Molecular simulation of the temperature- and density-dependence of ionic hydration in aqueous SrCl$_2$ solutions using rigid and flexible water models

Thomas Driesner$^a$ and Peter T. Cummings
Department of Chemical Engineering, The University of Tennessee, Knoxville, Tennessee 37996-2200

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Molecular dynamics simulations of aqueous SrCl$_2$ solutions have been performed with two flexible water models [the Bopp–Jancsó–Heinzinger (BJH) and modified Toukan–Rahman simple point charge model (SPC-mTR)] as well as the rigid simple point charge (SPC) model. Recent extended x-ray absorption fine structure spectroscopy (EXAFS) studies of Sr$^{2+}$ hydration reported a decrease of the average distance between Sr$^{2+}$ and water molecules in the first hydration shell with increasing temperature. The available Sr$^{2+}$–water potential for rigid SPC water and its variants is not able to reproduce this hydration shell contraction. Adding intramolecular flexibility in the form of the SPC-mTR potential only slightly improves the performance of the SPC model, while the BJH model performs significantly better. All models predict an expansion of the first hydration shell of the Cl$^-$ ion with increasing temperature. The degree of expansion is density and concentration dependent. Large shifts of the position of the first minimum in the $g_{\text{ClO}}(r)$ make the comparison of Cl$^-$ coordination numbers at different temperatures and densities difficult. We demonstrate that although the coordination number as determined from nearest neighbor hydrogen atoms (as preferred by neutron diffraction experimentalists) appears to decrease with increasing temperature, it is in fact increasing when the coordination number is properly defined as the number of nearest neighbor water molecules. When identical definitions for the hydration shells are used, the results for Cl$^-$ are in good agreement with the available experimental data. Hence, care has to be taken when discussing trends in hydration “strength” with temperature and density. © 1999 American Institute of Physics. [S0021-9606(99)52135-1]

I. INTRODUCTION

The microstructure of high temperature water and aqueous solutions has received a large degree of attention in recent years as a result of interest in industrial applications as well as the importance of such fluids in many geochemical processes such as the formation of hydrothermal ore deposits. In a constructive interplay of molecular simulation and experimental studies, during this decade significant progress in understanding the microstructure of pure water$^1$ has been achieved. Recent progress in experimental techniques has also promoted the collection of detailed data on the hydration/solvation of ions in high temperature aqueous solutions on an essentially molecular scale. Among the experimental methods, extended x-ray absorption fine structure spectroscopy (EXAFS)$^{2–9}$ and neutron diffraction with isotope substitution (NDIS)$^{10–14}$ methods appear to have a considerable potential in exploring the hydration environment around ions in great detail. In particular, the ion-water distance and the coordination number can be obtained with high precision (notice that we will follow the suggestions of Chialvo et al.$^{15}$ and strictly adhere to the term coordination number rather than hydration number or solvation number). The experimental studies of hydration/solvation of ions in high temperature aqueous solutions have been complemented by many molecular theoretic and simulation approaches, spearheaded by the groups of Chialvo and Cummings at the University of Tennessee and Oak Ridge National Laboratory, Rossky and Johnson at the University of Texas, and Tucker at UC-Davis. These theoretical and simulation approaches have been the subject of several recent reviews.$^{16–18}$

From the experimental data on ion hydration in high temperature aqueous solutions collected so far, two general trends seem to emerge; most EXAFS studies have found that the average cation–water distance decreases with increasing temperature, and a variety of methods indicates that the average anion–water distance increases with increasing temperature. For monovalent cations, the decrease is typically around 0.1 Å$^{2.5–7}$ when going from ambient to near critical temperatures. For divalent cations the decrease seems to be about half as large$^{4,5,7,8,19}$ although a recent study on Ni$^{2+}$ found an increase by about 0.02–0.03 Å.$^9$ NDIS studies of anion hydration [Cl$^-$ (Refs. 10,12,14)] show an apparent increase in the average anion–hydration water distance with a decrease of the coordination number. A similar trend was found in an EXAFS study of I$^-$ hydration.$^{20}$ Further evidence for the expansion of anion hydration shells with increasing temperature comes from redshifts in charge-transfer-to-the-solvent spectra such as those measured for HS$^-$ (Ref. 21) and Cl$^-$.$^{22}$
To date there has been no comprehensive theoretical explanation for these observations. Some insight comes from quantum chemical studies that demonstrate that the decrease of the dielectric constant of the solvent surrounding a divalent cation hydration complex leads to a decrease of the average cation–water distance. However, the quantum chemical approaches use an extremely simplified model of the solvent, that is, a continuous dielectric medium. It seems likely that molecular simulation methods (which include a structured and dynamic solvent) could be helpful in developing a much more detailed molecular understanding of the phenomena and resolve inconsistencies between the various experimental data sets. However, as yet only a few molecular simulation studies have tried to characterize changes in the hydration environment with temperature in some detail. Palmer et al. directly generated synthetic EXAFS spectra for Sr$^{2+}$ in water from molecular dynamics simulations using the rigid extended simple point charge (SPC/E) water model. Although the overall agreement between simulated and experimental spectra was quite reasonable, the simulations failed to reproduce the 0.05 Å decrease in the Sr$^{2+}$–oxygen distance that has consistently been reported in various experimental studies. On the other hand, a simulation of NaCl in the rigid simple point charge water model [SPC (Ref. 27)] showed an approximately 0.03 Å decrease in the Na$^{+}$–oxygen distance from ambient to near critical conditions. These contrasting results suggest that the failure or success in simulating the experimentally observed features may strongly depend on the molecular interaction potentials. The most likely sources are the ion–water intermolecular potential, intramolecular flexibility (or lack thereof), and polarizability.

