Molecular dynamics simulation of limiting conductances for LiCl, NaBr, and CsBr in supercritical water

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(Received 28 May 1999; accepted 6 October 1999)

We report molecular dynamics simulations of LiCl, NaBr, and CsBr in supercritical water in order to explain the experimental observations of the limiting conductances as a function of the density of water at supercritical state points. As was the case in our previous work on NaCl in supercritical water [Lee et al., Chem. Phys. Lett. 293, 289 (1998)], we find that the experimental trends in the limiting conductances as a function of water density are reproduced in our simulations—a clear change of slope from the assumed linear dependence of limiting conductances of LiCl, NaBr, and CsCl on the water density. We also found that the effect of the number of hydration water molecules around ions dominates in the higher-density region while the interaction strength between the ions and the hydration water molecules (as measured by the potential energy per hydration water molecule) dominates in the lower-density region. In the case of Cs\(^{+}\) and Br\(^{-}\), however, the latter factor in the lower-density region is not as dominant as in the cases of Na\(^{+}\) and Cl\(^{-}\) since a clear difference between the potential energy per hydration water molecule at densities above and below 0.45 g/cm\(^3\) was not clearly observed in the cases. In the case of Li\(^{+}\), the interaction between the ions and the hydration water in the lower-density region is almost a nonfactor since the potential energy per hydration water molecule is monotontically decreased with decreasing water density, which is consistent with the linear increase of the limiting conductance for the Li\(^{+}\) ion with decreasing water density. © 2000 American Institute of Physics.

I. INTRODUCTION

In the previous works,\(^{1,2}\) molecular dynamics (MD) simulations of the mobilities of the alkali metal ions (Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Rb\(^{+}\), and Cs\(^{+}\)) and the halides (F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\)) at 25°C were carried out using the TI4P and SPC/E models for water and ion–water potential parameters. The mobilities calculated from the mean squared displacements (MSD) and the velocity autocorrelation (VAC) functions were found to be in good agreement with each other. The calculations demonstrated, for the first time, cation and anion mobilities that fall on separate curves, as functions of ion size, with distinct maxima. This is in complete accord with experimental trends observed in water at 25°C.\(^{3-6}\) The residence times of water in the hydration shells around the ion were found to decrease dramatically with its size. The classical solvethermber model describes the mobility of the Li\(^{+}\) ion in water adequately but not those of the other ions. For the large ions, the steric effect due to large ion size and the large number of hydration water molecules restrict ionic mobility. As the size of ion decreases, the ion should diffuse more easily due to the small steric effect and the decreasing number of the hydration water molecules. But for the small ions, increase in the interaction between an ion and the hydrated water, reflected in the average potential energy per hydration water molecule (−222, −126, −84.2, −73.2, −55.7, −131, −77.8, −74.9, and −56.8 kJ/mol for Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Rb\(^{+}\), Cs\(^{+}\), F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\)),\(^{5}\) strongly decreases ionic mobility. This effect is seen in the residence time of the water in the first hydration shell around the ion (~400, 26.4, 9.4, 9.3, 9.5, 28.5, 9.0, 9.5, 7.7 ps for Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Rb\(^{+}\), Cs\(^{+}\), F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), and I\(^{-}\)).

Our understanding of solute speciation of dilute aqueous alkali halides at supercritical conditions is mostly based on conductimetric measurements.\(^{7,8}\) Two experimental results of the limiting molar conductances as a function of water density at high temperatures (supercritical points) showed two different trends.\(^{9,10}\) One displayed a clear change of slope from the assumed linear dependence of limiting equivalent conductances of LiCl, NaCl, NaBr, and CsBr on the water density\(^{9}\) and the other had a clear maximum in limiting equivalent conductance of NaOH.\(^{10}\) This phenomenon is closely related to the structure of water around an ion and to the shape of the anion, OH\(^{-}\).

In a previous study,\(^{11}\) we reported MD simulations of NaCl in supercritical water in order to explain the experimental observations of the limiting conductances as a function of the density of water supercritical state points. We found two important competing factors, the effect of the number of hydration water molecules around ions and the interaction strength between the ions and the hydration water molecules. In the cases of Na\(^{+}\) and Cl\(^{-}\), the number of hydration water molecules around ions dominated in the higher-density region while the interaction between the ions and the hydration water molecules dominated in the lower-
density region. The competition between these two factors was seen in the residence time of water in the first hydration shell around the ions. The different effects in the lower- and higher-density regimes led to different slopes for the limiting conductances as a function of density in the two regimes. Similar considerations explain the dependence of ion mobility on ion size at ambient conditions, as discussed above.

