Ion Solvation in Water–Acetonitrile Mixtures[1]

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The results of a preliminary molecular dynamics study of ion (Na^+ and Cl^-) solvation and association in water, acetonitrile, and aqueous acetonitrile are discussed. These mixtures are compositionally heterogeneous on the scale of a few molecular sizes, and this heterogeneity is expected to be an important factor governing ion solvation and association. Results for ions in pure water and pure acetonitrile are presented for ambient conditions. The degree of association is low in water, a high-density fluid, and high in acetonitrile, a low-density fluid. A separate set of simulations for water at supercritical temperatures demonstrates that the fluid density is more important than the temperature in determining the degree of ion association. Preliminary results for the mixtures are inconclusive except that they indicate the existence of an important sampling issue related to the compositional heterogeneity of the mixtures. An approach to resolving the sampling issue is suggested.

KEY WORDS: acetonitrile; aqueous acetonitrile; ion association; ion solvation; molecular dynamics; water.

1. INTRODUCTION

It has been known for some time that mixtures of water and acetonitrile are compositionally heterogeneous on the molecular length scale. Thermodynamic arguments suggest that the magnitudes and signs of the entropy of mixing and of the enthalpy of mixing are indications of small-scale compositional heterogeneity. The existence of the microheterogeneous character of these mixtures was determined using a combination of thermodynamic and fluctuation theory-based arguments [1–3]. The Kirkwood–Buff theory

of solutions [4] provides a formal link between the concentration fluctuations of a mixture and thermodynamic properties. The values of these integrals for water–acetonitrile mixtures indicate that these liquids contain water-rich regions and acetonitrile-rich regions. The size of these regions is probably on the scale of several molecular sizes. This has also been found for other water polar liquid mixtures where the high-quality thermodynamic property data needed to evaluate these integrals exist [2, 3].

Recently, molecular dynamics simulations of aqueous acetonitrile have confirmed this picture and have provided a more detailed description of the compositional heterogeneities [5, 6]. When X, the mole fraction of water is small, say 0.1, the water molecules form small clusters containing a few (5 to 10) molecules embedded in a space-filling acetonitrile matrix. Here, the term "clusters" refers to loose associations of molecules and NOT to compact, long-lived groupings. The criterion used to identify clusters is discussed at the end of Section 2. As X is increased to 0.3, the water clusters increase in size but are still isolated clusters in the acetonitrile matrix. For $X = 0.5$, one finds water clusters and acetonitrile clusters that interpenetrate and both clusters span the simulation cell. This continues with increasing X until $X = 0.9$, where one finds small, isolated acetontrile clusters embedded in a large water cluster. For a more detailed discussion, see the simulation papers.

Local compositional heterogeneity should have consequences for the solvation and distribution of third component solutes. One might expect to find third component solutes nonuniformly distributed in these mixtures, at least for some range of X. In this paper we use molecular dynamics simulations for a preliminary exploration of the distribution of Na^+ and Cl^- ions in water, in acetonitrile, and in their mixtures. In so doing, an important sampling issue is identified. An approach to the resolution of this issue is discussed. For comparison purposes, we also examine the solvation of the alkane molecule, butane. The behavior of partially hydrophobic and partially hydrophilic molecules, such as alcohols, will be considered elsewhere.

The following section describes the models and simulation methods used here. Section 3 contains the results of the simulations and some discussion of the results. The final section contains a brief statement of future directions for the simulation study of ions in aqueous acetonitrile.

2. MODEL AND SIMULATION DETAILS

Unless noted otherwise, all cases examined are for ambient conditions with the composition and density of the solvent matched to the experimental values [7]. In addition to pure water and pure acetonitrile, several compositions were simulated, with compositions ranging from 10 to 90%

water. Two types of solutes are examined. First, we examine ions in the form of one Na^+ ion and one Cl^- ion. Then we examine the solvation of the nonpolar molecule butane by water and by acetonitrile, but not by the mixtures.