In order to test at least some of these possible causes, we carried out a set of simulations of SrCl$_2$ in water using both rigid and flexible SPC/E water models as well as the flexible Bopp–Jancso–Heinzinger [BJH (Ref. 30)] water model. In the following we will briefly describe the simulation methods (the details of the potential models are described in the Appendix), and then report in detail the structural results obtained with the various water models. We will finally discuss the performance of the different models, as well as the bearings of our results on the interpretation of experimental results.

II. METHODS

Simulations with the rigid SPC water model were carried out in the NVT ensemble (constant particle number, volume, and temperature). The ion–water and ion–ion interactions were taken from Palmer et al. We did not modify the latter potentials because the structural differences between the SPC (used here) and SPC/E (used by Palmer et al.) are minor. As trial runs with 250 rigid SPC waters and 2 SrCl$_2$ showed that any temperature-dependent changes in the hydration shell position were less than 0.01 Å, the simulations were then run in a larger system of 26 SrCl$_2$ in 2127 water molecules in order to obtain better statistics in the radial distribution functions and hence possibly resolve very small changes in the hydration shell position. Since Ewald summation turned out to be unreasonably slow for the treatment of long range forces in such a large system, we used the particle–particle, particle–mesh algorithm [P3M (Ref. 31)] for long-range forces. In a similarly large system of water–NaCl, this approach had previously been shown to provide essentially identical results to Ewald summation while improving the simulation speed considerably.

Simulations with the flexible SPC water model were done with the intramolecular modified Toukan–Rahman (SPC-mTR) potential of Liew et al. and the ion–water and ion–ion interactions of Palmer et al. In the simulations with the BJH model, the ion–water and ion–ion interactions of Spoehr et al. were used. In both cases, long-range forces were treated with Ewald summation. All simulations with flexible water models were carried out with 250 water molecules, 2 Sr$^{2+}$ and 4 Cl$^{-}$ ions in a cubic box with periodic boundary conditions in the NVT ensemble and a time step of 0.15 fs. The simulations started from a fcc lattice that was “melted” and equilibrated at the desired temperature for at least 40 ps after the insertion of an appropriate number of ions. In order to collect good $g(r)$ with a high resolution of 0.001–0.005 Å, long simulation runs of 120–300 ps were necessary and carried out on an IBM SP2 parallel machine for the BJH model or using the multiple time step rRESPA algorithm with a short time step of 0.15 fs for the SPC-mTR model on normal workstation computers.

III. RESULTS

A. Rigid SPC water

The structural results from simulations using rigid SPC water essentially agree with those obtained by Palmer et al. for SPC/E. However, in order to better understand the temperature and density dependence of ionic hydration, we did a series of additional simulations along an isochoric path of 1.06 g cm$^{-3}$ at 300–800 K, and another set at two temperatures with densities somewhat higher than at the supposed liquid–vapor curve (see Table I).

Along the isochoric path there is some slight shift (less than 0.01 Å) of the first peak in the $g_{\text{Sr-O}}(r)$ towards a smaller Sr–O distance. The coordination number decreases slightly from 7.7 at ambient conditions, to 7.1 at the critical temperature and to 6.8 at 800 K. The position of the second peak (that is, the second hydration shell) shifts to larger distances, from 4.9 Å at 300 K to 5.17 at 800 K. Along the same path, the first peak in $g_{\text{Cl-O}}(r)$ shifts to larger distances by about 0.05 Å, a behavior that is in good agreement with results obtained by Driesner et al. for the NaCl–SPC system. A significant shift of the first minimum in the $g_{\text{Cl-O}}(r)$ (from 4.06 Å at 300 K to 4.6 Å at 590 K and 4.7 Å at 800 K, Table I) is observed, in good agreement with Balbuena et al., who reported a shift from 4.0 to 4.75 Å for Cl$^{-}$–SPC/E water. Since this minimum is usually taken as the geometric criterion for the definition of the first hydration shell, the “expansion” with increasing temperature results in an apparent increase of the coordination number from 8.4 (300 K) to 12 (590 K) and 13 (800 K). This effect has also been reported for the NaCl–SPC system and makes the di-
remains at 2.65 Å as was reported by Palmer et al. The first peak in $g_{Sr-O}(r)$ along the high-density isochoric path is even stronger than along the high-density isochoric path. Again, this is related to a strong outward shift of the first peak in $g_{Cl-O}(r)$ and is consistent with results found for the NaCl–SPC system. 25

### TABLE I. Characteristic points of various $g(r)$ for all simulation runs, coordination numbers, and intramolecular geometries. max 1=1st maximum in respective $g(r)$, min 1=1st minimum, etc.; positions are in Å, angles in deg. CN=coordination number.

