

## LETTERS

### Computer Simulation Studies of Ion Transport across a Liquid/Liquid Interface

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The mechanism for transporting a chloride ion or a cesium ion across a water–carbon tetrachloride liquid/liquid interface is characterized using molecular dynamics techniques. The results obtained in these studies provided new physical insight into both the free energies and solvent structures as the ion moved across the interface. The computed free-energy profiles of ion transfer for both ions increased monotonically from water to carbon tetrachloride. No free-energy minima were observed at the liquid/liquid interface. The first hydration shells of the ions were significantly reduced as the ions moved from the aqueous phase to the nonaqueous phase. A so-called “fingering” was created by the chloride ion in the nonaqueous phase, which has a similar characteristic found in the aqueous ionic cluster studies.

#### I. Introduction

The transfer of ions across the interface between water and an immiscible organic solvent is of importance in many fields of physical science.<sup>1–4</sup> An example is the charge transfer across the liquid/liquid interface.<sup>5,6</sup> Controlling the transfer rate of ions as they move across the interfaces between two phases can improve the efficiency of liquid extraction processes and is important to phase transfer catalysis.<sup>7,8</sup> The study of ion transfer is also important to environmental problems such as the interactions of contaminated organic solvents with groundwater and separation chemistry performed in binary solvent systems (i.e., organic and aqueous phases).<sup>9</sup> Little is known about the precise mechanism and dynamics of transfer processes and the molecular level structure of the interface where the transfer may take place. In particular, the differences between the mechanism of transferring a cation or an anion have not yet been completely characterized.

We have performed extensive classical molecular dynamics simulations to examine the mechanism and thermodynamics of the transfer of both a  $\text{Cl}^-$  or a  $\text{Cs}^+$  ion across a  $\text{CCl}_4\text{--H}_2\text{O}$  liquid/liquid interface. Due to low dielectric permittivity, there is very little available experimental data for ion free-energy

transfer of this system.<sup>10</sup> However, we believe this system is an interesting one, which deserves this kind of detailed study. In addition, another motivation in pursuing this system is its relevance to the national nuclear waste remediation effort, a significant environmental issue.<sup>9</sup> To our knowledge, the most important values of this work are the following: (1) The computed free-energy profiles of transfer for both ions increased monotonically from water to carbon tetrachloride and no free-energy minima were found at the liquid/liquid interface, (2) the first hydration shells of the ions are significantly modified and solvent structures around these ions are quite different as they moved across the liquid/liquid interface, (3) intermolecular interactions among the species are described using polarizable potential models that have been developed for use in liquid/liquid interface simulations.

In the past, molecular dynamics simulations have been used to study ion transfer across liquid/liquid interfaces. Examples include the pioneering work of Benjamin on the mechanism and dynamics of transferring a single  $\text{Cl}^-$  ion across a water/1,2-dichloroethane interface.<sup>3</sup> This study indicated that the ion transfer into the aqueous phase is an activated process due to the presence of a free-energy minimum ( $\sim 5$  kcal/mol) at the

liquid/liquid interface. Wipff and co-workers<sup>11</sup> reported a molecular dynamics study on the structural and energetic characteristics of ion-assisted transfer between water and chloroform and showed that the  $\text{Cs}^+$  diffuses spontaneously from the interface to water and displays apparently no free energy minimum. We note here, however, that the above studies employed effective pair potentials, and that polarization effects were not explicitly taken into account. Recent molecular dynamics studies have indicated that polarization effects must be included in order to properly model liquid/liquid interfaces.<sup>12,13</sup>

Our work differs from previous simulations of ion transfer in computational methodology and in the character of the interaction potential models. This paper is organized as follows. The polarizable model potentials and the method of simulation are summarized in Section II. Free-energy profiles and the solvation property of the liquid/liquid interface are presented and discussed in Section III. A summarization of this study is presented in Section IV.