The water–water interaction is taken as the SPC/E model [8]. The acetonitrile–acetonitrile interaction is the model potential of Edwards et al. [9, 10]. These are three-site models with Lennard–Jones interactions and Coulomb interactions between intermolecular sites. These potentials have been shown to provide qualitatively accurate liquid property estimates. The ion–ion interactions consist of Lennard–Jones plus Coulomb potentials [11]. The water–acetonitrile interaction parameters are determined using the Lorentz–Bertholot mixing rules [12]. These rules are also used to determine solute–solvent interaction parameters. The butane molecule is modeled as a set of four united atom interaction sites connected by harmonic stretch and bend interactions. Also, torsion motions are monitored. The alkane potentials are described elsewhere [13].

The simulations are conventional. Periodic boundary conditions were applied to mimic an infinite system, and the Ewald summation method was applied to the Coulomb interactions [14]. The equations of motion were integrated using an iterated form of Beeman's algorithm [15, 16] with a time step of 1 fs. The temperature was maintained at ambient conditions by a Nosé–Hoover thermostat [17]. As noted above, the volume was fixed so that the experimental density was realized. These conditions indicate that the simulations are performed in the canonical ensemble.

The results discussed below were obtained from productions runs of, at least, 100-ps duration that were preceded by stabilization runs of equal or greater duration. Clustering and solvation information was generated at 0.1-ps intervals using geometrical criteria based on the position of the minimum in the appropriate pair correlation function. If two molecules satisfy the cluster criterion, they are in the same cluster. Given that this pairwise clustering information is available, it is a straightforward sorting process to generate cluster information [18, 19]. These geometrical criteria are described next.

Two water molecules are in a cluster if the distance between the oxygen sites is less than 3.41 Å. Two acetonitrile molecules are in the same cluster if the distance between the nonmethyl carbon sites is less than 6.48 Å. A Na^+ ion and a Cl^- are in a cluster if the distance between the ions is less than 3.48 Å. Ions that are in ion–ion clusters are often referred to as speciated or associated ions.

Similar conditons for the solvation of the ion solutes were used. A Na^+ ion is solvated by a water molecule if the ion–oxygen distance is less than 3.41 Å, and it is solvated by an acetonitrile molecule if the ion–nitrogen

distance is less than 4.39 Å. The corresponding distances for the Cl^- ion are 2.84 Å for the ion–hydrogen separation and 5.59 Å for the ion–carbon and/or ion–methyl site separations.

The solvation shell for the butane molecule contains solvent molecules with their centers of mass within a specified distance from any of the carbon sites on the butane molecule. This distance is 5.10 Å for water and 6.60 Å for acetonitrile. These distances were found to produce a filled shell with one layer of solvent molecules. Smaller values produced incompletely filled shells, and larger values produced additional layers of solvent molecules.

The results described here are, of course, model dependent since the model parameters have been fit to specific properties. It is known that properties of ions in solution are quite sensitive to these parameters [20]. Therefore, the results should be taken as indicating the type of solvation structure expected rather than as a definitive description of the structure.

3. RESULTS

In this section, we examine the solvation of the solutes by the solvent molecules in two ways. The first way is in terms of the degree of association of the ions, and the second is in terms of the orientation of solvent molecules relative to the solutes. The measure of association, the association ratio, is the ratio of the number of samples with the ions associated to the total number of samples examined. For a 100-ps run, there is a total of 1000 samples. The measure of the orientation of the solvent molecule is in terms of

$$\cos \theta = (\boldsymbol{\mu} \cdot \mathbf{r})/|\boldsymbol{\mu}| \, |\mathbf{r}| \tag{1}$$

where $\boldsymbol{\mu}$ is the dipole moment of the solvating molecule and $\mathbf{r}$ is the vector from the center of mass of the solute to the center of mass of the solvating molecule. This measure will be displayed in terms of the distribution of values of $\cos \theta$. The quantity $P(\cos \theta) \, \Delta \cos \theta$ is the fraction of solvating molecules with orientation in the interval $\cos \theta$ to $\cos \theta + \Delta \cos \theta$. Here we take $\Delta \cos \theta = 0.02$ over the interval from -1 to 1 so $P = 0.01$ represents a uniform distribution of orientations.

