

# Structure and Dynamics of Hydrated Ions in a Water-Immiscible Organic Solvent

Ilan Benjamin

Department of Chemistry and Biochemistry, University of California Santa Cruz, California 95064

Received: August 19, 2008; Revised Manuscript Received: September 25, 2008

The structure and dynamics of *hydrated* alkali and halide ions in bulk 1,2-dichloroethane (DCE) are studied using molecular dynamics computer simulations. The number of water molecules in the ions' hydration shell and their orientational distribution, hydration water residence time, and ion diffusion constant are calculated and compared with the same quantities in bulk water. As the ion size increases, the average hydration number in DCE decreases, which is the opposite trend found in bulk water. The water molecules in the first hydration shell of the ion in bulk DCE are more tightly held to the ion, with a longer residence time than in bulk water. The hydrated ions in DCE are more mobile than in bulk water, and their mobility is much less sensitive to the ion size compared with the size dependence in bulk water.

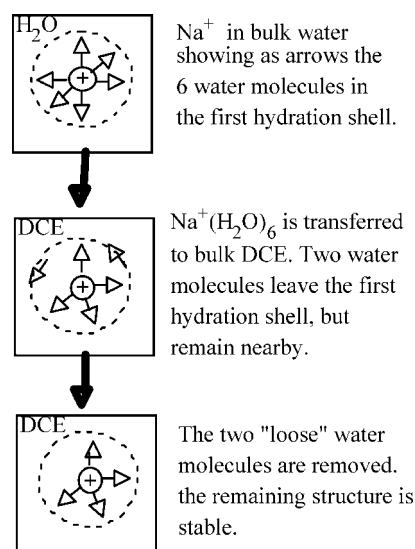
## I. Introduction

The observation that fully or partially hydrated ions are quite stable in the bulk of nonpolar, water-immiscible organic solvents is fundamental to many areas of science and technology. Hydrated ions of biological importance play an important role in environments that are quite hydrophobic, such as in ion channels,<sup>1,2</sup> the hydrophobic core of bacteriorhodopsin,<sup>3</sup> and lipid membranes. In phase-transfer catalysis, water molecules may accompany the transfer of an ionic reactant from water to the organic phase and thus significantly affect its reactivity.<sup>4</sup> In solvent extraction, when reagents such as tetraphenylborate are used to extract hydrophilic inorganic ions from water to nitrobenzene, UV-vis,<sup>5</sup> proton NMR,<sup>6–9</sup> IR,<sup>10</sup> and other experiments have confirmed that some water molecules are coextracted. Accurate numbers of the coextracted water molecules per ion have been established in nitrobenzene and under the influence of an extracting agent.<sup>11,12</sup>

Of particular relevance to the present paper are recent experiments on ion transfer, which show that the addition of trace amounts of water to neat 1,2-dichloroethane (DCE) induces the transfer of hydrophilic ions, and that these ions are transferred only as aqueous clusters disperse in the organic phase.<sup>13</sup>

Despite the clear importance of hydrated ions dissolved in bulk organic liquids, very little is known about their structure and dynamics. We mention that the idea of selective hydration of ions in mixed solvents is well-known,<sup>14</sup> and that the assumption that hydrophilic ions are transferred into the organic phase with all or some of their hydration shell has been used in simple continuum models of free energy of transfer.<sup>15</sup> In addition, there may be some similarities between the behavior of a hydrated cluster in the gas phase and in nonpolar solvents.<sup>16,17</sup> While molecular dynamics simulations of ion transfer have clearly shown that water molecules are transferred with small ions into the organic phase,<sup>18–23</sup> no systematic study of their structure and dynamics have been published.

In this paper, we present a detailed study of the structure and dynamics of hydrated clusters of four alkali ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) and four halide ions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) in bulk DCE, which, while considered water-immiscible, it does allow for a small amount of water to dissolve (2 g/L at 293 K).<sup>24</sup> Structural properties include the number of water molecules in the



**Figure 1.** Schematic representation of the method used in this work to study a hydrated ion in bulk DCE. This procedure (depicted with the example of  $\text{Na}^+$ ) is repeated for four alkali and four halide ions. See text for additional details.

hydration shell and their orientational distribution. Dynamical properties include water residence time and an ion diffusion constant. These properties are compared with the same properties calculated in bulk water.

The rest of this paper is organized as follows: In section II, the methodology we used is described. In section III, the structural and dynamical results are discussed. Our conclusions are presented in section IV.

## II. Systems and Method

**1. Methodology.** Our goal is to characterize the structure and dynamics of eight *hydrated* alkali and halide ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) in bulk DCE and to compare that with the same properties for the ions in bulk water. As mentioned above, the hydrated clusters dispersed in organic solvent are typically generated by an ion-transfer experiment (either by the use of a chemical extractant or with the help of an applied electric field). However, since the equilibrium

(structural and dynamical) properties of the hydrated ion should not depend on the history of how the cluster was formed, we choose a simpler method to generate them, which allows for direct and fast determination of the final equilibrium state and avoids the lengthy calculations of ion transfer for each of the eight ions we study here.

