A Molecular Dynamics Study of the Structure of an Aqueous KCl Solution

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A molecular dynamics simulation of a 2.2 molal aqueous KCl solution has been performed using the ST2 water model. The simulation extended over 5 ps at an average temperature of 288 K. The basic box has a sidelength of 18.74 Å and contained 200 water molecules, 8 cations and 8 anions. The structure of the solution is discussed by radial distribution functions, the orientation of the water molecules, and their geometrical arrangement in the first hydration shells. The first shells of K+ and Cl− extend up to 3.52 and 3.84 Å, respectively, with the corresponding hydration numbers 7.8 and 7.6. The results are compared with recent neutron and X-ray diffraction data and with findings of previous MC and MD simulations using various water-water potentials.

Introduction

The hydration of ions may determine the dynamical properties of aqueous electrolyte solutions and, in particular, it may affect the transport characteristics of the ions [1] and the ionic permeability through organized structures (e.g., biological membranes) [2]. This makes the study of ionic hydration a topic of considerable scientific interest.

In the last few years, results of several computer simulations of aqueous solutions of electrolytes have been published, particularly alkali or halide ions, using various water models. The simulations have been concerned with concentrated solutions [3–9] and with a single ion surrounded by 64, 125 or 216 water molecules [10–13]. Generally, a satisfactory agreement with experimental data has been found. Furthermore, simulations have proved to be capable of predicting properties which are not directly accessible by experiments [14].

In this paper, results of a molecular dynamics simulation of a 2.2 molal aqueous solution of KCl are reported. Very recently published neutron diffraction data on aqueous solutions of KCl [15] allow a detailed comparison of the present simulation results with experimental findings on the hydration shell of K+. Hydration features of Cl− are also compared with a rather large amount of experimental data that are available for the chloride ion [16].

Computational Details

The calculations were performed on a CRAY-XMP/12 computer. The simulation technique is the same as previously described [4]. The basic cube with a sidelength of 18.74 Å contained 200 water molecules, 8 potassium and 8 chloride ions; the experimental density of the 2.2 molal KCl solution is 1.06 g/cm3. The ST2 model [17] was assumed for the water-water interaction. The ion-ion potentials are based on the model of (12; 6) LJ spheres with a unit elementary charge in the center. The cation-cation LJ parameters are taken from the isoelectronic noble gas, and for anion-anion interaction they are calculated, as previously described [3], from the noble gas values with the help of Pauling radii. Cation-anion and anion-water LJ parameters

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were determined by applying Kong's combination rules [18]. The LJ parameters used are given in Table 1. The integration time-step was $2.18 \times 10^{-16}$ s and the simulation extended over $2 \times 10^4$ time-steps, equivalent to a total elapsed time of 5 ps. The fluctuations of the total energy $\Delta E/E$ over the run was smaller than $3 \times 10^{-5}$. The average value of the temperature was 288 K without rescaling. There was no systematic trend in the temperature.

**Results and Discussion**

**a) Radial Distribution Functions**

The ion-oxygen, $g_{\text{K-O}}(r)$, and ion-hydrogen, $g_{\text{K-H}}(r)$, radial distribution functions (RDF) for K$^+$ and Cl$^-$ are shown in Fig. 1 together with the corresponding running integration numbers, which are given by

$$n_{xy}(r) = 4\pi q \int_0^r g_{xy}(r') r'^2 \, dr',$$

where $q$ is the number density of the water molecules. Some characteristic values are reported in Table 2. The hydration number is defined as $n(r)$ at the first minimum of the ion-oxygen radial distribution function.

As one can see from Fig. 1, the first hydration shells of both K$^+$ and Cl$^-$ are not as well defined as for smaller monovalent ions such as Li$^+$ and F$^-$ [5, 7, 11, 12], but they are significantly more pronounced than for the larger Cs$^+$ and I$^-$ [5, 7].

The position of the first peaks in $g_{\text{K-O}}(r)$ and $g_{\text{K-H}}(r)$ and the hydration number of K$^+$ are compared in Table 3 with the corresponding data from other simulations and from experiments. In spite of the use of different water models there is good agreement between the various simulations, except for the MC calculation which leads to somewhat smaller numbers. Very good agreement exists for the X-ray data, where of course the K$^+$-H distance cannot be derived from the experiment [20]. Unfortunately the measurements of a 4 molal KCl solution by neutron diffraction measurements with isotopic substitution (NDIS) have not led to unambiguous data as far as the hydration shell of K$^+$ is concerned [15].