## II. Potential Models and Computational Methods

The rigid-body intermolecular interactions among  $\text{H}_2\text{O}$  and  $\text{CCl}_4$  are taken from earlier work.<sup>14</sup> The  $\text{Cs}^+$  and  $\text{Cl}^-$  potential parameters also are taken from our earlier work on ion solvation in aqueous solution. The cross interactions between  $\text{Cs}^+-\text{C}$ ,  $\text{Cs}^+-\text{Cl}$ ,  $\text{Cl}^--\text{C}$ , and  $\text{Cl}^--\text{Cl}$  are obtained via the Lorentz–Berthelot combining rule.<sup>15</sup> The predicted minima structures and energies are in good agreement with high-level electronic structure calculations.<sup>14</sup> A summary of the  $\text{Cs}^+-\text{CCl}_4$ ,  $\text{Cl}^--\text{CCl}_4$ ,  $\text{Cs}^+-\text{H}_2\text{O}$ , and  $\text{Cl}^--\text{H}_2\text{O}$  interaction energies as a function of ion–molecule separation is shown in Figure 1. The total interaction energy of the system is summarized as follows:

$$U_{\text{tot}} = U_{\text{pair}} + U_{\text{pol}} \quad (1)$$

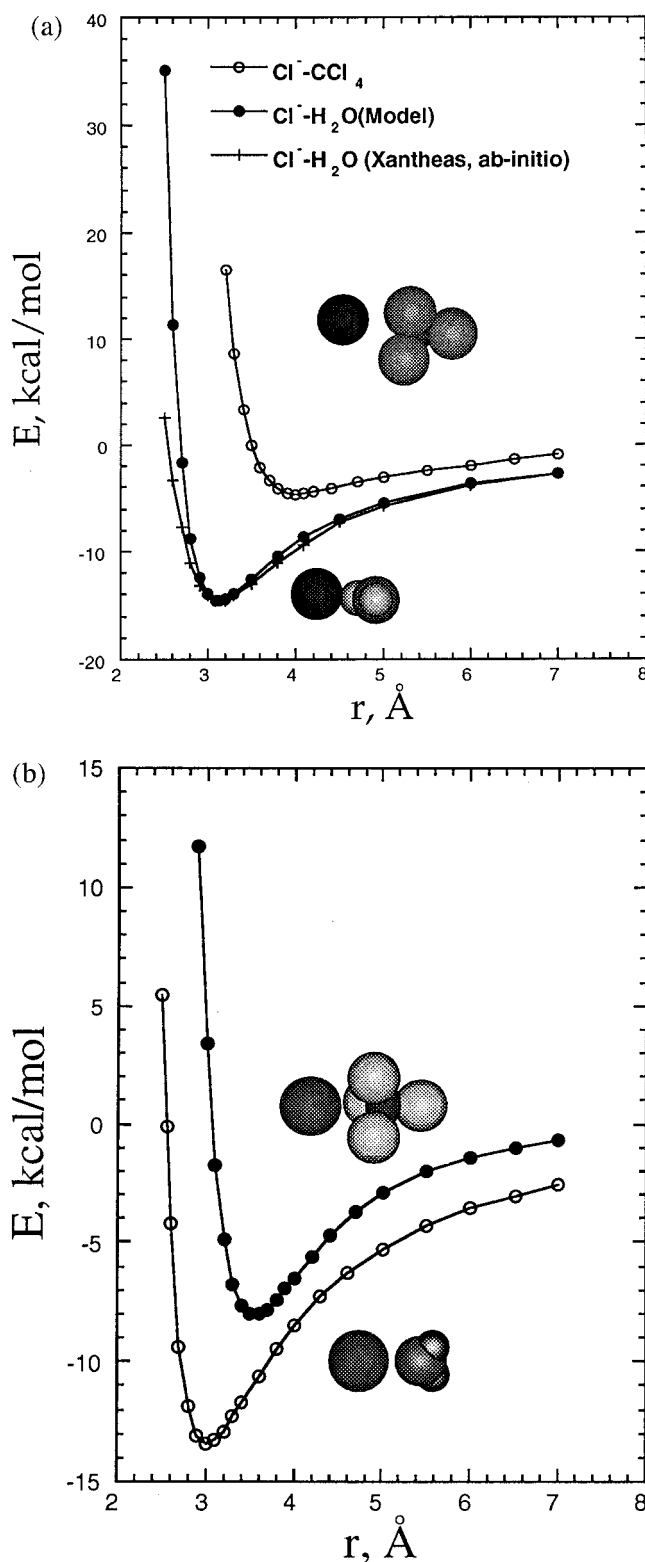
$$U_{\text{pair}} = \sum_i \sum_j \left( 4\epsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right) \quad (2)$$