The procedure we follow is comprised of the following steps:

(1) Each ion is equilibrated in bulk water for 100 ps. A 1 ns trajectory is used to determine the ion–water radial distribution function, the water molecule orientation in the first hydration shell, the ion time-dependent displacement for determination of the diffusion constant, and the water residence time-correlation function (defined below). The positions of the water and the ions are saved every 20 ps, giving rise to the 50 independent configurations used below.

(2) The ion together with the water molecules in the first hydration shell are removed and inserted in a cavity of approximately the same radius created in bulk DCE by removing the appropriate numbers of DCE molecules. The number of molecules in the first hydration shell is defined as

$$n_w = \int_0^{R_{\min}} 4\pi\rho_w g_{\text{IO}}(r)r^2 dr \quad (1)$$

where  $\rho_w$  is the water bulk number density,  $g_{\text{IO}}(r)$  is the ion–water oxygen radial distribution function, and  $R_{\min}$  is the location of the first minimum of  $g_{\text{IO}}(r)$ . Since  $n_w$  is typically a noninteger, we take the actual number of water molecules removed with the ion to be  $N_0$  = the smallest integer greater than  $n_w$ . However, we confirm that the selection of larger values of  $n_w$  by one or two water molecules does not change the final equilibrium size of the hydrated ion cluster in DCE.

This procedure is repeated to generate 50 independent configurations of hydrated ions in DCE.

(3) For each of the 50 independent configurations, while keeping the water molecules and the ion frozen, the system is equilibrated at constant temperature and pressure to remove high-energy repulsive interactions between the water and the DCE.

(4) The constraints on the water molecules and the ion are removed, and the system is followed until the cluster reaches an equilibrium, as determined by following a number of structural and energetic properties.

(5) Each of the 50 independent configurations is followed for 100 ps, and the same properties calculated in bulk water (step 1 above) are determined and averaged over the 50 configurations for the clusters in DCE. As will become clear below, the hydration number of the ion in DCE is smaller than the hydration number in water. As a result, a number of water molecules outside the hydration shell remain in close proximity to the ion. The properties calculated above may be influenced by these water molecules. We refer to this system as “wet” DCE.

(6) As a final step, we remove the water molecules outside the first hydration shell and repeat the calculations of step 5 for the ionic cluster in what we will refer to as “dry” DCE.

It should be stressed that the names “dry” and “wet” are used here only to distinguish the two simulation systems, and we are not claiming that the number of water molecules in “wet” DCE outside the ionic hydration shell corresponds to the solubility of water in DCE. Figure 1 sketches the different steps described above.

The residence time of water molecules in the ion’s first hydration shell has been the subject of numerous studies utilizing

the time-correlation approach method.<sup>25–29</sup> We use the same approach by defining a dynamical variable  $h_i(t)$  as follows:

$$h_i(t) = 1; \quad \text{if } r_i(t) \leq R_{\min} \text{ given that } r_i(0) \leq R_{\min} \\ = 0; \quad \text{if } r_i(t) > R_{\min} \text{ for a period of time } t > t_d(2)$$

where  $r_i(t)$  is the distance between the oxygen of the  $i$ th water molecule and the ion at time  $t$  and  $R_{\min}$  has been defined above. Thus,  $h_i(t)$  is a step function that is equal to 1 as long as the  $i$ th water molecule remains in the first hydration shell, or leaves and returns within a delay time of length  $t_d$ .

The correlation function is defined as

$$C(t) = \frac{1}{N} \sum_{i=1}^N \langle h_i(t) h_i(0) \rangle \quad (3)$$

where  $N$  is the number of water molecules in the first hydration shell and the ensemble average is taken over all of the time origins.

If  $C(t)$  is well approximated by an exponential  $e^{-t/\tau_R}$ ,  $\tau_R$  is the residence time, but in general we define the average residence time by

$$\tau_R = \int_0^\infty C(t) dt \quad (4)$$

A recent paper by Laage and Hynes<sup>29</sup> discussed the limitation of this method, which has to do with the fact that the selection of  $t_d$  is quite arbitrary, and  $\tau_R$  could be quite sensitive to  $t_d$ . In particular, the normal choice of  $t_d = 2$  ps was shown to lead to a large overestimation of  $\tau_R$ , as determined from a detailed examination of the barrier recrossings. To avoid the problem of the arbitrary nature of  $t_d$ , we have selected the value of  $t_d = 0$ . While this underestimates the “correct” value of  $\tau_R$  for the larger ions, it still allows for a comparison of the results in the different systems studied here.

The calculations described above represent a total simulation time of about 75 ns. All of the calculations were done at  $T = 298$  K using an integration time step of 0.5 fs.

**2. Systems and Potentials.** The calculations in bulk water are done using a truncated octahedral box of size 39.1 Å containing one ion and 999 water molecules. The initial DCE box contains 256 molecules in a truncated octahedral box of size 40.6 Å. The actual number of DCE molecules remaining in the box after the hydrated cluster is inserted depends on the size of the cluster and varies in the range 252–249.