In this paper, we extend our MD simulations of the systems to LiCl, NaBr, and CsBr in supercritical water at 673 K. In the following section, we describe the technical details of simulation. We present our results in Sec. III and the concluding remarks in Sec. IV.

II. MOLECULAR MODELS AND MOLECULAR DYNAMICS SIMULATION DETAILS

The SPC/E (extended simple point charge) model was adopted for the water molecule. All ions were represented by a point charge having a Lennard-Jones (LJ) center. The potential parameters for ion–water of Li$^+$, Cs$^+$, and Br$^-$ are the same as those used in Ref. 2; for Li$^+$, Cs$^+$, and Br$^-$, the ion-oxygen $\sigma_{i0}$ is 2.337, 3.526, and 3.896 Å, respectively, and $\epsilon_{i0}$ is 0.6700 and 0.5216 kJ/mol for the cations and 0.4948 kJ/mol for the anion (for comparison, $\sigma_{i0}$ = 2.876 and 3.875 Å, respectively, and $\epsilon_{i0}$ = 0.5216 kJ/mol for Na$^+$ and Cl$^-$ ions$^{1,21}$). These ion–water potentials were originally developed by Pettit and Rossky. A spherical cutoff $r_c$ of half the simulation box length was employed for all the pair interactions. This is a simple truncation in which two molecules are considered as interacting if the distance between their centers is less than the cutoff radius $r_c$ and the interaction is neglected if the distance is larger than $r_c$. This simple truncation of all interactions for water containing a single ion was shown by Perera et al.$^{14}$ to be comparable in accuracy to the use of Ewald summation or reaction field methods.

The experimental critical properties of water are $T_c$ = 647.13 K, $\rho_c$ = 0.322 g/cm$^3$, and $P_c$ = 220.55 bar,$^{15}$ and the critical properties of SPC/E water are $T_c$ = 640 K, $\rho_c$ = 0.29 g/cm$^3$, and $P_c$ = 160 bar.$^{16}$ We chose the simulation state points for the calculation of the limiting conductance of LiCl, NaBr, and CsBr at the reduced temperature, $T_r = T/T_c = 1.05$ (673 K) and at the reduced densities, $\rho_r = \rho/\rho_c = 0.76, 1.07, 1.38, 1.66, 2.10, and 2.55$, corresponding to real densities of about 0.22, 0.31, 0.40, 0.48, 0.61, and 0.74 g/cm$^3$ for the SPC/E model; this spans the range of densities around 0.45 g/cm$^3$, where the clear change of slope from the assumed linear dependence of limiting equivalent conductances of LiCl, NaCl, NaBr, and CsBr on density$^9$ and the maximum in limiting equivalent conductance of NaOH (Ref. 10) are located.

We used Gaussian isokinetics$^{17-20}$ to keep the temperature of the system constant and the quaternion formulation$^{21,22}$ of the equations of rotational motion about the center of mass of the SPC/E water molecules. For the integration over time, we adopted Gear’s fifth-order predictor-corrector algorithm$^{23,24}$ with a time step of 0.5 × 10$^{-13}$ s (0.5 fs). Each MD simulation of a single ion system with 215 SPC/E water were carried out for Li$^+$, Cs$^+$, and Br$^-$ ions for 1 200 000 time steps after equilibration of 600 000 time steps. The equilibrium properties are averaged over 6 blocks of 200 000 time steps and the configurations of water molecules and an ion are stored every 10 time steps for further analysis.

The diffusion coefficient $D_i$, of each ion is calculated from the mean square displacement (MSD) and from the velocity autocorrelation function (VAC), and the ion mobility is obtained by $u_i = D_i e/k_B T = D_i e/F R T$ (Einstein relation), where $k_B$ is the Boltzmann constant, $R$ is the gas constant, $F$ is the Faraday constant, $e$ is the charge on the ion in units of the electronic charge, $T$ is the absolute temperature, and $i = +$ and $-$ . The limiting conductance of each ion can be calculated from $\lambda^{0} = u_i e F$. The total limiting conductance of LiCl (NaBr or CsBr) is the sum of each ion, $\lambda^{0} = \lambda^{+} + \lambda^{-}$.