and

$$U_{\text{pol}} = - \sum_{i=1}^N \mu_i \cdot E_i^0 - \frac{1}{2} \sum_{i=1}^N \sum_{j=1, i \neq j}^N \mu_i \cdot T_{ij} \cdot \mu_j + \sum_{i=1}^N \frac{|\mu_i|^2}{2\alpha_i} \quad (3)$$

Here,  $r_{ij}$  is the distance between site  $i$  and  $j$ ,  $q$  is the charge, and  $\sigma$  and  $\epsilon$  are the Lennard–Jones parameters.  $E_i^0$  is the electric field at site  $i$  produced by the fixed charges in the system,  $\mu_i$  is the induced dipole moment at atom site  $i$ , and  $T_{ij}$  is the dipole tensor. The first term in eq 3 represents the charge–dipole interaction, the second term describes the dipole–dipole interaction, and the last term is the energy associated with the generation of the dipole moment  $\mu_i$ . During molecular dynamics simulations, a standard iterative self-consistent field procedure is used to evaluate the induced dipoles.

The molecular dynamics simulations are performed on a system consisting of 1 ion, 1430 water, and 266 carbon tetrachloride molecules in a rectangular simulation cell with linear dimensions of  $35 \times 35 \times 70$  Å. This yields liquid densities of 0.997 and 1.584 g/cm<sup>3</sup> for water and carbon tetrachloride at room temperature, respectively. The initial configuration of the liquid/liquid interface is obtained by joining two bulk liquid slabs, which have been equilibrated separately to give the correct bulk liquid densities. The interface is chosen to be perpendicular to the  $z$ -axis. The water molecules are



**Figure 1.** (a) The gas-phase  $\text{Cl}^-$ - $\text{H}_2\text{O}$  and  $\text{Cl}^-$ - $\text{CCl}_4$  interaction energies as a function of ion–molecule separations. Insets are the lowest-energy structures. The ab initio data is taken from the work of Xantheas.<sup>22</sup> (b) Same as (a) for  $\text{Cs}^+$ .

located in the region of  $z > 35$  Å, while the carbon tetrachloride molecules occupy the region of  $z < 35$  Å. The simulations are performed at a constant volume and temperature and periodic boundary conditions are applied in all three directions. The temperature of the system is maintained at 298 K by coupling the  $\text{H}_2\text{O}$  and  $\text{CCl}_4$  to separate external thermal baths with a time constant of 0.2 ps.<sup>16</sup> The initial velocity assigned to each atom

**TABLE 1: Potential Parameters for CCl<sub>4</sub>, H<sub>2</sub>O, Cl<sup>-</sup>, and Cs<sup>+</sup> Used in the MD Simulations<sup>a</sup>**

molecule	atom type	$\sigma(\text{\AA})$	$\epsilon(\text{kcal/mol})$	$q(e)$	$\alpha(\text{\AA}^3)$
CCl <sub>4</sub>	C	3.410	0.1000	-0.1616	0.878
	Cl	3.450	0.2600	0.0404	1.910
H <sub>2</sub> O	H	0.000	0.0000	0.5190	0.000
	O	3.234	0.1825	0.0000	0.000
	M	0.000	0.0000	-1.0380	1.444
Cl <sup>-</sup>	Cl	4.410	0.1000	-1.0000	3.690
Cs <sup>+</sup>	Cs	3.831	0.1000	1.0000	2.440

<sup>a</sup> The potential parameters are taken from ref 14.  $\sigma$  and  $\epsilon$  are the Lennard-Jones parameters,  $q$  is the atomic charge, and  $\alpha$  is the atomic polarizability.