For the water and DCE molecules’ potentials, we use those of ref 30. The ion–solvent potential is given by a pairwise sum of atom-based Lennard-Jones plus Coulomb terms:

$$u_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right] + \frac{q_i q_j}{4\pi r \epsilon_0} \quad (5)$$

where “ $i$ ” refers to the ion and “ $j$ ” denotes an atom on a solvent molecule separated by a distance  $r$ . The Lennard-Jones parameters  $\sigma_{ij}$  and  $\epsilon_{ij}$  are determined from the standard (Lorentz–Berthelot) mixing rules:<sup>31</sup>

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2, \quad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \quad (6)$$

**TABLE 1: Ions' Lennard-Jones Parameters**

ion	$\sigma$ (Å)	$\epsilon$ (kcal/mol)
Li <sup>+</sup>	1.594	0.133
Na <sup>+</sup>	2.275	0.115
K <sup>+</sup>	3.154	0.110
Cs <sup>+</sup>	3.650	0.149
F <sup>-</sup>	2.734	0.534
Cl <sup>-</sup>	3.934	0.832
Br <sup>-</sup>	4.234	0.537
I <sup>-</sup>	4.734	0.357

**TABLE 2: Calculated and Experimental Ion Properties in Bulk Water**

ion	$R_{\max}$ (Å) calcd (exptl) <sup>a</sup>	$R_{\min}$ (Å)	$-\Delta G_{\text{hyd}}$ (kcal/mol) calcd (exptl) <sup>b</sup>
Li <sup>+</sup>	1.98 (2.08)	2.75	122.5 (126.4)
Na <sup>+</sup>	2.3 (2.36)	3.10	102.3 (101.3)
K <sup>+</sup>	2.75 (2.8)	3.42	81.5 (84.1)
Cs <sup>+</sup>	3.02 (3.14)	3.85	74.1 (73.1)
F <sup>-</sup>	2.55 (2.63)	3.10	112.4 (102.5)
Cl <sup>-</sup>	3.25 (3.19)	3.85	71.6 (72.7)
Br <sup>-</sup>	3.37 (3.37)	3.95	65.3 (66.2)
I <sup>-</sup>	3.6 (3.65)	4.20	57.7 (57.4)

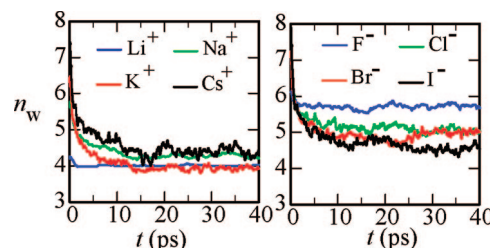
<sup>a</sup> Reference 46. <sup>b</sup> Reference 56.

where the Lennard-Jones parameters for the different ions  $\sigma_{ii}$  and  $\epsilon_{ii}$  are summarized in Table 1 and the parameters for the different sites on the solvent molecules are given in ref 30. While different sets of ion parameters have been suggested in the literature,<sup>27,32–35</sup> the parameters we use give reasonable values for the hydration free energy<sup>36</sup> and for two structural properties (Table 2).

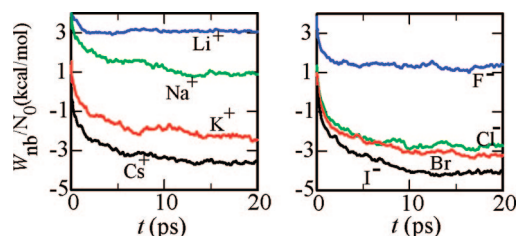
Note that the intermolecular potential energy functions used in this work are pairwise additive. Thus, the polarizable nature of the solvent and the ions is effectively included by proper adjustment of the Lennard-Jones parameters and the point charges. While a more accurate approach, which employs many-body polarizable potentials, could be used,<sup>37–45</sup> we postpone this for a future study, using the results given here as a useful comparison.

### III. Results and Discussion

**1. Time-Dependent Formation of the Hydrated Ion in DCE.** Before discussing the properties of the hydrated ion in bulk DCE, we briefly look at the nonequilibrium dynamics leading to the formation of the final equilibrated cluster. Starting from an ensemble of 50 independent hydrated ions, each with its complete hydration shell after it has been inserted in bulk DCE and equilibrated (with the water molecules frozen around the ion), the constraints on the water are removed. The integral of eq 1 is calculated and averaged over 50 fs intervals and over the 50 independent trajectories. Figure 2 shows the time-dependent  $n_w(t)$  for the cations and the anions on separate panels. Each curve starts from the value in bulk water, given in Table 3, which is in reasonable agreement with experiments<sup>46</sup> and other calculations.<sup>27,35</sup> It reaches a fixed (on average) lower value 10–20 ps later. The behavior of the cations and the anions is quite different: each of the four cations reaches a hydration number around 4, although this number fluctuates significantly for Cs<sup>+</sup>, somewhat less so for K<sup>+</sup> and Na<sup>+</sup>, and almost no fluctuations are observed for Li<sup>+</sup>. We will see below that this is related to the residence time of water in these clusters. The final equilibrium hydration number for the anions varies from 5.8 for F<sup>-</sup>, to 5 for Cl<sup>-</sup> and Br<sup>-</sup>, and to 4.5 for I<sup>-</sup>. This is the *reverse* trend of the hydration number with the ion size in bulk



**Figure 2.** Time-dependent average hydration number of the hydrated ions in bulk DCE, starting from the full bulk water hydration shell. Each line represents an ensemble average of 50 independent starting configurations.