It is important to note how these calculations are performed. We calculate the individual diffusion coefficients of the each individual ion in a molecular dynamics simulation consisting of water and the lone ion. By combining the conductances of the individual ions to obtain the conductance of the salt, we do not allow for the possibility of ionic association to influence the calculated value of the limiting conductance. Hence, by construction, our simulations of limiting conductances do not include the effects of ion pairing.

III. RESULTS AND DISCUSSION

The diffusion coefficients $D_i$ of Li$^+$, Cs$^+$, and Br$^-$, calculated from the mean square displacement (MSD) and from the velocity autocorrelation function (VAC), are listed in Table I. The limiting conductances $\lambda^{0}$ determined from these diffusion coefficients are also listed in the same table. The
limiting conductances of Li⁺, Cs⁺, and Br⁻ calculated from the MSD are compared, in Fig. 1, with those of Na⁺ and Cl⁻. ¹¹

In Fig. 1, the behavior of the limiting conductance of Br⁻ in the higher-density regime shows almost the same trend as that of Cl⁻ reflecting that the limiting conductances of Cl⁻ and Br⁻ at ambient conditions are almost the same (76.3 and 78.1 cm²/mol at 298.15 K). As the density of water decreases, the deviation from the assumed linear dependence of limiting conductance of Br⁻ on the water density is smaller than that of Cl⁻. On the other hand, the similarity of the limiting conductances of Na⁺ and Cs⁺ over the whole range of water density is in contrast to the large difference in the limiting conductances of those ions at ambient conditions (50.1 and 77.2 cm²/mol at 298.15 K). The deviation from the assumed linear dependence of limiting conductance of Cs⁺ on the water density is slightly larger than that of Na⁺. The limiting conductances of Li⁺ over the whole range of water density calculated from our MD simulation are too small compared with the experimental results⁹ and exhibit almost linear dependence of limiting conductance on the water density. A possible explanation for this may be the strong polarizing effect of Li⁺ due to its small size and recalculation of the limiting conductances of Li⁺ using polarizable models¹⁵ for water and the Li⁺ ion is presently under study.

The limiting conductances of LiCl, NaCl, NaBr, and CsBr, calculated from those of the individual ions by λᵣ = λ⁺⁺λ⁻, are plotted in Fig. 2. The overall agreement is quite good except for LiCl when compared with the experimental results.⁹ The poor result for LiCl is evidently a reflection of the poor prediction for the limiting conductance of Li⁺. We have once more confirmed that the experimental trends in the limiting conductances as a function of water densities are reproduced in our simulations—a clear change of slope from the simple linear dependence of limiting conductances of LiCl, NaBr, and CsCl on the water density. This is similar to what was found for NaCl.¹¹ Except for LiCl, the calculated values are essentially exact in the higher- and medium-density regions, and are slightly higher than the experimental values in the lower-density region.

Several thermodynamic, structural, and dynamic quantities have been calculated and listed in Table II. The average ion–water potential energies for Li⁺, Cs⁺, and Br⁻ ions increase nearly linearly with decreasing water density except for a relatively sudden increment at 0.22 g/cm³ as was observed in the cases of Na⁺ and Cl⁻. This can be seen in Fig. 3. The calculated ion–water potential energy for Cl⁻ is closer to that for Cs⁺ rather than that for Br⁻.

The hydration number n is found by integrating the water number density from the inner to the outer boundary of the first solvation shell,²⁶

\[ n = 4\pi \rho \int_a^b g_{i0}(r) r^2 dr, \]

where ρ is the bulk water number density, a is the point at which the ion–oxygen radial distribution function g_{i0}(r) first rises from zero, and b is the point at which the first minimum