is chosen from a Maxwell-Boltzmann distribution corresponding to the desired simulation temperature. During the MD simulations, the SHAKE algorithm<sup>16</sup> is employed to fix the H<sub>2</sub>O and CCl<sub>4</sub> geometry by constraining all the bond lengths. A time step of 2 fs is used in integrating the equations of motion. The nonbonded interactions (i.e., Lennard-Jones, Coulombic, and polarization) are truncated at molecular center-of-mass separations (i.e., H<sub>2</sub>O-H<sub>2</sub>O and ion-H<sub>2</sub>O, interactions are truncated at a molecular separation of 9 Å, while the CCl<sub>4</sub>-CCl<sub>4</sub>, CCl<sub>4</sub>-H<sub>2</sub>O, and ion-CCl<sub>4</sub> interactions are truncated at longer distances of 15, 12, and 12 Å, respectively, due to oscillations observed in the radial distribution functions at larger separations) (See Table 1). This approach has been shown to provide comparable results to the reaction field or Ewald summation techniques.<sup>17</sup>

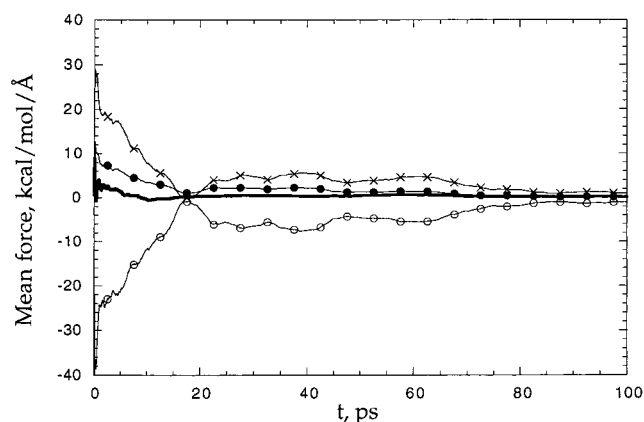
To evaluate the free energies associated with the transfer of an ion across the liquid/liquid interface, we use the constrained molecular dynamics techniques similar to the approach used for ionic association.<sup>18</sup> The reaction coordinate for ion transfer can be considered as the  $z_s$  position of the ion. The Helmholtz free energy difference,  $\Delta F(z_s)$ , between a state where the ion is located at  $z_s$ ,  $F(z_s)$ , and a reference state where the ion is at  $z_0$ ,  $F_0$ , is simply

$$\Delta F(z_s) = F(z_s) - F_0 = - \int_{z_0}^{z_s} \langle f_z(z_s') \rangle dz_s' \quad (4)$$

where  $f_z(z_s')$  is the  $z$  component of the total force exerting on the ion at a given  $z$  position,  $z_s'$ , averaged over the canonical ensemble. Here,  $F_0$  is chosen as the free energy of the system with the ion located in the bulk water region. During the simulation, the  $z$  coordinate of the ion is reset to the original value after each dynamical step and the average force acting on the ion is evaluated. The average forces are subsequently integrated to yield the free energy profile or the potential of mean force (PMF). For the present calculations, the position of the ion ranges between  $z = 22$  to  $50$  Å, with a position increment of  $1.0$  Å. The total simulation time at each ion position is at least 200 ps with 100 ps for equilibration. We found the average forces for a given ion position are converged to within a 100 ps simulation time as demonstrated in Figure 2.

### III. Results and Discussion

In Figure 3a, the PMF for transferring a Cl<sup>-</sup> ion across the CCl<sub>4</sub>/H<sub>2</sub>O interface at 298 K as a function of  $Z$ -axis normal to the interface is shown. The free-energy profile exhibits a monotonic increase from the aqueous phase into the organic phase and the estimated free energy of transfer is  $19 \pm 2$  kcal/mol. The computed free energy undergoes major changes as the ion begins to cross the interface. The change in free energy is positive because of the fact that the Cl<sup>-</sup> ion prefers to be in water rather than in carbon tetrachloride. This could be anticipated by comparing the Cl<sup>-</sup>-H<sub>2</sub>O and Cl<sup>-</sup>-CCl<sub>4</sub> dimer