**Figure 3.** Time-dependent water intermolecular potential energy per water molecule, starting from the equilibrated bulk water hydrated shell in DCE.

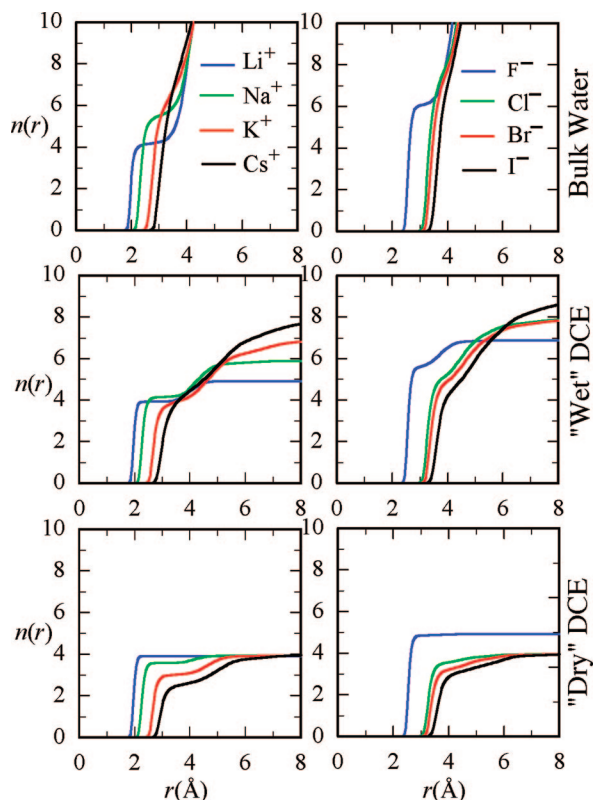
**TABLE 3: Calculated Ionic Hydration Numbers in Bulk Water and in DCE**

ion	$n_w$	"wet" DCE	"dry" DCE
Li <sup>+</sup>	4.2	4.0	4.0
Na <sup>+</sup>	5.5	4.2	3.6
K <sup>+</sup>	6.6	3.9	3.1
Cs <sup>+</sup>	8.4	4.2	2.6
F <sup>-</sup>	6.1	5.7	4.9
Cl <sup>-</sup>	7.6	5.1	3.6
Br <sup>-</sup>	7.6	4.9	3.2
I <sup>-</sup>	8.2	4.5	3.0

water. While we could not find experimental data for these ions in DCE, these hydration numbers are similar to those reported in nitrobenzene.<sup>12</sup>

The equilibrium hydration number is determined by a competition between three main factors: (1) water–ion electrostatic energy, (2) water–DCE interaction energy, and (3) ability of water molecules to maintain favorable water–water hydrogen bonding. Both the water–ion and water–water interactions within the hydration shell are strongly influenced by the ion size. Larger ions have less favorable ion–water electrostatic interactions, but they allow the water to more easily interact and form hydrogen bonds with each other.

Figure 3 shows the time-dependent total water–water non-bonded energy per water molecule during the process where the final equilibrium hydrated cluster is established in DCE. In bulk water, the pair interaction energy of  $-10$  kcal/mol accounts for approximately four hydrogen bonds, so we can take each hydrogen bond to be roughly equivalent to  $-2.5$  kcal/mol. We first note that, at  $t = 0$ , all of the energies in Figure 3 are positive. Since the initial water–ion configurations were taken from bulk water, this suggests that in bulk water the ion–water hydration complex structure prevents water–water hydrogen bonding among the first shell water molecules (of course, hydrogen bonding exists between these water molecules and those in the second shell). As the cluster structure and composition change toward the formation of the equilibrium structure in DCE, water–water hydrogen bonding is formed between the remaining water in the first hydration shell and



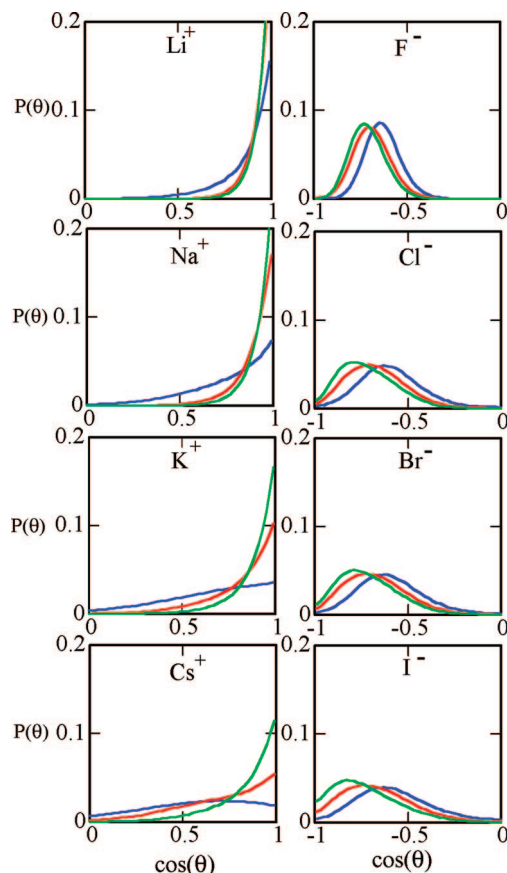
**Figure 4.** Running hydration number (eq 7) vs oxygen-ion distance  $r$  for all of the ions studied. Top two panels, bulk water; middle two panels, equilibrated hydrated ion in DCE with all of the water molecules from the original hydration shell in bulk water ("wet" DCE); bottom two panels, equilibrated hydrated ion in bulk DCE with the water molecules that left the hydration shell removed from the system ("dry" DCE). The line color key for the middle and bottom panels is as in the top two panels.

