such cases. Even though the excess Born free energy of solvation for alkali metal ions such as  $\text{Na}^+$  and  $\text{Cs}^+$  in methanol-water solutions shows non-ideality in a direction opposite to that found in experiments, the experimentally observed ion size dependence is well captured by the present theory.

Next we discuss the mole fraction dependence of excess Born free energy of solvation ( $-\Delta F_{\text{Born}}$ ) for these ions and compare them with the experimental excess free energy of solvation ( $-\Delta G$ ) in ethanol-water mixtures. Interestingly, in water-ethanol mixtures (middle panels) the nonideality in  $-\Delta F_{\text{Born}}$  for all the ions is qualitatively similar to that found in experimentally obtained  $-\Delta G$ . From the arguments given for methanol-water solutions,  $-\Delta F_{\text{Born}}$  for  $\text{C}_4$  in ethanol-water mixture is expected to show qualitative agreement with the corresponding experimental  $-\Delta G$ . However, the reasons for the qualitative agreement between theory and experiments for alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{Cs}^+$ ) are not obvious to us. It might be that since  $-\Delta F_{\text{Born}}$  in the present theory is dictated by a combination of ion size, solvent-solvent size ratio, dipole moments, and solution density (obtained from experiments), the calculation explores the right parameter space which leads to such a qualitative agreement with experiment. It could also be that such an agreement is fortuitous if one keeps in mind the complexity of the interactions involved in these systems and also the simplified model that the present theory is using to study them. Therefore, one should use sophisticated theories such as those proposed by Yoshida *et al.*<sup>49</sup> and Omelyan *et al.*<sup>50</sup> in order to explore how subtle differences in the hydrophobic and H-bonding interactions and their effects on microscopic solution structure lead to a different behavior of excess free energy of solvation for alkali metal ions in methanol-water and ethanol-water solutions. Similar comparisons for TBA-water systems could not be made as the experimental data at all TBA mole fractions are not available. However, for larger