<table>
<thead>
<tr>
<th>Species</th>
<th>300 K</th>
<th>520 K</th>
<th>590 K</th>
<th>800 K</th>
<th>300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.06 g cm$^{-3}$</td>
<td>0.88 g cm$^{-3}$</td>
<td>0.62 g cm$^{-3}$</td>
<td>1.06 g cm$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>2.64</td>
<td>2.61</td>
<td>2.61</td>
<td>2.64</td>
<td>2.64</td>
</tr>
<tr>
<td>SrH</td>
<td>3.33</td>
<td>3.298</td>
<td>3.290</td>
<td>3.32</td>
<td>3.32</td>
</tr>
<tr>
<td>ClO</td>
<td>3.14</td>
<td>3.15</td>
<td>3.2</td>
<td>3.22</td>
<td>3.22</td>
</tr>
<tr>
<td>CIH</td>
<td>4.68</td>
<td>6.0</td>
<td>5.8</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>CN</td>
<td>9.7</td>
<td>10.0</td>
<td>9.3</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>$r_{OH}$ (bulk)</td>
<td>0.9742</td>
<td>0.9754</td>
<td>0.9715</td>
<td>1.019</td>
<td>1.019</td>
</tr>
<tr>
<td>$r_{OH}$ (Cl$^-$)</td>
<td>0.9803</td>
<td>0.9774</td>
<td>0.9787</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$a_{OH}$ (bulk)</td>
<td>100.0</td>
<td>100.04</td>
<td>101.24</td>
<td>105.46</td>
<td>105.85</td>
</tr>
<tr>
<td>$a_{OH}$ (Cl$^-$)</td>
<td>100.4</td>
<td>99.5</td>
<td>99.4</td>
<td>105.42</td>
<td>105.63</td>
</tr>
<tr>
<td>$a_{OH}$ (SrCl$^-$)</td>
<td>99.05</td>
<td>97.1</td>
<td>97.23</td>
<td>104.72</td>
<td>104.73</td>
</tr>
</tbody>
</table>

*Reference 19.

A direct comparison of chloride coordination numbers at different temperatures problematic.

Along the low-density path, the first peak in $g_{Sr-O}(r)$ remains at 2.65 Å as was reported by Palmer et al. for the SrCl$_2$–SPC/E system. The second peak shifts outward by about the same small amount as along the isochoric path. However, the coordination number decreases strongly from 7.7 at 300 K to 5.0 at 590 K. This is the result of the formation of ion clusters in the rather concentrated (0.68 molal) solution (see Table II). For all conditions, the position of the first peak in $g_{Sr-H}(r)$ remains essentially unchanged (3.31 ±0.01 Å). The first peak in $g_{Cl-O}(r)$ shifts outward from 3.22 to 3.32 Å, that is, the expansion of the Cl$^-$ hydration shell is even stronger than along the high-density isochoric path (see Table I and Fig. 1). Also, the Cl$^-$ coordination number increases, but less strongly than along the isochoric path. Again, this is related to a strong outward shift of the first minimum in $g_{Cl-O}(r)$ and is consistent with results found for the NaCl–SPC system. 25

### TABLE II. Strontium chloride speciation in 0.68 molal solution, simulated with rigid SPC water. The species were defined geometrically, that is, ions were considered to be associated when having distances smaller than 4.2 Å [i.e., the first minimum in $g_{SrCl}(r)$].

<table>
<thead>
<tr>
<th>Species</th>
<th>300 K</th>
<th>520 K</th>
<th>590 K</th>
<th>590 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>single ions</td>
<td>68%</td>
<td>36%</td>
<td>24%</td>
<td>49%</td>
</tr>
<tr>
<td>ion pairs (SrCl$^-$)</td>
<td>21%</td>
<td>30%</td>
<td>26%</td>
<td>26%</td>
</tr>
<tr>
<td>triplets (≈SrCl$_2$,aq)</td>
<td>11%</td>
<td>18%</td>
<td>26%</td>
<td>25%</td>
</tr>
<tr>
<td>quadruplets (mainly SrCl$_4$)</td>
<td>...</td>
<td>4%–5%</td>
<td>15%</td>
<td>very rare (0.2%)</td>
</tr>
<tr>
<td>quintuplets (mainly SrCl$_5$)</td>
<td>...</td>
<td>1%–2%</td>
<td>14%</td>
<td>...</td>
</tr>
<tr>
<td>sixduplets and higher</td>
<td>...</td>
<td>...</td>
<td>11%</td>
<td>...</td>
</tr>
</tbody>
</table>