the water in the partial second shell. Thus, in the case of the smallest ions  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{F}^-$ , where most of the water molecules remain in the first hydration shell due to the strong ion-water electrostatic interactions, the total of the water-water interactions remains positive. As the ion size increases and the water-ion electrostatic energy decreases, water molecules leave the first hydration shell and form hydrogen bonding with those that remain. The final interaction energy corresponds to one hydrogen bond per water molecule for  $\text{K}^+$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  and to almost two hydrogen bonds per water molecule for  $\text{Cs}^+$  and  $\text{I}^-$ .

**2. Structure.** The top two panels of Figure 4 show the running hydration number  $n(r)$  of all of the ions in bulk water from which the hydration numbers given in Table 3 were determined.

$$n(r) = \int_0^r 4\pi\rho_w g_{\text{IO}}(r)r^2 dr \quad (7)$$

The peak position of  $g_{\text{IO}}(r)$  is the same in bulk water and for the hydrated ion in DCE (not shown), but the peak value is generally lower, reflecting the smaller number of the water molecules in the first hydration shell. The middle two panels of Figure 4 depict the running hydration number as a function of  $r$  for the hydrated ion in bulk DCE. This is calculated using eq 7 after the equilibrium structure of the hydrated ion in bulk DCE is reached. Obviously, for each ion,  $n(\infty) = N_0$  is the total number of water molecules in the first hydration shell in bulk water (adjusted upward to be an integer, as explained above).



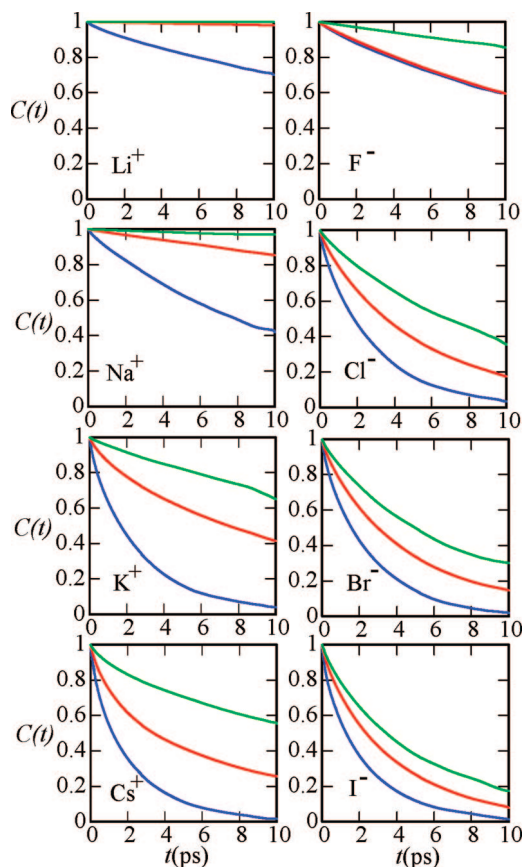
**Figure 5.** Orientational probability distribution for first shell water molecules. The angle  $\theta$  is between the water dipole and the ion-oxygen vector. In each panel, the blue, red, and green lines are for the ion in bulk water, in "wet" DCE, and in "dry" DCE, respectively.

Consistent with the data presented in Figure 2, Figure 4 shows that, except for  $\text{Li}^+$  and  $\text{F}^-$ , the first hydration shell of the ions in bulk water suffers a loss of one or more water molecules, depending on the ion size. These water molecules remain near the cluster during the simulation time scale. More precisely, all of these water molecules remain within a 7–8 Å distance from the ion, still interacting with the first hydration shell water, except for one water molecule in the case of  $\text{Cs}^+$  and  $\text{I}^-$ . We refer to this situation as the hydrated ion in "wet" DCE.

When the water molecules outside the first hydration shell of the cluster in bulk DCE are removed ("dry" DCE), the remaining water molecules stay near the ion (see bottom two panels). However, as the ion gets larger, some of these water molecules spend a larger fraction of time outside the first hydration shell radius, resulting in an average hydration number that is lower than that in "wet" DCE (Table 3). Because there is no water-water hydrogen bonding in "dry" DCE, the water nonbonded interaction remains positive or near small negative values (data not shown). Obviously, in the space available around a large ion, the solvation by DCE molecules is possible, resulting in a mixed solvation shell. The structure of a mixed solvation shell of  $\text{Na}^+$  and  $\text{Cl}^-$  ions in DCE following ion transfer has been previously discussed.<sup>19</sup>

Information about the arrangement of water molecules in the first hydration shell around the ions can be obtained by computing the probability distribution  $P(\theta)$  for the angle  $\theta$  between the water dipole and the water oxygen-ion vectors, as shown in Figure 5. As is well-known from simulations in bulk water,<sup>47</sup> the water dipole is oriented directly along the cation-oxygen vector (peak near  $\theta = 0$  in the panels on the