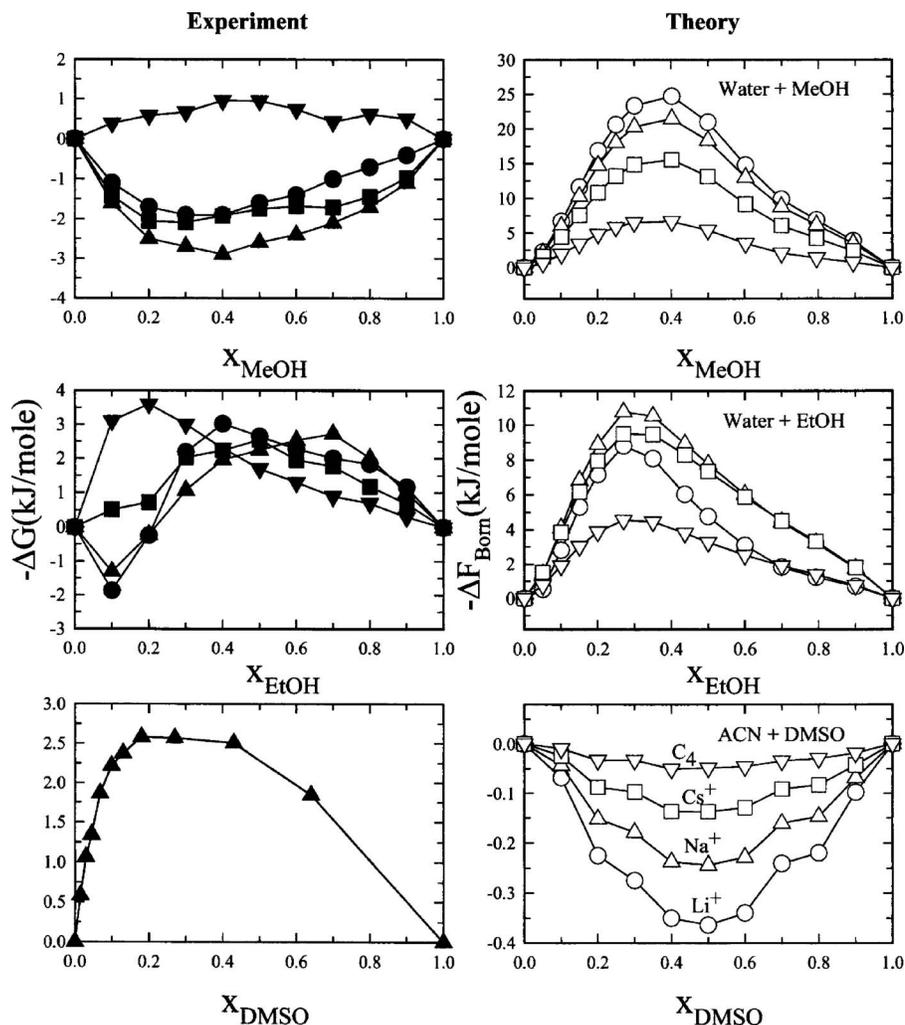


FIG. 7. Comparison between the calculated excess Born free energy of solvation ( $-\Delta F_{\text{Born}}$ ) and experimental excess free energy of solvation ( $-\Delta G$ ) for  $\text{Li}^+$  (circles),  $\text{Na}^+$  (triangles),  $\text{Cs}^+$  (squares), and  $\text{C}_4$  (inverted triangles) ions in binary mixtures of methanol-water (upper panels), ethanol-water (middle panels), and DMSO-acetonitrile (bottom panel). These excess functions are shown as a function of mole fraction of one of the components in the mixture. The experimental data are represented by the solid symbols, while the predictions from the extended MSA theory are shown by the open symbols.

ions such as  $\text{Cs}^+$  and  $\text{C}_4$ , the available data on free energy of solvation are showing the same qualitative trend as predicted by the present theory.

Let us now focus our attention on similar studies in a nonassociating binary liquid mixture where both the solvent components are polar yet not involved in H-bonding interaction either between molecules of same species or between different species. We have chosen DMSO-acetonitrile mixture<sup>65</sup> as an example of the above type. In addition, the molecular diameter and dipole moment of DMSO are slightly larger (4.1 D and 5.3 Å) than those of acetonitrile (3.5 D and 4.5 Å). Therefore, a competition between the size mediated and electrostatic interactions would lead to a nonideality much less pronounced compared to the systems composed of molecules with dissymmetric size and dipole moments. This is indeed the scenario as shown by the calculated  $-\Delta F_{\text{Born}}$  in the bottom panel of Fig. 7. However, the predicted nonideality is not only growing in a direction opposite to that found in experiments<sup>63(b)</sup> (data available only for  $\text{Na}^+$ ) but also differs in magnitude. This is probably due to the specific ion-solvent interaction between the dissolved ion and DMSO molecule (through the lone pair of electrons). Effects of such specific ion-solvent interactions have also been found while studying ion mobility in DMSO-acetonitrile mixtures. Such ion-solvent specific interaction

may drastically alter the solution structure around a dissolved ion which cannot be accounted for by the extended MSA approach. This is definitely a limitation of the present theory.

Although the above comparison tests the applicability of the extended MSA theory in describing the experimentally observed nonideality of the excess Born free energy of solvation for unipositive rigid ions in aqueous solutions of several alcohol and DMSO-acetonitrile mixtures, these results do not indicate whether the nonideality of solutions themselves is described adequately. This check is necessary for the following reason. Note that the nonideality in the presence of an ion in a binary mixture is guided by the ion-dipole and dipole-dipole interactions, whereas the same in binary mixtures (absence of any ion) is governed by only the dipole-dipole interactions. Since the nonideality in the presence and the absence of ion is guided by different types of interactions, the nonideality seen in the presence of ion does not automatically ensure the same in the binary mixture in the absence of the ion. This aspect of solution chemistry is addressed below.