<table>
<thead>
<tr>
<th>Ion</th>
<th>Density (g/cm³)</th>
<th>Ion–water p. c. (kJ/mol)</th>
<th>Hydration number (n)</th>
<th>Ion–water p. c./n</th>
<th>Residence time of water (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>0.22 ± 0.06</td>
<td>4.12 ± 0.12</td>
<td>180 ± 3</td>
<td>3.45 ± 0.19</td>
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<tr>
<td>Li⁺</td>
<td>0.31 ± 0.06</td>
<td>4.12 ± 0.14</td>
<td>182 ± 2</td>
<td>3.41 ± 0.36</td>
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</tr>
<tr>
<td>Li⁺</td>
<td>0.40 ± 0.06</td>
<td>4.19 ± 0.11</td>
<td>184 ± 2</td>
<td>3.36 ± 0.31</td>
<td></td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.48 ± 0.06</td>
<td>4.20 ± 0.08</td>
<td>185 ± 2</td>
<td>3.26 ± 0.25</td>
<td></td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.48 ± 0.06</td>
<td>4.20 ± 0.08</td>
<td>185 ± 2</td>
<td>3.26 ± 0.25</td>
<td></td>
</tr>
<tr>
<td>Cs⁺</td>
<td>0.22 ± 0.06</td>
<td>4.21 ± 0.15</td>
<td>68.8 ± 2.4</td>
<td>3.06 ± 0.10</td>
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<tr>
<td>Cs⁺</td>
<td>0.31 ± 0.06</td>
<td>6.70 ± 0.30</td>
<td>65.9 ± 2.4</td>
<td>1.92 ± 0.04</td>
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<tr>
<td>Cs⁺</td>
<td>0.40 ± 0.06</td>
<td>6.98 ± 0.39</td>
<td>63.6 ± 2.6</td>
<td>1.82 ± 0.07</td>
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<tr>
<td>Cs⁺</td>
<td>0.48 ± 0.06</td>
<td>7.25 ± 0.38</td>
<td>61.8 ± 2.8</td>
<td>1.72 ± 0.05</td>
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</tr>
<tr>
<td>Cs⁺</td>
<td>0.61 ± 0.06</td>
<td>7.85 ± 0.20</td>
<td>58.3 ± 0.8</td>
<td>1.67 ± 0.07</td>
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<tr>
<td>Cs⁺</td>
<td>0.74 ± 0.06</td>
<td>8.69 ± 0.32</td>
<td>53.5 ± 1.3</td>
<td>1.59 ± 0.09</td>
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</tr>
<tr>
<td>Br⁻</td>
<td>0.22 ± 0.06</td>
<td>7.25 ± 0.33</td>
<td>55.3 ± 2.2</td>
<td>2.09 ± 0.17</td>
<td></td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.31 ± 0.06</td>
<td>7.70 ± 0.24</td>
<td>53.9 ± 1.6</td>
<td>1.86 ± 0.11</td>
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<tr>
<td>Br⁻</td>
<td>0.40 ± 0.06</td>
<td>7.99 ± 0.33</td>
<td>53.2 ± 0.9</td>
<td>1.74 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.48 ± 0.06</td>
<td>8.37 ± 0.58</td>
<td>51.1 ± 1.0</td>
<td>1.71 ± 0.12</td>
<td></td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.61 ± 0.06</td>
<td>8.88 ± 0.35</td>
<td>49.4 ± 1.0</td>
<td>1.69 ± 0.09</td>
<td></td>
</tr>
</tbody>
</table>
in g_{i0}(r) occurs. Table II lists the hydration number of water in the first solvation shell around Li\(^+\), Cs\(^+\), and Br\(^-\) ions. Figure 4 shows that the hydration numbers for these ions are monotonically decreased with decreasing water density, but the slopes for Li\(^+\), Cs\(^+\), and Br\(^-\) are not very different in the ranges of density above and below 0.45 g/cm\(^3\) unlike those of Na\(^+\) and Cl\(^-\). The hydration number for Li\(^+\) is nearly unchanged over the whole range of water density.

The potential energy per hydration water molecule, defined as the average ion–water potential energy divided by the hydration number, for Li\(^+\), Cs\(^+\), and Br\(^-\) ions is also listed in Table II. In the cases of Na\(^+\) and Cl\(^-\), the difference between these potential energies at densities above and below 0.45 g/cm\(^3\) was clearly observed. Figure 5, however, shows that these potential energies for Cs\(^+\) and Br\(^-\) decrease nearly linearly with decreasing water density over the whole range of water density. As a result, the potential energy per hydration water molecule decreases nearly linearly with decreasing water density over the whole range of water density.