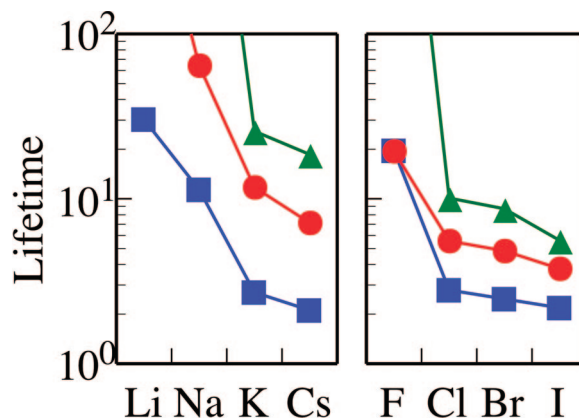




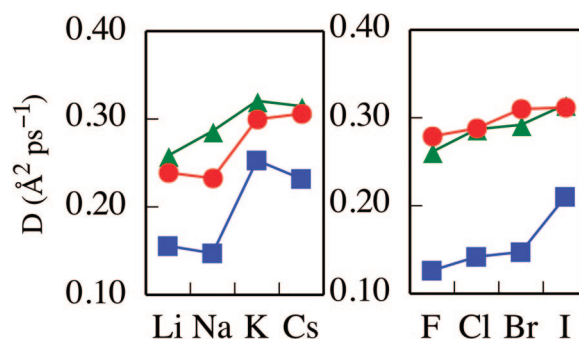
**Figure 6.** Water residence time-correlation function (eq 3) for the water molecules in the hydration shell of all the ions studied. In each panel, the blue, red, and green lines are for the ion in bulk water, in "wet" DCE, and in "dry" DCE, respectively.

left). In contrast, the anion–oxygen vector lies approximately along the water OH bond,<sup>48,49</sup> so that the water dipole forms an angle of  $\theta = 128^\circ$  ( $\cos \theta = -0.6$ ) with respect to the anion–oxygen vector. These configurations maximize hydrogen bonding between first shell and second shell water molecules. Figure 5 demonstrates that, as the hydrated ion is transferred to bulk "wet" DCE and then to "dry" DCE, the probability distribution gets narrower, especially for the cations, reflecting a tighter hydration shell. The larger the ion, the bigger the difference between the bulk water and the DCE results. In addition, for the anions, the peak of the distribution shifts to a larger angle ( $\cos \theta$  approaching  $-1$ ) as the hydrated ion is moved to the organic phase. This reflects the tendency of the water dipole to point directly toward the ion as the number of water molecules outside the first hydration shell available to form hydrogen bonds with the first shell water is decreased.

**3. Water Residence Time.** The correlation functions  $C(t)$  (eq 3) for each ion in bulk water, "wet" DCE, and "dry" DCE are shown in Figure 6. Each curve of Figure 6 is reasonably well approximated by a single exponential, except for the case of  $\text{I}^-$  and  $\text{Cs}^+$  (the largest ions with the fastest dynamics), but in all cases, a double exponential gives an excellent fit and is used to compute the average residence time according to eq 4. These residence times are shown in Figure 7. The points not shown on the graph ( $\text{Li}^+$  in "wet" and "dry" DCE and  $\text{F}^-$  and  $\text{Na}^+$  in "dry" DCE) are those outside the scale corresponding to relaxation times  $\tau_R > 100$  ps, which are thus unreliable given the length of the present simulations. The residence times calculated in bulk water are generally similar to those calculated using other water models and other water–ion interaction models.<sup>27,29,50</sup>



**Figure 7.** Water residence time for first shell water molecules in the hydration shell calculated according to eq 4. In each panel, the blue squares, red circles, and green triangles are for the ion in bulk water, in "wet" DCE, and in "dry" DCE, respectively. The "missing" data points correspond to residence times larger than 100 ps.



**Figure 8.** Ions' diffusion constant. In each panel, the blue squares, red circles, and green triangles are for the ion in bulk water, in "wet" DCE, and in "dry" DCE, respectively.

Besides the well-known observation that the residence time decreases as the ion gets larger, Figures 6 and 7 demonstrate an important new finding. Except for the case of  $\text{F}^-$ , the residence time of the water molecule in the first hydration shell is significantly longer when the hydrated ion cluster is in bulk DCE compared with bulk water. This is the result of two factors. First, it is unfavorable for water molecules to migrate into the lower dielectric medium surrounding the hydrated ion. Second, the successful exchange of water molecules depends on the availability of nearby water molecules and this is greatly diminished when the hydrated ion cluster is in "wet" DCE (compared with bulk water). This also explains the further increase in the residence time when the hydrated ion is in "dry" DCE. These results are also consistent with the increase in hydrogen-bond lifetimes calculated at the interface between water and nonpolar liquids,<sup>51</sup> as well as with the increase in the barrier height for a water molecule to exit the first hydration shell computed for  $\text{Li}^+$  and  $\text{Na}^+$  at the water–nitrobenzene interface.<sup>21</sup> In the latter case, an increase in the residence time as the ion moves from water to nitrobenzene was observed.