In Fig. 8 we compare experimentally obtained excess Gibbs free energy of mixing<sup>66</sup>  $\Delta G_{\text{mix}}$  (left panels) with an equivalent quantity ( $\Delta U/2$ ) obtained from the theory (right panels) for alcohol-water (upper panels) and DMSO-

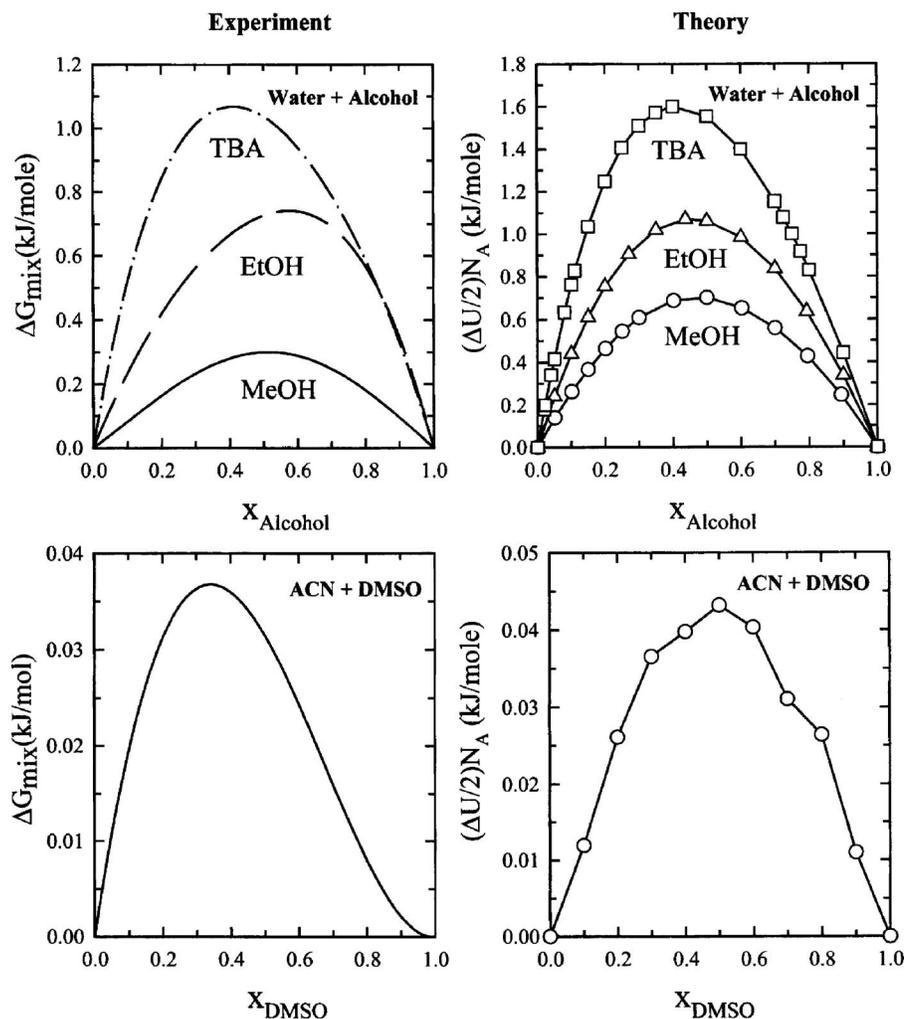


FIG. 8. Comparison between experiment (left panels) and theory (right panels) for excess free energy of mixing in alcohol-water (upper panels) and DMSO-acetonitrile mixtures (lower panels). The solid line represents the experimental results for methanol-water mixture, dashed line the ethanol-water, and the dot-dashed line the TBA-water results. The line going through the symbols (squares, triangles, and circles) is simply a guide for the eye. Note that no experimental data exist for  $\Delta G_{\text{mix}}$  for DMSO-acetonitrile mixture; only the excess enthalpy of mixing  $\Delta H_{\text{mix}}$  is available. The excess volume of mixing for dimethylsulfoxide-acetonitrile mixture is very small compared to that in alcohol-water mixture which are known to possess a large volume contraction (Ref. 66). Under certain approximations, Hildebrand and Wood (Ref. 68) and Scatchard (Ref. 69) showed that  $\Delta G_{\text{mix}} \cong \Delta H_{\text{mix}}$ .