B. Flexible SPC-TR and SPC-mTR

In a first series of simulations we tried the flexible SPC version of Toukan and Rahman, 29 usually called SPC-TR. However, the simulations were numerically unstable at high temperatures. It turned out that this instability was related to the ‘‘dissociation’’ of water molecules in the vicinity of Sr$^{2+}$-ions. The dissociation behavior could be traced back to the improper shape of the intramolecular potential at large O–H displacements that were occasionally induced by the strong ion–water interactions. Therefore, we switched to a modified version of the Toukan–Rahman model (SPC-mTR) as proposed by Liew et al. 28 which led to stable simulations
because the water molecules did not dissociate with this improved potential. Simulations were done at a density of 1.04 g cm$^{-3}$ at 300 and 600 K.

At 300 K, the results for the flexible SPC model are essentially identical and resemble those from the rigid SPC model, that is, a $g_{\text{Sr-O}}(r)$ first peak around 2.64 Å and peak shifts to larger distances in $g_{\text{Cl-O}}(r)$. There is only a small but distinct shift of the first peak in $g_{\text{Sr-O}}(r)$ to 2.63 Å at 600 K (Fig. 2). For the $g_{\text{Sr-H}}(r)$, the position of the first peak remains essentially constant at 3.32 Å (Fig. 3). The high temperature peaks are somewhat broadened and reduced in height, reflecting the enhanced dynamics of the hydration shell waters. The coordination number increases slightly from 7.3 to 7.6 from ambient to supercritical conditions. The absence of a decrease of the coordination number (that was observed for the rigid model) may be related to the somewhat lower SrCl$_2$ concentration at high density and to the smaller system size, preventing the formation of larger clusters. At both conditions the H–O–H angle changes from its gas phase value of 109.47° to about 105° with only little variation between bulk water and water in the Sr$_2^+$ and Cl$^-$ first hydration shells (see Table I and Fig. 4). The average intramolecular O–H bond length in bulk water is stretched to 1.019 Å (at 300 K) and 1.016 Å (at 600 K) compared to the SPC–mTR gas phase equilibrium value of 1.0 Å.

C. BJH water

In contrast to both types of SPC results, the BJH simulations show a significant change in the Sr$_2^+$ hydration shell geometry. When going from 300 to 600 K, the first peak in $g_{\text{Sr-O}}(r)$ shifts towards shorter ion–water distances from 2.64 to 2.61 Å (Fig. 2). This is accompanied by a similar shift in $g_{\text{Sr-H}}(r)$ from 3.34 to 3.29 Å, independent of the solution density (see Table I and Fig. 3). The latter behavior is in strong contrast to that of the SPC water–Sr$_2^+$ systems that exhibit state independent Sr$_2^+$ hydration shell diameters.

The position of 2.64 Å for the first peak in $g_{\text{Sr-O}}(r)$ at ambient conditions compares very well with the EXAFS results of Pfund et al. and Palmer et al. but is somewhat smaller than for the free water molecules in both cases. Notice, however, that the BJH geometry is much more sensitive to the local environment. Sr denotes Sr$_2^+$ first hydration waters, Cl the same for Cl$^-$. 

FIG. 1. First peak of $g_{\text{Cl-O}}(r)$ for rigid SPC water vs BJH water. With increasing temperature, the peak shifts to larger Cl–O distances, i.e., the hydration shell expands.

FIG. 2. First peak of $g_{\text{Sr-O}}(r)$ for BJH and SPC-mTR water. BJH shows a shift to smaller distances by about 0.03 Å with increasing temperature whereas a possible shift for SPC-mTR is within statistical uncertainty.

FIG. 3. First peak of the $g_{\text{Sr-H}}(r)$ for BJH and SPC-mTR water. The peak shifts by 0.05 Å towards shorter distances with increasing temperature in the BJH system but remains stationary for SPC-mTR.

FIG. 4. H–O–H angle in various environments at 600 K and 1.04 g cm$^{-3}$ for BJH and SPC-mTR water. Bulk water values are approximately 4°–5° smaller than for the free water molecules in both cases. Notice, however, that the BJH geometry is much more sensitive to the local environment. Sr denotes Sr$_2^+$ first hydration waters, Cl the same for Cl$^-$. 

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larger than the Sr–O distances obtained by Seward et al. Notice however, that Palmer et al. used molecular dynamics simulations to generate synthetic EXAFS, which showed somewhat smaller Sr–O distances than the real $g_{\text{Sr-O}}(r)$. Their Sr–O distances from the synthetic EXAFS appear to be in much better agreement with the results of Seward et al. rather than those of Pfund et al.