There were two important competing factors in the explanation of the limiting conductance of NaCl in supercritical water at 673 K—the number of hydration water molecules around ions and the interaction between the ions and the hydration water molecules. In the cases of Na\(^+\) and Cl\(^-\), the effect of the number of hydration water molecules around ions dominated in the higher-density region while the interaction strength between the ions and the hydration water molecules dominated in the lower-density region. The same explanation may apply for the limiting conductances of Cs\(^+\) and Br\(^-\), but the latter factor in the lower-density region is not very dominant as in the cases of Na\(^+\) and Cl\(^-\); that is, a difference between the potential energy per hydration water molecule at densities above and below 0.45 g/cm\(^3\) was not clearly observed in the cases of Cs\(^+\) and Br\(^-\). That is why the sudden decrease of the limiting conductance at the water density of 0.22 g/cm\(^3\) is not observed in the cases of Cs\(^+\) and Br\(^-\) as seen in Fig. 1, unlike in the cases of Na\(^+\) and Cl\(^-\). In the case of Li\(^+\), the latter factor in the lower-density region is almost a nonfactor since the potential energy per hydration water molecule is monotonically decreasing with decreasing water density, which is consistent with the linear increase of the limiting conductance for the Li\(^+\) ion with decreasing water density.

Another quantity to elucidate the environment around the ion is the residence time of the hydrated water. The residence time correlation function is defined by

\[
R(r,t) = \frac{1}{N_r} \sum_{i=1}^{N_r} [\theta_t(r,t) \theta_t(r,0)],
\]

where \(\theta_t(r,t)\) is the Heaviside unit function, which is 1 if a water molecule \(i\) is within a spherical region of radius \(r\) within the first hydration shell of the ion and 0 otherwise, and \(N_r\) is the average number of water molecules in this region \(r\) at \(t=0\). The characteristic decay time (residence time), \(\tau\), is obtained by fitting the time correlation function to an exponential decay \((R(r,t)) = \exp(-t/\tau)\), which is useful particularly when \(\tau\) is large. The residence times for Li\(^+\), Cs\(^+\), and Br\(^-\) are listed in Table II and plotted in Fig. 6 together with Na\(^+\) and Cl\(^-\). All the ions show the clear difference between the higher- and lower-density regions above and below 0.45 g/cm\(^3\). The slope of the calculated residence time for Cs\(^+\) in the lower-density region below 0.45 g/cm\(^3\) is
less than that for Na\(^+\) in the same region which coincides with the slow decrease of the limiting conductance at the water density of 0.22 g/cm\(^3\) observed in the case of Cs\(^+\) as seen in Fig. 1. The calculated residence times, however, and the slope of the residence time for Br\(^-\) in the lower-density region below 0.45 g/cm\(^3\) are larger than those for Cl\(^-\) though the diffusion coefficients of Br\(^-\) are larger than those of Cl\(^-\) and the potential energy per hydration water molecule for Br\(^-\) is smaller than that for Cl\(^-\). The same trends in the residence time, the diffusion coefficient, and the potential energy per hydration water molecule are observed at ambient conditions for both ions.\(^2\) This suggests that there is another factor in explaining the limiting conductance of ions in supercritical water and in ambient water, for example, the hydrogen-bond dynamics of water molecules within the first hydration shell of ions. Note that the slope of the residence time for Li\(^+\) in the lower-density region is smaller than in the higher-density region, which is consistent with the behavior of the limiting conductance for Li\(^+\).

### IV. CONCLUDING REMARKS

In our previous study,\(^1\) we performed MD simulations of NaCl in supercritical water in order to explain the experimental observations of the limiting conductances as a function of the density of water supercritical state points. We found two important competing factors, the effect of the number of hydration water molecules around ions and the interaction strength between the ions and the hydration water molecules. The former dominated in the higher-density region while the latter dominated in the lower-density region. The competition between these two factors was seen in the residence time of water in the first hydration shell around the ions. The different effects in the lower- and higher-density regimes lead to different slopes for the limiting conductances as a function of density in the two regimes.