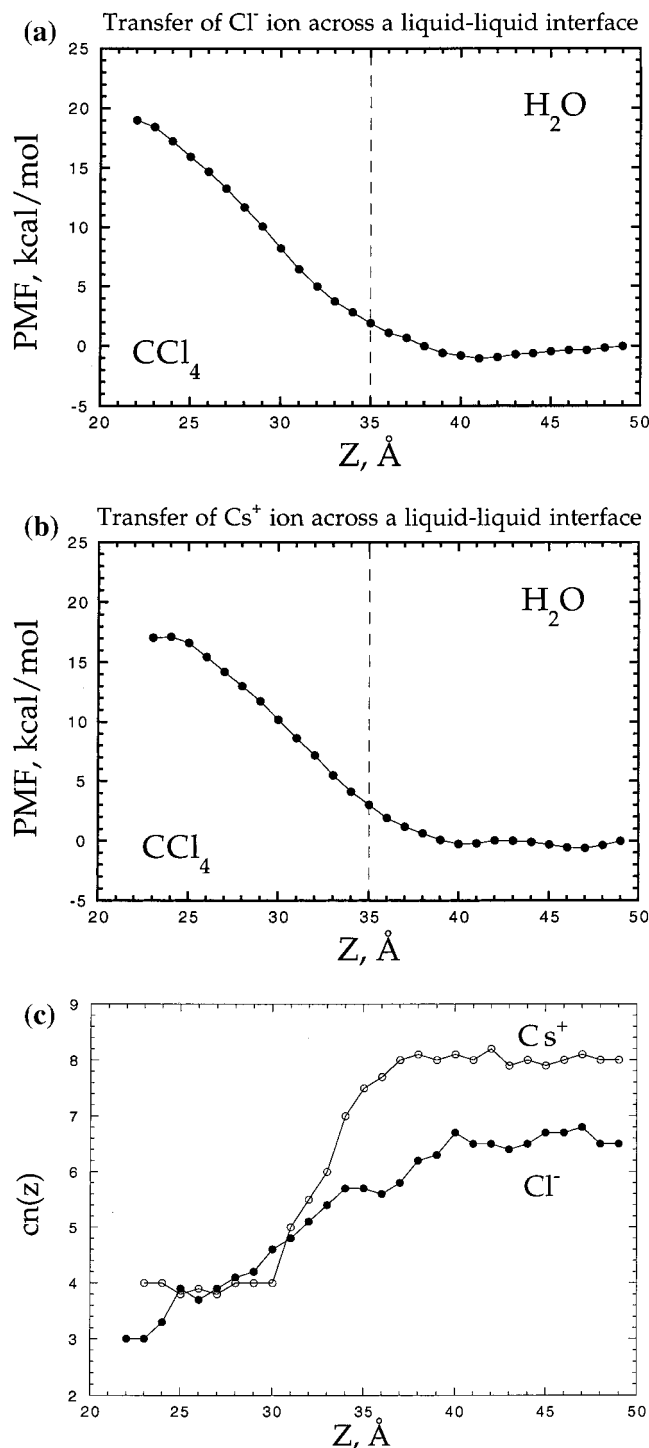
**Figure 2.** The cumulative forces (for a given ion position) acting on the ion as a function of time. Solid line (total), solid circles (polarization), open circles (Lennard-Jones), and open circle (Coulombic).

potential energy surfaces shown in Figure 1a. There apparently is no experimental data for this process. However, the result from this study can be qualitatively related to the value of 14 kcal/mol for the free energy of transferring a Cl<sup>-</sup> ion across the C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>/H<sub>2</sub>O interface and 11 kcal/mol for the CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O interface.<sup>20</sup> Both C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> should be better solvents for Cl<sup>-</sup> because they both have a finite dipole moment. So the free energy of transfer for those solvents should be lower.