acetonitrile (lower panels) mixtures. The approximations and logic required for the equivalence of these two quantities for binary mixtures considered here could be found in the relevant literature.<sup>14,47</sup> The expression for the internal energy (due to dipole-dipole interaction) per particle for completely asymmetric dipolar liquid mixture is given by<sup>54</sup>

$$\begin{aligned}
 U &= -\frac{4\pi}{3} \sum_{i=1}^2 \sum_{j=1}^2 \sqrt{x_i x_j} \sqrt{\rho_i \rho_j} \mu_i \mu_j \int_{R_{ij}}^{\infty} \frac{h_{ij}^D(r)}{r} dr \\
 &= -\frac{4\pi}{3} \sum_{i=1}^2 \sum_{j=1}^2 \sqrt{x_i x_j} \sqrt{\rho_i \rho_j} \mu_i \mu_j \kappa_{ij}.
 \end{aligned} \quad (39)$$

In Eq. (39),  $x_i$  is the mole fraction of the  $i$ th species constituting the binary mixture. In the MSA the excess free energy of mixing per mole is approximately given by<sup>14,54,67</sup>  $(\Delta U/2)N_A$ , where  $N_A$  is the Avogadro number.  $\Delta U$  is calculated by the equation similar to Eq. (38). It is evident from Fig. 8 that the MSA is comparing well with the experiments for both the alcohol-water and DMSO-acetonitrile systems. This is indeed surprising, particularly for alcohol-water systems, as the solution structure here is governed by specific interactions. Note that the mole fraction at which the peak of the nonideality occurs also matches semiquantitatively with those found in experiments. For acetonitrile-DMSO mixture,

the agreement is even better as no specific interactions govern the solution structure in this mixture.<sup>68,69</sup>

#### IV. CONCLUSION

In this article we have presented analytical expressions for Born free energy of solvation of a singly charged rigid ion in a binary mixture of dipolar hard spheres of unequal radii and different dipole moments. The relevant expressions are derived within the framework of mean spherical approximation (MSA). Analytical expressions for the partial solvent polarization density about an ion in such a completely asymmetric mixture are also presented. The analytical tractability of MSA is preserved in the present formalism, which is important for a quick and qualitative understanding of solution structure in complex liquid mixtures. It has been found that the excess Born free energy of solvation depends both on the ion size and size disparity between solvent molecules in a binary mixture. This is in addition to the contribution arising out of difference in dipole moments. Note here that ion solvation in an asymmetric dipolar mixture has already been studied by several authors.<sup>5,58</sup> In these studies,<sup>5,58</sup> however, the MSA was not solved by consistently incorporating the ion size. Instead, solvent intra- and intermolecular correlations were obtained from the solutions of dipolar MSA. Systematic incorporation of ion size is crucial because the po-

larization structure at the surface of the ion is very different from that at two or three molecular diameter away. The present work therefore reveals that not only the size of the solvent molecules but also the size of the ion plays an important role in determining the extent of nonideality.

When the present theory is applied to binary mixtures with solvent parameters representing water and several monohydroxyl alcohols, the excess Born free energy of solvation shows a nonmonotonic mole fraction dependence. The peak in the excess Born free energy of solvation has been found to decrease with the increase in the size of the alcohol molecule. Also, the peaks are occurring at lower mole fraction of alcohol as the alcohol size becomes larger. These results are surprisingly similar to what have been found earlier in several experimental studies. In the present work the nonmonotonic alcohol mole fraction dependence of the excess Born free energy of solvation arises due to a novel interplay among size mediated electrostatic interactions between ion, alcohol, and water molecules, and between alcohol-alcohol, alcohol-water, and water-water molecules. The calculated microscopic partial polarization densities around a dissolved ion indicate the molecular origin of the preferential solvation and explain the nonideality in excess Born free energy of solvation in terms of intra- and intermolecular correlations. These results also indicate that for a system of equal size and dipole moments, the nonideality will be either very weak or nonexistent in the absence of any specific interactions. Dimethyl sulfoxide (DMSO) and acetonitrile molecules are both very close in size and dipole moments, and our studies with DMSO-acetonitrile mixtures indeed show a very weak nonideality.<sup>65</sup> However, experimental data on mobility for small alkali ions in DMSO-acetonitrile mixtures<sup>52</sup> indicate the presence of a donor-acceptor bond between ion and a DMSO molecule, probably through the interaction of the ion with the lone pair of electrons on the oxygen atom of a DMSO molecule. Therefore, the experimental data with small alkali ions in this mixture are expected to show a stronger nonideality than predicted by the present theory. Formation of donor-acceptor-type ion-solvent complex is unfavorable with large symmetrical organic ions due to steric reasons, and hence the theoretical predictions for these ions would be closer to experimental results. When the excess functions for the binary mixtures themselves (that is, in the absence of any ion) have been calculated from the MSA and compared with the relevant experimental results, a good qualitative agreement has been found for all these complex liquid mixtures.