In contrast to the SPC-mTR results, the BJH H–O–H angle shows a strong dependence on temperature and local environment. At 300 K, the H–O–H angle in bulk water and in the Cl–hydration shell are almost identical but are different by almost 2° at the 600 K, low-density run. The strontium ion hydration water H–O–H angle is always the smallest, that is, 1.3° (at 300 K) to 4° (at 600 K) smaller than the bulk water value. While the bulk water H–O–H angle increases with increasing temperature, it decreases in the hydration shells of both types of ions. At 600 K, the H–O–H angle in bulk water is density dependent while the H–O–H angles in the hydration shells of both types of ions remain constant. All intramolecular O–H bond lengths are stretched by 0.014–0.03 Å compared to the free BJH water molecule. The smallest stretch is always for the bulk water molecules, the biggest primarily for the strontium ion hydration shell waters, except at ambient conditions. The BJH simulations predict similar outward shifts in the $g_{\text{Cl-O}}(r)$ as the SPC models (Figs. 1 and 5).

**IV. DISCUSSION**

**A. Sr\(^{2+}\) hydration**

Assuming that the interpretation of the experimental EXAFS data are correct (in that there is a decrease of the average Sr–O distance in the first hydration shell by about 0.05 Å), then the BJH model clearly captures this effect best. Intuitively, one would expect this to be the result of molecular flexibility, allowing the molecule to relax its geometry as a response to the field of the ion. However, when adding flexibility to the SPC model, improvements over the rigid model are very small. Thus, it seems that molecular flexibility by itself is not the key parameter. Besides the different partial charges and molecular geometries, the main difference between the two sets of potentials is the kind of interactions involving the hydrogens which is purely electrostatic for the SPC-type models but has an additional non-Coulombic term in the BJH potentials. At this stage, we see no possibility to unequivocally decide which of the differences between the potentials is responsible for the better performance of the BJH model.

However, in order to gain some insight, we calculated the potential energy of a system of one Sr\(^{2+}\) ion and one water molecule in a $C_{2v}$ geometry as a function of the Sr–O distance. At each Sr–O distance the minimum potential energy was found by relaxing the water geometry. The resulting potential energy curves are shown in Fig. 6. There clearly is some difference with respect to both the curve shape and the position of the minimum and, most important, the BJH Sr–O system exhibits a somewhat flatter potential energy surface (inset in Fig. 6). In a combined effect of enhanced kinetic energy at high temperatures and a reduction of the influence of first shell–second shell interactions [as seen in the outward shift of the second maximum of the $g_{\text{Sr-O}}(r)$], this feature in the potential energy surface would allow BJH water molecules to approach the ion more closely than any type of SPC water.

This demonstrates that in order to model and understand the intricacies of ionic hydration in detail, care has to be taken in the choice of the intra- and intermolecular potential models. Apparently, the various SPC models fail in this respect while the BJH potentials, which were fitted to $ab\ ini\ tuo$ and spectroscopic data, do a much better job. The addition of polarizability to the water model (e.g., as in the Chialvo and Cummings models) will possibly improve the results. However, the sensitivity of the BJH intramolecular geometry to the local environment indicates that polarizability alone will probably not be appropriate. Advanced models that include both flexibility and polarizability to some degree [e.g.,
likely that there are some problems in either the experiment or the data treatment in the study by Fulton et al.\textsuperscript{3} Notice also that their data set is also the only one predicting a hydration shell expansion for a cation (Ni\textsuperscript{2+}).

The rather large changes in the anion hydration process have also consequences for the interpretation and comparison of experimental data, in particular from neutron diffraction or EXAFS studies. Neutron diffraction experimentalists have repeatedly emphasized that the coordination number of the chloride ion is difficult to define appropriately.\textsuperscript{10,12,14} It depends on which \(g(r)\) is integrated and to what distance. In addition, it may be biased by bulk water molecules partly entering the first shell. Driesner et al.\textsuperscript{25} could not characterize this latter effect in detail because of the very dynamic nature of the chloride ion hydration shell. They determined the average residence time of a water molecule in the chloride ion first hydration shell at ambient conditions to be 11 ps, which—when combined with a coordination number of around 7–8—indicates one exchange event with bulk water every 1.5 ps. With residence times down to about 2 ps at near critical conditions, a static characterization of the hydration shell seems even less appropriate. Nevertheless, when examining the current results in detail, some important conclusions that also pertain to the interpretation of experimental data, can be drawn.

This can be seen, for example, in the interpretation of Cl\textsuperscript{−} hydration data by de Jong et al.\textsuperscript{10} The authors found a slight expansion of the hydration shell from 2.30\(\pm\)0.03 Å at 100 °C to 2.39\(\pm\)0.04 Å at 300 °C, which is consistent with the present simulation results. For the determination of the

### TABLE III. Coordination numbers (CN) for the Cl\textsuperscript{−} ion at various characteristic points of the respective \(g(r)\).