3.1. Ions and Water

The solvation shells of the Na^+ and Cl^- ions by water contain on average 6.2 and 7.0 water molecules, respectively, with a width of the distribution of these numbers of the order of 0.6 molecules. The corresponding numbers for the solvation of these ions by acetonitrile molecules are 6.9

molecules solvating the Na^+ and 9.8 molecules solvating the Cl^- ion. These numbers are for ions that are not associated. When the ion pair is associated in water, the number of solvating molecules in water is only slightly decreased [21], as is also the case for acetonitrile.

The distribution of the orientation of the solvating water molecules is shown in Fig. 1. The solid line is for the Na^+ ion water orientation. The maximum near $\cos\theta = 1$ indicates that the solvation shell contains primarily molecules with the oxygen site (with a negative charge) aligned so that the dipole moment points away from the ion. The dashed line is for the Cl^- ion water orientation. The maximum near $\cos\theta = -0.4$ indicates the solvation shell primarily contains molecules with one hydrogen site (with a positive charge) located so that it points toward the ion, with the other hydrogen orientated away from the ion. This is an example of how ions disrupt the hydrogen bond network that is present in water, at least in the immediate vicinity of the ion. The disruption is local since the solvating molecules are in turn hydrogen bonded to water molecules located outside the solvation shell.

At ambient conditions, the ion pair is usually in a nonassociated configuration. For this state, the association ratio is 0.23. The association ratio is much larger for ions in supercritical water [21] so it is of interest to determine the relative importance of temperature and fluid density in determining the degree of association of the ions.
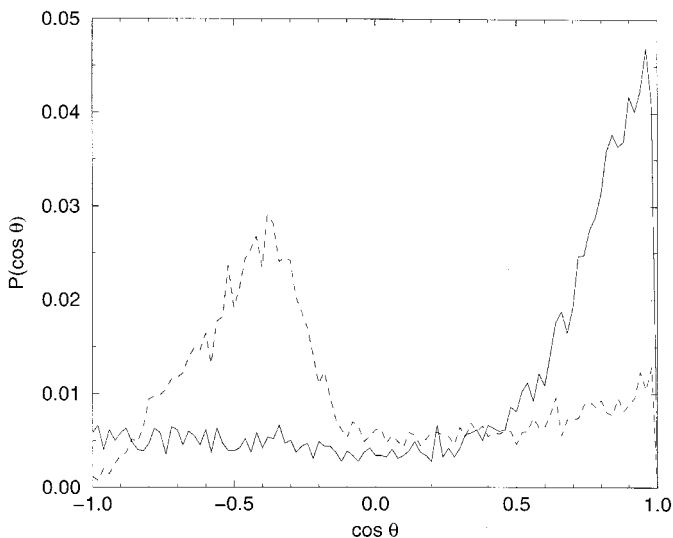

Fig. 1. The orientation distributions of water molecules about a Na^+ ion (solid line) and about a Cl^- ion (dashed line).

A series of simulations was made for one Na^+ ion and one Cl^- ion in water at the supercritical temperature 673 K for four fluid densities. The critical temperature and density of water are 647 K and $332 \, kg \cdot m^{-3}$ [22]. The association ratio at the supercritical temperature is 0.34 for $1000 \, kg \cdot m^{-3}$, 0.67 for $500 \, kg \cdot m^{-3}$, 0.81 for $400 \, kg \cdot m^{-3}$, and 0.93 for $300 \, kg \cdot m^{-3}$. Density is clearly more important than temperature in determining the association ratio for these ions in water.