It is to be noted here that since the present work is based on the mean spherical approximation (MSA), the effects of shape of the molecules and specific interactions among them have not been incorporated. Therefore, the correlations derived from the present work are qualitative in nature. Needless to say, a full nonlinear treatment with a systematic incorporation of the shape and specific interaction effects will lead to a quantitative description of solution structure in binary dipolar mixtures. Integral equation theory coupled with RISM approach by Yoshida *et al.*<sup>49</sup> and Omelyan *et al.*<sup>50</sup> has been found to be successful in describing qualitatively many of the experimental data in water-alcohol systems discussed

here. However, this approach is nontrivial and numerically involved. The present approach, on the other hand, is based on the MSA framework, which is simple and analytically tractable, yet capable of describing *qualitatively* the nonideality in alcohol-water mixtures in terms of microscopic solvent structure.

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## APPENDIX A: ORNSTEIN-ZERNIKE RELATIONS FOR IONS IN BINARY MIXTURES

The Ornstein-Zernike (OZ) relations for the correlation functions in an electrolyte solution of binary dipolar mixture are written as<sup>16</sup>

$$\begin{aligned}
 h_{\alpha\beta}(r) &= c_{\alpha\beta}(r) + \sum_{\gamma} \rho_{\gamma} \int ds c_{\alpha\gamma}(|\mathbf{r}-\mathbf{s}|) h_{\gamma\beta}(s) \\
 &\quad + \sum_k \rho_k \int ds \langle c_{\alpha k}(\mathbf{r}-\mathbf{s}) h_{k\beta}(\boldsymbol{\omega}_3, \mathbf{s}) \rangle_{\boldsymbol{\omega}_3}, \\
 h_{\alpha j}(\mathbf{r}, \boldsymbol{\omega}_2) &= c_{\alpha j}(\mathbf{r}, \boldsymbol{\omega}_2) + \sum_{\gamma} \rho_{\gamma} \int ds c_{\alpha\gamma}(|\mathbf{r}-\mathbf{s}|) h_{\gamma j}(\mathbf{s}, \boldsymbol{\omega}_2) \\
 &\quad + \sum_k \rho_k \int ds \langle c_{\alpha k}(\mathbf{r}-\mathbf{s}, \boldsymbol{\omega}_3) h_{kj}(\boldsymbol{\omega}_3, \mathbf{s}, \boldsymbol{\omega}_2) \rangle_{\boldsymbol{\omega}_3}, \\
 h_{i\beta}(\boldsymbol{\omega}_1, \mathbf{r}) &= c_{i\beta}(\boldsymbol{\omega}_1, \mathbf{r}) + \sum_{\gamma} \rho_{\gamma} \int ds c_{i\gamma}(\boldsymbol{\omega}_1, \mathbf{r}-\mathbf{s}) h_{\gamma\beta}(s) \\
 &\quad + \sum_k \rho_k \int ds \langle c_{ik}(\boldsymbol{\omega}_1, \mathbf{r}-\mathbf{s}, \boldsymbol{\omega}_3) h_{k\beta}(\boldsymbol{\omega}_3, \mathbf{s}) \rangle_{\boldsymbol{\omega}_3}, \\
 h_{ij}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2) &= c_{ij}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2) \\
 &\quad + \sum_{\gamma} \rho_{\gamma} \int ds c_{i\gamma}(\boldsymbol{\omega}_1, \mathbf{r}-\mathbf{s}) h_{\gamma j}(\mathbf{s}, \boldsymbol{\omega}_2) \\
 &\quad + \sum_k \rho_k \int ds \langle c_{ik}(\boldsymbol{\omega}_1, \mathbf{r}-\mathbf{s}, \boldsymbol{\omega}_3) \\
 &\quad \times h_{kj}(\boldsymbol{\omega}_3, \mathbf{s}, \boldsymbol{\omega}_2) \rangle_{\boldsymbol{\omega}_3}, \tag{A1}
 \end{aligned}$$