<table>
<thead>
<tr>
<th>Water model</th>
<th>(T) (K)</th>
<th>(r) (Å)</th>
<th>(CN_{\text{hydrogen}})</th>
<th>(CN_{\text{oxygen}})</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>BJH</td>
<td>300</td>
<td>2.9</td>
<td>6.4</td>
<td>0.1</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>16</td>
<td>7.3</td>
<td>0.2</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>19</td>
<td>8.2</td>
<td>0.3</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>2.9</td>
<td>6.2</td>
<td>0.3</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>15.9</td>
<td>7.3</td>
<td>0.4</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>26.8</td>
<td>12.5</td>
<td>0.5</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>23</td>
<td>10.6</td>
<td>0.6</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td>SPCnTR</td>
<td>300</td>
<td>3.0</td>
<td>5.9</td>
<td>0.1</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>13</td>
<td>6.6</td>
<td>0.2</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>18.6</td>
<td>8.8</td>
<td>0.3</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>2.9</td>
<td>5.6</td>
<td>0.1</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>14</td>
<td>7</td>
<td>0.2</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
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<td>4.7</td>
<td>27</td>
<td>13</td>
<td>0.3</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>22</td>
<td>11</td>
<td>0.4</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
<td>SPC</td>
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<td>0.1</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
<tr>
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<td>8.4</td>
<td>0.2</td>
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<td>0.3</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
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<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
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<td>ambient</td>
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<td>6.4(\pm)0.3</td>
<td>0.1(\pm)0.4</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
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<td>3.1</td>
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<td>0.2(\pm)0.4</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
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<td>573\textsuperscript{b}</td>
<td>2.8</td>
<td>4.9(\pm)0.5</td>
<td>0.1(\pm)0.5</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
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<td>648\textsuperscript{c}</td>
<td>2.8?</td>
<td>2.5(\pm)0.2</td>
<td>0.1(\pm)0.2</td>
<td>(g_{\text{Cl}-\text{Br}}(r)) ambient</td>
</tr>
</tbody>
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\textsuperscript{a}Reference\textsuperscript{34}.
\textsuperscript{b}Reference\textsuperscript{10}.
\textsuperscript{c}Reference\textsuperscript{14}.

RWK2 (Refs. 37–39) may be good candidates. Fitting of both water–water and ion–water intermolecular potentials to \textit{ab initio}-derived potential energy surfaces may turn out to be superior to fitting to thermodynamic and/or diffraction data. Since all models studied here qualitatively predict a trend towards shorter cation–water distances, the interpretation of the EXAFS data in terms of a contracting hydration shell appears to be at least qualitatively correct.

#### B. Cl\textsuperscript{−} hydration

In contrast to cation hydration, all models predict an expansion of the Cl\textsuperscript{−} hydration shell with increasing temperature. Such shifts have recently been reported from EXAFS studies of I\textsuperscript{−} hydration\textsuperscript{7} and comparable shifts for Cl\textsuperscript{−} have been found in neutron diffraction experiments.\textsuperscript{10,11,14} Additional evidence comes from redshifts in charge-transfer-to-the-solvent spectra such as those measured for HS\textsuperscript{−} (Ref. 21) and Cl\textsuperscript{−}.\textsuperscript{22} It therefore appears that the anion hydration shell expansion as predicted by the current simulations is not a simulation artifact. Also, the successful simulation of this feature appears to be largely model-independent.

In contrast, Fulton et al.\textsuperscript{3} reported a contraction of the Br\textsuperscript{−} hydration shell with increasing temperature in their EXAFS experiments. There is no \textit{a priori} reason why Br\textsuperscript{−} should behave differently from Cl\textsuperscript{−} or I\textsuperscript{−}. If one considers the variety of methods (EXAFS, UV-VIS, MD) that provide evidence for an anion hydration shell expansion, it seems likely that there are some problems in either the experiment...
coordination number, they used the total distribution function $G_{\text{Cl}}(r)$ that has a rather constant first minimum at around 2.8 Å, which is approximately coincident with the first minimum in $g_{\text{Cl-H}}(r)$. When 2.8 Å was used for the definition of the hydration shell, a decrease in the coordination number from 6.9±0.5 (100 °C) to 4.9±0.5 (300 °C) was found. Powell et al.,40 who got accurate $g_{\text{ClO}}(r)$ and $g_{\text{ClO}}(r)$ by NDIS on the second difference level, reported 6.4±0.3 at ambient conditions (in very good agreement with the present simulation results, Table III). In order to demonstrate the importance of the exact criterion of the definition of the hydration shell on the determination of coordination numbers, we calculated the coordination number at various characteristic points of the $g_{\text{Cl-H}}(r)$ and $g_{\text{Cl-O}}(r)$. These are compiled in Table III. When we take the first, largely temperature-independent minimum in $g_{\text{Cl-H}}(r)$, then the results of all models are quantitatively comparable to the neutron diffraction results, that is, they predict a similar decrease in the coordination number. The higher concentrations in the experiments explain the larger coordination number decrease compared to most simulations. This is implied by the simulation results with rigid SPC water, in which a higher concentration was used and a larger coordination number decrease occurred. However, when the first minimum in $g_{\text{Cl-O}}(r)$ is used, there is no decrease in the coordination number. Instead the apparent coordination number increases, in particular, when the first minimum in $g_{\text{Cl-O}}(r)$ at the temperature of interest is used. It also increases in most cases when the second minimum in the $g_{\text{Cl-H}}(r)$ is used. The penetration of second shell waters into the geometrically defined first hydration shell is indicated by the fact that at the position of the second minimum of $g_{\text{Cl-H}}(r)$ the oxygen-based coordination number is usually smaller than the hydrogen-based coordination number. Similar, but less drastic trends were also found by Balbuena et al.24