To further characterize the ion transfer free energy across the liquid-liquid interface, the PMF were decomposed into energy contributions that correspond to the individual ion-solvent interactions. These energy contributions indicated that the computed free energy of ion transfer is the resultant of a competition between the Lennard-Jones and the electrostatic interactions (Coulombic and polarization). This finding is significantly different from the transferring of a neutral solute molecule (methane or chloroform) across this interface, where the free energy required to create a cavity is a major contribution.<sup>19</sup>

As the ion moves across the interface, the first hydration shell of the Cl<sup>-</sup> ion as a function of  $z$ -axis normal to the interface is significantly reduced as shown in Figure 3c. Thus, the mechanism of ion transfer that involves changes in the hydration shell of the ion is shown. The interface for various ion positions along the  $z$ -axis, were examined and found to be distorted to some degree as the ion is pushed from the aqueous phase to the nonaqueous phase. As already mentioned in previous work by Benjamin,<sup>3</sup> at short distances ( $< 12$  Å), the fingering effects were observed as the Cl<sup>-</sup> ion moved into the nonaqueous phase.<sup>3</sup> They persist during the course of at least 200 ps of the simulation, because of the strong hydrogen-bonding network between water molecules. Upon examining this fingering, several observations can be made: (1) the chloride ion is partially solvated and is located on the top of the fingering, (2) the water molecules formed the fingering orient themselves to preserve their hydrogen-bonding networks, and (3) this phenomenon is analogous to the observations found in previous studies of aqueous anion clusters.<sup>21,22</sup> The fingering effects are finally broken off as the Cl<sup>-</sup> ion moved further into the CCl<sub>4</sub> liquid phase. In Figure 4a, a snapshot was taken at the end of a 200 ps of the molecular dynamics simulation when the Cl<sup>-</sup> ion was located 13 Å away from the interface in the CCl<sub>4</sub> liquid phase.

One important finding in this study is that no interfacial minimum is observed in the free-energy profile. Thus, we can view the mechanism of ion transport across this interface as



**Figure 3.** (a) The computed free-energy profile of transferring a  $\text{Cl}^-$  ion across a water–carbon tetrachloride liquid/liquid interface; (b) the computed free-energy profile of transferring a  $\text{Cs}^+$  ion across a water–carbon tetrachloride liquid/liquid interface; and (c) the computed hydration numbers of the ions as a function of  $z$ -axis normal to the interface.

just a simple diffusive process. This result is far different from the conclusion of Benjamin's study of mass transfer of  $\text{Cl}^-$  ion across the water/dichloroethane interface.<sup>3</sup> We note here that, a comparison between the result of this study and Benjamin's results may not be appropriate, in part, due to significant differences between the calculations. For instance, because the nature of the nonaqueous solvents is different (i.e., carbon tetrachloride versus dichloroethane), it may be more difficult to displace dichloroethane molecules than carbon tetrachloride

molecules. The computational methods used to compute the free-energy profile and the potential models employed in describing the intermolecular interactions are completely different. Most importantly, the nature of solvent structures was not fully taken into account in Benjamin's PMF calculations, i.e., because of the fingering effect, only water molecules near the ion are included in the calculations of the electrostatic component of the total free energy.<sup>3</sup> It is important that further research is needed to clarify this discrepancy.

In addition to the  $\text{Cl}^-$  ion simulations, a detailed study of the transport properties for the  $\text{Cs}^+$  ion across a  $\text{CCl}_4/\text{H}_2\text{O}$  interface was also carried out. The PMF of transferring a  $\text{Cs}^+$  ion across the  $\text{CCl}_4/\text{H}_2\text{O}$  interface at 298 K as a function of  $z$ -axis normal to the interface is shown in Figure 3b. As one can see, the PMF is very similar to that of the  $\text{Cl}^-$  ion. For instance, the free-energy profile exhibits a monotonic increase from the aqueous phase into the organic phase, and no minimum was found at the interface. The increase in the free energy is expected due to the fact that the  $\text{Cs}^+$  ion interacts more strongly with water than with carbon tetrachloride. This can be seen in the dimer energies shown in Figure 1b. We have also performed a reverse transfer for the  $\text{Cs}^+/\text{H}_2\text{O}/\text{CCl}_4$  system and found the computed PMF for both directions are nearly identical. Thus, our results presented in this paper represent the equilibrium free energy of the system.