where  $c$  and  $h$  denote the direct and total (or indirect) correlation functions, respectively.  $\langle \rangle_{\boldsymbol{\omega}} = 1/4\pi \int d\boldsymbol{\omega}$ , denoting angular convolution. The MSA closure conditions here are given by<sup>16</sup>

$$h_{IJ}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2) = -1, \quad r < R_{IJ}^c,$$

$$c_{IJ}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2) = -(k_B T)^{-1} u_{IJ}(\boldsymbol{\omega}_1, \mathbf{r}, \boldsymbol{\omega}_2), \quad r > R_{IJ}^c, \quad (\text{A2})$$

where  $I = \alpha, i$ ;  $J = \beta, j$  and for other notations we refer to the works of Morrillo *et al.*<sup>16</sup>  $k_B T$  is the Boltzmann constant times the absolute temperature. The angular functions  $1, E_i, D_{ij}$ , and  $\Delta_{ij} = \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_i) \cdot \hat{\boldsymbol{\mu}}(\boldsymbol{\omega}_j)$  form a closed set under the angular convolution  $\langle A(\boldsymbol{\omega}_1, \boldsymbol{\omega}_3) B(\boldsymbol{\omega}_3, \boldsymbol{\omega}_2) \rangle_{\boldsymbol{\omega}_3}$ . Multiplication table for these quantities can be found in Ref. 15.

## APPENDIX B: CONNECTION BETWEEN $F$ AND $f$ FUNCTIONS

The relation between the ‘‘one-dimensional’’ functions  $F$  and their ‘‘three-dimensional’’ counterpart  $f$  are given by<sup>15,16</sup>

$$\begin{aligned} F_{\alpha\beta}^C(x) &= 2\pi \int_x^\infty dr P_0(x/r) r f_{\alpha\beta}^C(r), \\ F_{\alpha j}^E(x) &= 2\pi \int_x^\infty dr P_1(x/r) r f_{\alpha j}^E(r), \\ F_{i\beta}^E(x) &= 2\pi \int_x^\infty dr P_1(x/r) r f_{i\beta}^E(r), \\ F_{ij}^\Delta(x) &= 2\pi \int_x^\infty dr P_0(x/r) r f_{ij}^\Delta(r), \\ F_{ij}^D(x) &= 2\pi \int_x^\infty dr P_2(x/r) r f_{ij}^D(r), \end{aligned} \quad (\text{B1})$$

where  $P_0(x) = 1$ ,  $P_1(x) = x$ ,  $P_2(x) = (1/2)(3x^2 - 1)$  are Legendre polynomials. In an equivalent way, one can write as

$$\begin{aligned} 2\pi r f_{\alpha\beta}^C(r) &= -\frac{d}{dr} F_{\alpha\beta}^C(r), \quad 2\pi r f_{\alpha j}^E(r) = \left(\frac{1}{r} - \frac{d}{dr}\right) F_{\alpha j}^E(r), \\ 2\pi r f_{i\beta}^E(r) &= \left(\frac{1}{r} - \frac{d}{dr}\right) F_{i\beta}^E(r), \quad 2\pi r f_{ij}^\Delta(r) = -\frac{d}{dr} F_{ij}^\Delta(r), \\ \pi^2 f_{ij}^D(r) &= -r^2 \left(\frac{1}{r} \frac{d}{dr}\right)^2 \frac{1}{r} \int_0^r dx F_{ij}^D(x). \end{aligned} \quad (\text{B2})$$