This has important consequences for our understanding of hydration as a function of temperature. Clearly, one would expect that a definition of “coordination shell” comprises the nearest neighbor water molecules of the ion rather than solely the nearest neighbor hydrogen atoms. Ideally, the position of the molecule would be defined by the center of mass, which can very well be approximated by the oxygen position in the water molecule. Hence, the more intuitive choice of the first minimum in $g_{\text{Cl-O}}(r)$ (ambient or at temperature of interest) will predict an increase in the number of nearest neighbors rather than a decrease as inferred from the $g_{\text{Cl-H}}$ first minimum. Since a decrease or increase of the coordination thus solely depends on the definitions used, care has to be taken when reporting and interpreting both experimental and simulation results. The exact criteria for determining coordination numbers have to be given with the reported numbers and conclusions that hydration becomes “weaker” or “stronger” require an exact definition of these terms.

The apparent paradox of simultaneously decreasing and increasing coordination numbers is very likely to be the result of the increased dynamics of hydration water molecules. The decreasing number of nearest neighbor hydrogens is readily explained by increased dynamics since orientational disorder can be expected to increase (see, for example, the discussion by Balbuena et al.24 on the strength of the Cl–water interactions) while there is enough space for water molecules in different orientations to let the number of nearest neighbor molecules increase. In addition, the large outward shifts of the first minimum and second hydration shell peak in $g_{\text{Cl-O}}(r)$ (Fig. 5) can be interpreted as a change in the hydrogen bonding style and dynamics similar to that in pure water as described by Guissani and Guillot.41 In fact, the $g_{\text{Cl-H}}(r)$ is essentially structureless beyond the first hydration shell while $g_{\text{Cl-O}}(r)$ still exhibits some structure. First shell hydration water molecules will be less confined by bulk water than they are at ambient conditions. It should be emphasized that in the discussion of their neutron diffraction results, Yamaguchi et al.14 already addressed some of these issues correctly but their statement that “calculated Cl–H radial distribution functions overestimate the hydrogen bonding between the chloride ion and water” appears to be questionable in the light of the present results. The simulations do very well in predicting the $g_{\text{Cl-H}}(r)$-based coordination number and, hence, probably the simulated $g_{\text{Cl-O}}(r)$-based coordination numbers are correct as well. It seems likely that reanalyzing the neutron diffraction results in terms of the present results may indicate that the “dehydration” of the chloride ion inferred from the $g_{\text{Cl-H}}(r)$ based interpretation may simply be nonexistent. Notice however, that the very high concentrations used in the experiments may have promoted ion clustering, which would force water molecules out of the hydration shell. This, however, would only indirectly be a temperature effect and rather be a concentration effect. At high temperatures, the hydration shell geometry and coordination number of the chloride ion depends on density and concentration (see Table I and Driesner et al.25). Generalization from data at only one concentration and density should be avoided.

V. CONCLUSIONS

Our simulation results provide clear evidence that the contractions of cation hydration shells (that have been inferred from EXAFS experiments) and expansions of anion hydration shells (inferred from EXAFS, NDIS, and other methods) with increasing temperature are real. The quantitative simulation of the cation hydration shell using classical molecular dynamics simulations is sensitive to the chosen interaction potentials while the anion hydration shell expansion is rather model-insensitive. Both experimental and simulated chloride–water distances and coordination numbers are in essentially quantitative agreement as long as the same criteria are used in the determination of these properties. The simulation results clearly demonstrate that the use of only one of these criteria can lead to a highly incomplete and misleading characterization of hydration, at least for the chloride anion.