In this study, we have once more confirmed that the experimental trends in the limiting conductances as a function of water densities are reproduced in our simulations; as for NaCl,\(^1\) a clear change of slope from the assumed linear dependence of limiting conductances of LiCl, NaBr, and CsCl on the water density. We also found that the number of hydration water molecules around ions dominates in the higher-density region while the interaction between the ions and the hydration water molecules dominates in the lower-density region. The latter factor, however, in the lower-density region is not very dominant as in the cases of Na\(^+\) and Cl\(^-\), that is, the difference between the potential energy per hydration water molecule at densities above and below 0.45 g/cm\(^3\) was not clearly observed in the cases of Cs\(^+\) and Br\(^-\). That is why the sudden decrease of the limiting conductance at the water density of 0.22 g/cm\(^3\) is not observed in the cases of Cs\(^+\) and Br\(^-\) as seen in Fig. 1, unlike in the cases of Na\(^+\) and Cl\(^-\). In the case of Li\(^+\), the latter factor in the lower-density region is almost a nonfactor since the potential energy per hydration water molecule is monotonically decreasing with decreasing water density, which is consistent with the linear increase of the limiting conductance for the Li\(^+\) ion with decreasing water density. A possible explanation for the discrepancy between the Li\(^+\) result and experiment may be the strong polarizing effect of Li\(^+\) due to its small size and recalculation of the limiting conductances of Li\(^+\) using polarizable models\(^2\) for water and the Li\(^+\) ion is presently under study.

Some insight can be gained into the discrepancy between simulation and experiment for the Li\(^+\) ion by considering the possibility that the combination of the Li\(^+\) model and water (SPC/E) that we have used underestimates the hydration number around Li\(^+\). Several ambient condition simulations of Li\(^+\)-water have predicted coordination numbers of around six, e.g., Mezei and Beveridge\(^2\) find a coordination number of 5.97 using the MC and MCY models for water; and Lee et al.\(^1\) find a coordination number of 6.0 using the TIP4P model for water. So the question that arises is whether the coordination number of around 6 will persist to the supercritical conditions studied in this paper, or at least be higher than what we have found for Li-SPC/E water. There are several ways to probe this question. The first is to ask what is the coordination number for Li\(^+\)-water at supercritical conditions if water is modeled by TIP4P, a model which gives a coordination number of 6.0 at ambient conditions. We performed a simulation for Li\(^+\)-TIP4P water at a density of 0.48 g/cm\(^3\) and temperature of 673.15 K. The results are reported in Tables I and II. We found that the coordination number is 4.89, which is higher than the value for SPC/E (4.20). Earlier simulations by Lee et al.\(^2\) of Li\(^+\)-SPC/E water at ambient conditions yielded a coordination number of 4.1. From this set of results, it is clear that SPC/E predicts a lower coordination number than TIP4P at both ambient and supercritical conditions (although the difference between the two is less at supercritical conditions), and thus there is some evidence to conclude that SPC/E may be less accurate than TIP4P in predicting the Li\(^+\)-water coordination number. However, the impact of this difference on the mobility is very small, as is clear from Table I, and in the wrong direction, since TIP4P will predict a slightly lower limiting conductance for Li\(^+\)-water than will SPC/E. Hence, the inaccuracy of the results for Li\(^+\)-water are probably more related to the inadequacy of the model for Li\(^+\)-water than the model for water, and will require further investigation.

As noted at the end of Sec. II, these calculations are performed in such a way that ion-pairing cannot contribute to the simulation results. On the other hand, it is widely be-
believed that ion-pairing has a significant impact on experimentally-measured limiting conductances. This is because the limiting conductances measured experimentally are obtained as the infinite-dilution extrapolation of experiments performed at very low (but still finite) concentration. Since ion-pairing is so strong at supercritical conditions, the reasoning then is that the experimental measurements must reflect ion-pairing. However, we have seen in this paper that much of the behavior of the limiting conductance of the salts (other than Li-containing salts) is fitted quantitatively by a model which, by construction, does not include ion pairing. This raises the possibility that ion-pairing effects may not be as important in salts composed of the larger ions as is generally supposed. However, there remains the other possible interpretation of our results, namely, that the good agreement between experiment and simulation may be fortuitous, and to explore this issue is beyond the scope of the current paper. It would be interesting, however, to investigate this problem of the effect of ion pairing on conductance completely within the simulation model by performing a series of simulations with finite concentrations of salts in solution and employing an extrapolation scheme as is used experimentally. This would require very large simulations to obtain meaningful statistics on very dilute solutions containing enough ions to yield statistically meaningful ion-pairing statistics, and so would most likely require massively parallel supercomputers. We hope to be able to perform such simulations in the near future.

ACKNOWLEDGMENTS

The work of S.H.L. was supported by the nondirected Research Fund of the Korea Research Foundation, 1996. S.H.L. thanks the Tongmyung University of Information Technology (Pusan, South Korea) for access to its IBM SP/2 computer. The work of P.T.C. was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.