3.2. Ions and Acetonitrile

The situation in acetonitrile is similar to that in water for the non-associated ions. This is indicated in Fig. 2. Since acetonitrile is a linear molecule, the orientation of the molecules around the Cl^- ion is dominated by orientations of the dipole moment that are antiparallel to the vector from the ion to the solute. For the Na^+ ion, the solvating molecules are oriented mainly with the dipole moment vector parallel to the ion solute vector. When the ion pair is associated, the structure shown in Fig. 2 is significantly reduced, as shown in Fig. 3. It should be noted that several hundred picoseconds was required for the ion pair that was initially well separated to associate. This indicates that considerable care must be taken if physically significant samples of ion solvation and association in acetonitrile
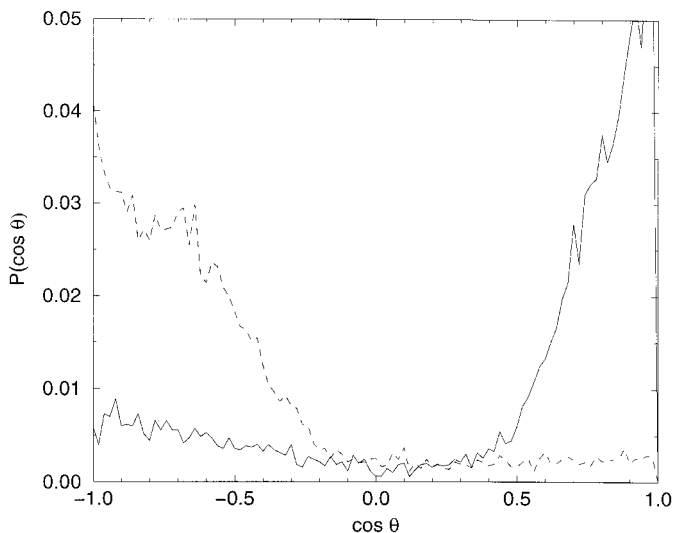

Fig. 2. The orientation distributions of acetonitrile molecules about a nonassociated Na^+ ion (solid line) and about a nonassociated Cl^- ion (dashed line).
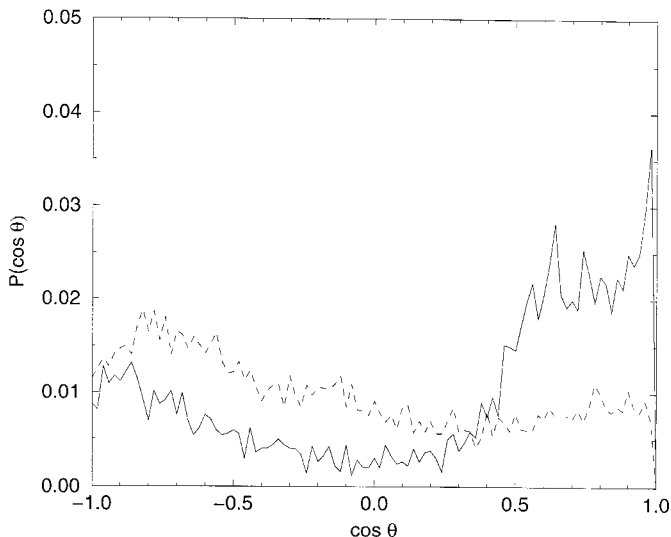
Fig. 3. The orientation distributions of acetonitrile molecules about an associated ion pair. The solid line is for the Na^+ ion, and the dashed line is for the Cl^- ion.

and its mixtures are to be realized. Once the pair was associated, the ions remain in close proximity, if not always satisfying the association condition, for long time intervals. The association ratio is larger than 0.9.