The great challenge in the future will be to link these local, molecular scale observations to solution thermodynamics. Coordination numbers and hydration shell geometries are the primary features available from experiments, and small variations in hydration shell geometries and stoichiometries as reported here can have significant influence...
on the success or failure of empirical or semiempirical formulations of equations of states. This can, for example, be seen in the revision of the HKF model.²² The interplay between simulation and experiment will be essential for the improvement or re-engineering of such equations. A first step to link molecular scale observations to thermodynamics has been done by Chialvo and Cummings, who developed a strict solvation formalism.⁴³,⁴⁴,¹⁵,⁴⁵ Unfortunately, coordination numbers are not part of the solvation formalism (but solvation numbers are, see Chialvo et al.,¹⁵ for a definition of coordination vs solvation number). Also, the solvation formalism is currently only available for infinitely dilute solutions while experiments are carried out at finite, sometimes very high, concentrations. To extend the theoretical approaches to accessible variables in such “real world” systems will be a challenge that very likely will require a close interplay between simulation and experiment.

ACKNOWLEDGMENTS

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APPENDIX: POTENTIAL PARAMETERS

1. SPC water simulations

The non-Coulombic intermolecular potential is of the form¹⁹,²⁷

\[ U_{\text{pot}} = \left( \frac{c_{12}}{r} \right)^{12} - \left( \frac{c_{6}}{r} \right)^{6}, \]

with the potential parameters¹⁹

\[ c_{12} = \left( \text{kJ/Å}^{12} \right) = 3.428 \text{ (O–O)}, 0.00 \text{ (O–H)}, 0.00 \text{ (H–H)}, \]

\[ c_{6} = \left( \text{kJ/Å}^{6} \right) = 4.3437 \text{ (Sr–Sr)}, 4.0267 \text{ (Sr–Cl)}, 4.5940 \text{ (Cl–Cl)}; \]

For the Coulombic part, the partial charges for the O and H sites are \( q_{O} = -0.82e \) and \( q_{H} = 0.41e \), respectively. The intramolecular O–H distance is 1.0 Å, the H–O–H angle is 109.47°. In the flexible SPC-mTR water model, the intramolecular potential is described by²⁸

\[ U_{\text{intra}} = U_{\text{OH}} + U_{\text{HOH}}. \]

2. BJH water simulations

The intramolecular part of the BJH water potential³⁰ can be written as

\[ U_{\text{intra}} = \sum_{i=1}^{18} a_i \rho_i^b \rho_i^c (\Delta \alpha)^d, \]

with \( \rho_1 = (r_{\text{OH1}} - r_{\text{eq}})/r_{\text{OH1}}, \) and \( \rho_2 = (r_{\text{OH2}} - r_{\text{eq}})/r_{\text{OH2}}, \)

where \( r_{\text{OH1}} \) and \( r_{\text{OH2}} \) denote the instantaneous O–H distances for the two hydrogens, and \( r_{\text{eq}} \) denotes the equilibrium O–H distance of 0.9572 Å. \( \Delta \alpha = \alpha - \alpha_{\text{eq}} \) is the deviation of the instantaneous H–O–H angle \( \alpha \) (in rad) from the equilibrium value \( \alpha_{\text{eq}} = 1.3424 \) (i.e., 104.52°). The values of the potential constants are given in Table IV.

It must be emphasized that the non-Coulombic part of the intermolecular water–water potential has been reported differently in different publications,²⁰,⁴⁶,⁴⁷ apparently in most cases as a result of typographical errors. For the present study, we implemented the potential according to the original computer code by P. Bopp. With \( U_{ij} \) in kJ mol⁻¹ and \( r \) in Å, the non-Coulombic formulations are

\[ U_{ij} = \begin{cases} 
111904.7 - 1.045443e^{-4(r - 3.4)^2} & \text{for } r > 3.91 \\
-1.045443e^{-1.5(r - 4.5)^2} & \text{for } r < 3.91 
\end{cases}. \]
The Coulombic interactions were computed with partial charges of 0.33\(e\) for the hydrogen sites and \(-0.66e\) for the oxygen sites.

The ion–water and ion–ion interactions are as follows (units as for the water–water potential):

\[
U_{\text{SO}} = \frac{-1191.781}{r^2} + 176388.4 \, e^{-3.11r},
\]

\[
U_{\text{SH}} = \frac{352.295}{r^2} + 14.45313 \, e^{-0.158r},
\]

\[
U_{\text{ClO}} = \frac{-111.3493}{r^2} + 379635.5 \, e^{-3.209r},
\]

\[
U_{\text{CH}} = \frac{1.889746 \times 10^{26}}{r^6} \, e^{-34.0r},
\]

\[
U_{\text{SrO}} = \frac{-60.1611456}{r^6} + 26.7202 \, e^{-0.617r},
\]

\[
U_{\text{SrCl}} = \frac{-1370.04}{r^6} + 80937.5 \, e^{-2.14r},
\]

\[
U_{\text{ClCl}} = \frac{28671.393}{r^6} + 91.717142 \, e^{-3.39r}.
\]

17. K. P. Johnston and P. J. Rossky, in NATO Advanced Study Institute on Supercritical Fluids, July 12–24, edited by E. Kiran (Kemer, Antalya, Turkey, 1999) (to be published).