**4. Diffusion.** The mobility of ions in aqueous solutions has been the subject of numerous experimental and theoretical studies. The experimental determination of limiting ionic conductivities can be used to determine the drift velocity of the ion  $u$ , and with the help of Einstein's relation,  $u = D/kT$  gives the diffusion constant  $D$ . Theoretically, one can determine the diffusion constant from either the integral of the ion's velocity autocorrelation function or from the slope of the ion's mean square displacement.<sup>52</sup>

To our knowledge, no studies of hydrated ion mobility in nonpolar solvents have been published, despite the obvious importance of these species. Figure 8 shows the calculated diffusion constant of the alkali and halide ions in bulk water and of the hydrated ion clusters in DCE, determined from the slope of the mean square displacement. Our results for the diffusion constants in bulk water are in general agreement with experiments and previous calculations, and show a maximum in the cationic mobilities as a function of ion size. We find two new significant results: (1) The translational diffusion of each hydrated ion in bulk DCE ("dry" or "wet") is faster than that of the same ion in bulk water. (2) The diffusion constant of the hydrated ion in bulk DCE is much less sensitive to the ion size compared with the size dependence in bulk water.

These results can be understood as follows. The mobility of small single-charge ions in bulk water is the result of the competition between two main opposing effects: As the ion size is increased, hydrodynamic friction due to the ion's larger mass will increase. However, the ion's ability to hold onto its hydration shell will decrease with a corresponding decrease in the dielectric drag. This gives a reasonable explanation for the observed maximum in ionic mobility as a function of ion size. As the hydrated ion is transferred to bulk DCE, the dielectric drag between the first shell water and the bulk liquid is greatly reduced compared with that in bulk water, which generally leads to faster mobility. This effect is more significant for the small ions, and thus, they will experience a more dramatic increase in mobility, leading to a flattening of the curve of mobility vs ionic size. In the limit of very small size (or larger charge), when the ion's first hydration shell is the same in water and DCE, one can consider the hydrated ion as a large, rigid cluster whose mobility in water and in DCE should follow a simple hydrodynamic relation.<sup>53</sup> It is important to point out, however, that a detailed understanding of ion mobility is not completely resolved, and other explanations have been proposed for the dependence of ion mobility on size.<sup>54</sup>

#### IV. Conclusions

The molecular dynamics simulations described in this paper suggest that hydrated alkali and halide ions in bulk DCE are stable species whose structure and dynamics can be well-characterized. Starting from an  $\text{Li}^+$  ion whose hydration number (4) in DCE is unchanged relative to that in bulk water, as the ion size increases, the average hydration number in DCE decreases relative to that in bulk water. The hydration number in DCE decreases as the ion size increases, which is the opposite trend found in bulk water. The water molecules in the first hydration shell are more tightly held, with substantial increase in their residence time relative to that in bulk water. The increase in the average lifetime of a water molecule in the ions' first hydration shell is significant for understanding the process of ion transfer between water and nonpolar liquids,<sup>13,21</sup> as well as in affecting the reactivity of nucleophilic ions in nonpolar solvents.<sup>55</sup>

Much more work is needed to understand hydrated ion clusters in nonpolar media. Forthcoming publications will address the effect of ion polarizability and will examine the energetics of these clusters, as well as compare them to available gas phase cluster data.

**Acknowledgment.** This work has been supported by a grant from the National Science Foundation (CHE-0809164).

#### References and Notes

(1) Eisenman, G.; Dani, J. A. *Annu. Rev. Biophys. Biophys. Chem.* **1987**, *16*, 205.