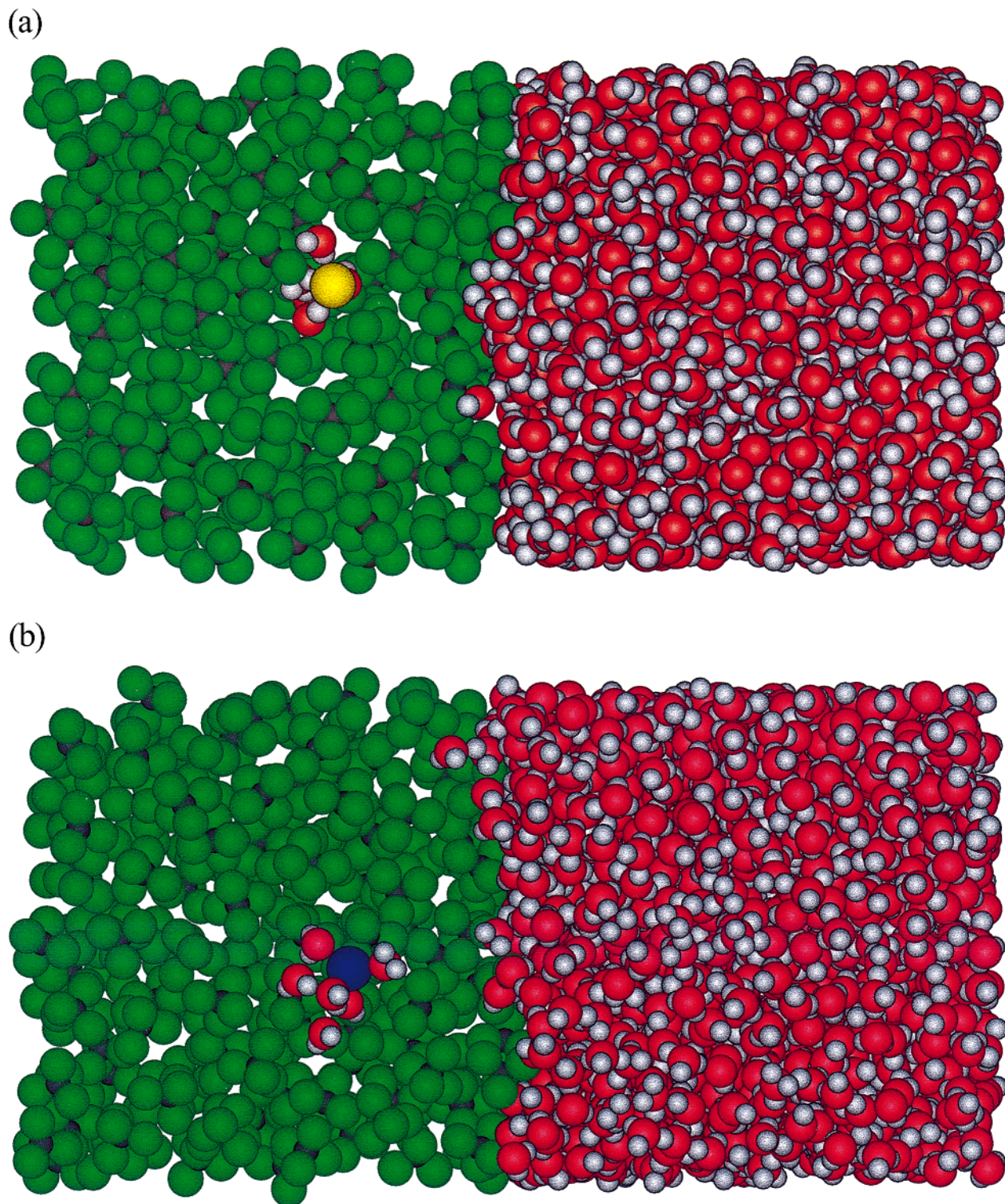
The estimated free energy of transfer is  $17 \pm 1$  kcal/mol. There is experimental data available for the Gibbs transfer energy of  $\text{Cs}^+$  ion from the aqueous phase into a mixed organic phase (nitrobenzene (NB)–carbon tetrachloride).<sup>10</sup> For example, the net free energy of transfer from water into a mixed organic phase (i.e., 60% NB and 40%  $\text{CCl}_4$ ) is about 5 kcal/mol. The electrochemical measurements on Gibbs transfer energy from aqueous phase into neat carbon tetrachloride has not yet been carried out, due to complications in experimental techniques. The results on mixed organic phase systems indicated that with decreasing dielectric permittivity the value of the Gibbs transfer energy of the  $\text{Cs}^+$  ion increases. Thus, we can expect that the value of the Gibbs transfer energy of the  $\text{Cs}^+$  ion from water to neat carbon tetrachloride will be greater than 5 kcal/mol.