3.3. Ions in Water–Acetonitrile Mixtures

The results obtained for ions in water acetonitrile mixtures are not conclusive. This is because it is necessary to average over a number of "initial conditions" for the ions, something that has not yet been done. The mixtures are locally heterogeneous, and the solvation of the ions appears to vary considerably with the local environment of the ion. We find that different initial conditions lead to quite different numbers of solvating water and acetonitrile molecules. At this point, the most one can say is that when the mole faction of water is less than 0.3, the association fraction for the ions is of the order of 0.9. For higher water concentrations, the association fraction decreases to about 0.2. This trend is consistent with the observed variation of the Gibbs energies of transfer of Na^+ ions from water to aqueous acetonitrile [23].

There is a suggestion in these preliminary results that the ions tend to be solvated simultaneously by both water and acetonitrile molecules. This

possibility needs to be explored. Also, an examination of how ions behave when initially placed in water-rich regions or in acetonitrile-rich regions is needed.

3.4. Butane

The solvation of a single butane molecule in water [13] and in acetonitrile has been examined. There are some differences in the solvation shell molecule organization in the two cases. First, the average number of acetonitrile molecules in the shell is 19, while 27 water molecules solvate the butane. The orientation of the solvating molecules is different as well. These distributions are displayed in Fig. 4. This indicates that the water molecules tend to be oriented so that the dipole moment is roughly perpendicular to the vector between the water molecule and the center of the butane molecule. This is an example of how water molecules are arranged near a small hydrophobic entity. This arrangement minimizes the loss of hydrogen bonds [24]. In contrast, there is little orientational order of the acetonitrile molecules in the solvation shell. The solvation of small hydrophobic solutes by both solvents is seen to differ substantially from the solvation of ions.
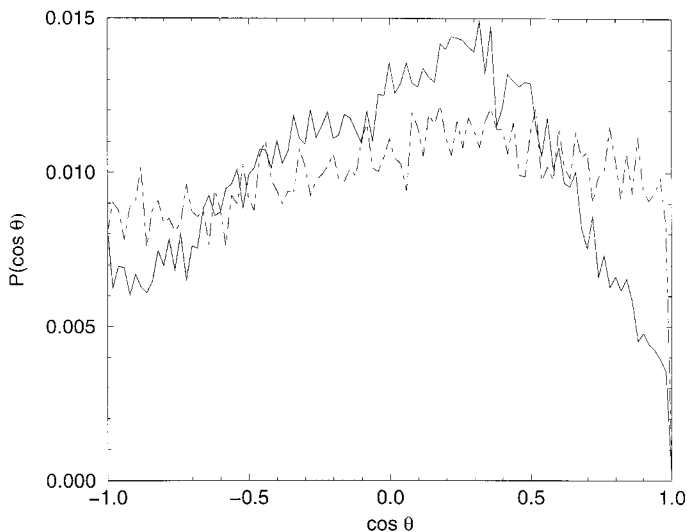

Fig. 4.   The orientation distributions for the water molecules (solid line) and for the acetonitrile molecules (dashed line) in the solvation shell of a butane molecule.

4. CONCLUDING COMMENTS

The simulations are based on model potentials that are known to provide physical properties that are qualitatively correct for the pure liquids. They also produce mixture properties that are consistent with what is observed. This gives us confidence that these models will provide the proper trends in properties as ions are introduced. The current studies of ions in aqueous acetonitrile are suggestive but not conclusive due to the sampling issues mentioned earlier. The compositional heterogeneity of the mixtures means that attention must be directed to improved sampling. What follows is a suggestion on how to avoid a brute-force, time-expensive approach.

The density of water has been shown to be an important quantity for the value of the association ratio, while the temperature is less important. This may provide a guide to the future examination of the solvation and association of ions in aqueous acetonitrile, as the number density of the mixtures decreases rapidly with increasing acetonitrile content. For example, the volume per molecule in bulk acetonitrile at ambient conditions is roughly the same as the volume per molecule of supercritical water at $300 \text{ kg} \cdot \text{m}^{-3}$. Some careful determinations of how ions are partitioned in the mixtures would clarify the importance of the fluid volume per molecule in determining the solvation and association of the ions. It would also indicate the type of sampling of initial conditions needed to obtain reliable estimates for these properties.

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