## APPENDIX C: EXPRESSIONS FOR $a_{ij}$ AND $b_{ij}$

The value of  $a_{ij} \equiv [b]$  can be obtained by the following equation:

$$[b] = [R][B] \left\{ I - \frac{1}{6} [\rho][R^3][B] \right\}^{-1} \quad (\text{C1})$$

and  $a_{ij} \equiv [a]$  is given by

$$[a] = 2 \left\{ I + \frac{1}{2} [b][R^2][\rho] \right\} \left\{ I - \frac{1}{6} [B][R^3][\rho] \right\}^{-1} [B], \quad (\text{C2})$$

where

$$[\rho]_{ij} = \rho_i \delta_{ij}, \quad [R^n]_{ij} = R_i^n \delta_{ij}, \quad \text{and} \quad [B]_{ij} = 2\pi \kappa_{ij}, \quad (\text{C3})$$

where  $\kappa_{ij} = \int_{R_{ij}}^\infty (h_{ij}^D(r)/r) dr = \kappa_{ji}$  are obtained by solving the following set of equations:<sup>14,54</sup>

$$\begin{aligned} 3y_{11} &= \Phi_{11}(2\rho_1 \kappa_{11}, 2\rho_2 \kappa_{12}^2 / \kappa_{11}) \\ &\quad - \Phi_{11}(-\rho_1 \kappa_{11}, -\rho_2 \kappa_{12}^2 / \kappa_{11}), \\ 3y_{22} &= \Phi_{22}(2\rho_1 \kappa_{12}^2 / \kappa_{22}, 2\rho_2 \kappa_{22}) \\ &\quad - \Phi_{22}(-\rho_1 \kappa_{12}^2 / \kappa_{22}, -\rho_2 \kappa_{22}), \\ 3y_{12} &= \frac{\kappa_{12}}{\kappa_{11}} \{ \Phi_{12}(2\rho_1 \kappa_{11}, 2\rho_2 \kappa_{22}) - \Phi_{12}(-\rho_1 \kappa_{11}, -\rho_2 \kappa_{22}) \}, \end{aligned} \quad (\text{C4})$$

where  $3y_{ij} = (4\pi/3)\beta\rho_i\mu_i\mu_j$ .

$\Phi_{ij}(\rho_i, \rho_j)$  is given by

$$\Phi_{ij} = \rho_i \frac{\partial \beta \mu_i}{\partial \rho_j} \quad (\text{C5})$$

$\mu_i$  is the chemical potential of  $i$ th species in the mixture which is given by

$$\begin{aligned} \beta \mu_i(\rho_1, \rho_2) &= \ln(\rho_i \Lambda_i^3) - \ln(1 - s) + \frac{\pi}{6} R_i^3 \beta p \\ &\quad + \frac{3R_i^2}{(1-s)} (\eta_1 R_1 + \eta_2 R_2) \\ &\quad + \frac{9R_i^2}{2(1-s)^2} (\eta_1 R_1^2 - \eta_2 R_2^2)^2 \\ &\quad + \frac{3R_i}{(1-s)} (\eta_1 R_1^2 + \eta_2 R_2^2), \end{aligned} \quad (\text{C6})$$

where  $s = s_1 + s_2$ ,  $s_i = (\pi/6)\rho_i R_i^3$ , and  $\eta_i = (\pi/6)\rho_i$ . In Eq. (C6),  $p$  is the compressibility pressure which is given by

$$\begin{aligned} \beta p &= (\rho_1 + \rho_2)(1 + s + s^2)(1 - s)^{-3} - \frac{18}{\pi} \eta_1 \eta_2 (R_2 - R_1)^2 \\ &\quad \times \{ (R_1 + R_2) + R_1 R_2 (\eta_1 R_1^2 + \eta_2 R_2^2) \} (1 - s)^{-3}. \end{aligned} \quad (\text{C7})$$

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