Similar to the  $\text{Cl}^-$  ion transfer, as the  $\text{Cs}^+$  ion moves across the interface, the first hydration shell of the  $\text{Cs}^+$  ion as a function of  $z$ -axis normal to the interface is significantly reduced (i.e., 8 to 4) as shown in Figure 3c. In Figure 4b, a snapshot was taken when the  $\text{Cs}^+$  ion was located deep in the  $\text{CCl}_4$  liquid phase. It is clear that the  $\text{Cs}^+$  is completely solvated even though its hydration number in the first solvation shell is reduced by a half. A similar observation was reported in previous studies of aqueous cation clusters.<sup>21</sup> The computed density profiles for various ion positions along the  $z$ -axis were found to be far less distorted when compared to the corresponding results for the  $\text{Cl}^-$  ion.

#### IV. Conclusion

In summary, we have demonstrated a detailed molecular-level mechanism for transporting an ion (i.e., chloride ion or cesium ion) across the water–carbon tetrachloride liquid/liquid interface using molecular dynamics computer simulation techniques. The results obtained in these studies provided new physical insight into both the free energies and solvent structures as the ions moved across the interface. The computed free-energy profiles of transfer for both ions increased monotonically from water to carbon tetrachloride and no free-energy minima were observed at the liquid/liquid interface. Thus, these ions are not surface active. These results are not in accordance with earlier theoretical studies on the ion transfer processes of a similar system.<sup>3</sup>





**Figure 4.** Snapshots were taken at the end of 6 ns of the molecular dynamics simulations when the ions were pulled away from the interface in the  $\text{CCl}_4$  liquid phase: (a)  $\text{Cl}^-$  and (b)  $\text{Cs}^+$ . A thickness of  $\text{CCl}_4$  molecules have been removed to expose the hydration shells of the ions.

The first hydration shells of the ions were found to be significantly reduced as they moved from the aqueous phase to the organic phase. The detailed water structures around these ions were analyzed and found to be quite different. For example, as the ions move from the aqueous phase to the organic phase, the  $\text{Cl}^-$  ion dragged a trace of water molecules along with it. The trace of water molecules is finally broken off as the  $\text{Cl}^-$  ion moved further into the  $\text{CCl}_4$  liquid phase. In contrast, the  $\text{Cs}^+$  ion is always solvated with a few water molecules as the

ion moved across the interface. Another important finding is that these ions are not surface active as indicated in the PMFs.

In this study, the counterion effects on the ion transport across the interface have not yet been studied. In the past, we have examined the role of the counterion on the ion-crown ether association in water. These simulation studies indicated that including the counterion lowers the free-energy profile, but the characteristics of the free-energy profile remains the same. Wipff and co-workers<sup>11</sup> have examined the counterion effects ( $\text{Pic}^-$ /

$\text{Cl}^-$ ) on the free energy profiles of transporting a  $\text{Cs}^+$  ion across the water/chloroform interface and found a couple of kcal/mol difference between both simulations. Thus, it would be of interest in future work on the liquid/liquid interface to include counterions to evaluate their effects on the PMFs as well as on the fingering phenomenon, to directly compare with experimental values.

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