- (2) Gouaux, E.; MacKinnon, R. *Science* **2005**, *310*, 1461.
- (3) Grigorieff, N.; Ceska, T. A.; Downing, K. H.; Baldwin, J. M.; Henderson, R. *J. Mol. Biol.* **1996**, *259*, 393.
- (4) Albanese, D.; Landini, D.; Maia, A.; Penso, M. *Ind. Eng. Chem. Res.* **2001**, *40*, 2396.
- (5) Symons, M. C. R.; Jackson, S. E. *J. Chem. Soc., Faraday Trans.* **1979**, *75*, 1919.
- (6) Kawasaki, M.; Toei, K.; Iwachido, T. *Chem. Lett.* **1972**, *1*, 417.
- (7) Benoit, R. L.; Lam, S. Y. *J. Am. Chem. Soc.* **1974**, *96*, 7385.
- (8) Ito, K.; Iwamoto, E.; Yamamoto, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2290.
- (9) Osakai, T.; Hoshino, M.; Izumi, M.; Kawakami, M.; Akasaka, K. *J. Phys. Chem. B* **2000**, *104*, 12021.
- (10) ID Kuntz, J.; Cheng, C. J. *J. Am. Chem. Soc.* **1975**, *97*, 4852.
- (11) Osakai, T.; Ogata, A.; Ebina, K. *J. Phys. Chem. B* **1997**, *101*, 8341.
- (12) Osakai, T. The role of water molecules in ion transfer at the oil/water interface In *Interfacial Catalysis*; Volkov, A. G., Ed.; Marcel Dekker: New York, 2003; p 53.
- (13) Sun, P.; Laforge, F. O.; Mirkin, M. V. *J. Am. Chem. Soc.* **2007**, *129*, 12410.
- (14) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.
- (15) Osakai, T.; Ogata, A.; Ebina, K. *J. Phys. Chem. B* **1997**, *101*, 8341.
- (16) Arshadi, M. R.; Yamdagni, R.; Kebarle, P. *J. Phys. Chem.* **1970**, *74*, 1475.
- (17) Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.
- (18) Benjamin, I. *Science* **1993**, *261*, 1558.
- (19) Schweighofer, K. J.; Benjamin, I. *J. Phys. Chem.* **1995**, *99*, 9974.
- (20) Schweighofer, K. J.; Benjamin, I. *J. Phys. Chem. A* **1999**, *103*, 10274.
- (21) Chorny, I.; Benjamin, I. *J. Phys. Chem. B* **2005**, *109*, 16455.
- (22) Dang, L. X. *J. Phys. Chem. B* **1999**, *103*, 8195.
- (23) Wick, C. D.; Dang, L. X. *J. Phys. Chem. C* **2008**, *112*, 647.
- (24) *Encyclopedia of Chemical Technology*; Grayson, E. M., Ed.; Wiley: New York, 1979; Vol. 5.
- (25) Impey, R. W.; Madden, P. A.; McDonald, I. R. *J. Phys. Chem.* **1983**, *87*, 5071.
- (26) Lee, S. H.; Rossky, P. J. *J. Chem. Phys.* **1994**, *100*, 3334.
- (27) Koneshan, S.; Rasaiah, J. C.; Lynden-Bell, R. M.; Lee, S. H. *J. Phys. Chem. B* **1998**, *102*, 4193.
- (28) Bizzarri, A. R.; Cannistraro, S. *J. Phys. Chem. B* **2002**, *106*, 6617.
- (29) Laage, D.; Hynes, J. T. *J. Phys. Chem. B* **2008**, *112*, 7697.
- (30) Benjamin, I. *J. Chem. Phys.* **1992**, *97*, 1432.
- (31) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*, 2nd ed.; Academic: London, 1986.
- (32) Pettitt, B. M.; Rossky, P. J. *J. Chem. Phys.* **1986**, *84*, 5836.
- (33) Lee, S. H.; Rasaiah, J. C. *J. Chem. Phys.* **1994**, *101*, 6964.
- (34) Obst, S.; Bradaczek, H. *J. Phys. Chem.* **1996**, *100*, 15677.
- (35) Jensen, K. P.; Jorgensen, W. L. *J. Chem. Theory Comput.* **2006**, *1499*.
- (36) Rose, D.; Benjamin, I. Manuscript to be submitted, 2009.
- (37) Sprik, M.; Klein, M. L. *J. Chem. Phys.* **1988**, *89*, 7556.
- (38) Ahlstrom, P.; Wallqvist, A.; Engstrom, S.; Jonsson, B. *Mol. Phys.* **1989**, *68*, 563.
- (39) Sprik, M.; Klein, M. L.; Watanabe, K. *J. Phys. Chem.* **1990**, *94*, 6483.
- (40) Wallqvist, A. *Chem. Phys.* **1990**, *148*, 439.
- (41) Dang, L. X.; Rice, J. E.; Caldwell, J.; Kollman, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 2481.
- (42) Bader, J. S.; Berne, B. J. *J. Chem. Phys.* **1996**, *104*, 1293.
- (43) Small, D. W.; Matyushov, D. V.; Voth, G. A. *J. Am. Chem. Soc.* **2003**, *125*, 7470.
- (44) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. A* **2002**, *106*, 379.
- (45) Vrbka, L.; Mucha, M.; Minofar, B.; Jungwirth, P.; Brown, E. C.; Tobias, D. J. *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 67.
- (46) Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475.
- (47) *The Chemical Physics of Solvation, part A*; Dogonadze, R. R.; Kalman, E.; Kornyshev, A. A.; Ulstrup, J., Eds.; Elsevier: Amsterdam, 1985.
- (48) Cummings, S.; Enderby, J. A.; Neilson, G. W.; Newsome, J. R.; Howe, R. A.; Howells, W. S.; Soper, A. K. *Nature* **1980**, *287*, 714.
- (49) Powell, D. H.; Barnes, A. C.; Enderby, J. E.; Neilson, G. W.; Salmon, P. S. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 137.
- (50) Lee, S. H.; Rasaiah, J. C. *J. Phys. Chem.* **1996**, *100*, 1420.
- (51) Benjamin, I. *J. Phys. Chem. B* **2005**, *109*, 13711.
- (52) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon: Oxford, U.K., 1987.
- (53) Wolynes, P. G. *Annu. Rev. Phys. Chem.* **1980**, *31*, 345.
- (54) Ghorai, P. K.; Yashonath, S.; Lynden-Bell, R. M. *J. Phys. Chem. B* **2005**, *109*, 8120.
- (55) Landini, D.; Maia, A.; Rampoldi, A. *J. Org. Chem.* **1989**, *54*, 328.
- (56) Tissandier, M. D.; Cowen, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D.; Coe, J. V.; Tuttle, T. R. *J. Phys. Chem.* **1998**, *102*, 7787.