For the comparison with the NDIS data the neutron weighted K$^+$-water RDF from the simulation rescaled for a concentration of 4 molal is shown in Fig. 2 as full line together with the experimental data reproduced from [15]. The dotted and dashed lines result from Fourier transforms of the differ-

| **Table 1**. (12; 6) Lennard-Jones parameters used in the simulation of the aqueous KCl solution. $\sigma$ (first row) is given in Å and $\varepsilon$ (second row) is expressed in units of $10^{-16}$ erg. |
| --- | --- | --- |
| **K$^+$** | **Cl$^-$** | **H$_2$O** |
| K$^+$ | 3.36 | 4.08 | 3.25 |
| | 186.0 | 67.7 | 94.32 |
| Cl$^-$ | 4.86 | 4.02 | |
| | 27.87 | | |
| H$_2$O | 3.1 | 52.61 |

| **Table 2**. Characteristic values of the radial distribution functions $g_{xy}(r)$ for the 2.2 molal KCl solution. $r_{M1}$, $r_{m1}$ and $r_{M2}$ are the positions, in Å, of the first maximum, the first minimum and second maximum of $g_{xy}(r)$, respectively. The binning is 0.04 Å. |
| --- | --- | --- | --- | --- | --- |
| *xy* | $r_{M1}$ | $g_{xy}(r_{M1})$ | $r_{m1}$ | $g_{xy}(r_{m1})$ | $r_{M2}$ | $g_{xy}(r_{M2})$ | $n_{xy}(r_{m1})$ |
| KO | 2.80 | 5.9 | 3.52 | 0.3 | 4.6 | 1.5 | 7.8 |
| KH | 3.32 | 3.2 | 4.32 | 0.7 | 5.4 | 1.2 | 23.4 |
| ClO | 3.16 | 3.6 | 3.84 | 0.6 | 4.8 | 1.3 | 7.6 |
| ClH | 2.20 | 3.1 | 3.04 | 0.4 | 3.6 | 1.5 | 7.3 |

| **Table 3**. Comparison of the ion-oxygen and ion-hydrogen most frequent first neighbor distances and hydration numbers from the simulation of the 2.2 molal KCl solution with results from various other computer simulations and experiments. |
| --- | --- | --- | --- | --- | --- |
| K$^+$—O | K$^+$—H | $n$(K$^+$) | Cl$^-$—O | Cl$^-$—H | $n$(Cl$^-$) | Method | Ref. |
| 2.80 | 3.32 | 7.8 | 3.16 | 2.20 | 7.6 | MD | this work |
| 2.76 | 3.35 | 7.5 | 3.29 | 2.35 | 7.2 | MD | [12] |
| 2.86 | 3.32 | 7.6 | 3.23 | 2.29 | 5.9 | MD | [13] |
| 2.80 | 3.32 | 8.1 | 3.14 | 2.26 | 5.7 | NDIS | [19] |
| 2.80 | 3.32 | | | | 6 | X-ray | [20] |

*a* Data from measurements of NaCl and RbCl solutions.
The Structure of an Aqueous KCl Solution

Fig. 2. Neutron weighted K⁺-water radial distribution function in barn from the simulation of the 2.2 molal KCl solution (rescaled for 4 molal; full) and from a neutron diffraction measurement with isotopic substitution (dots, dashed).

Fig. 3. Difference structure functions for a 4 molal KCl solution from neutron diffraction measurements with potassium isotope substitution (dots) and rescaled results from the simulation of a 2.2 molal KCl solution (full).
ence structure function point by point and after
smoothing, respectively. Obviously there is a strong
discrepancy between the simulation and the NDIS
measurement. In the case where the $K^+ - O$ and
$K^+ - H$ contributions are resolved in the experi­
mental curve (dotted line) both peaks are shifted to
smaller distances by about 0.25 Å relative to the
simulation, which is in good agreement with the X­
ray measurements as far as the $K^+ - O$ distance
(first peak) is concerned (Table 3). In the un­
resolved curve (dashed line) the maximum is
positioned at 3.1 Å between the two peaks resulting
from the simulation.

In order to check the reason for this discrepancy
the difference structure functions for the 4 molal
solution from the NDIS experiment and the simula­
tion are compared in Fig. 3, where the simulation
data are again rescaled. The difference which exists
in the amplitude of the first minimum and the first
maximum cannot be responsible for the difference
in $g_K(r)$ shown in Figure 2. Obviously, the problem
arises from the difficulty to draw a smoothed line
through the experimental points at higher $k$-values.
As this difficulty arises already for a 4 molal
solution it is easy to imagine the problem at lower
concentrations. This example demonstrates again
that the analysis of scattering data can be significant­
ly improved by computer simulations as has been
shown before in the case of an aqueous NaCl
solution [3] and liquid chloroform [21].

In Fig. 4 the neutron weighted $Cl^-$-water RDF is
drawn and in Table 3 the positions of the first peaks in $g_{ClO}(r)$ and $g_{ClH}(r)$ are compared with results from other simulations and from experiments.
Experimental NDIS data for $Cl^-$-water from a KCl
solution are not available, therefore the numbers
given in the table are taken from measurements of a
5.32 molal NaCl and a 4.36 molal RbCl solution
[19]. All $Cl^-$-O and $Cl^-$-H distances agree reason­
able well while quite some differences exist for the
hydration numbers. These discrepancies might be a
consequence of the rather shallow first minimum in
$g_{ClO}(r)$ which indicates that the end of the first
hydration shell of $Cl^-$ is not well defined.

Comparing Fig. 4 with $g_C(r)$ from NDIS
measurements of the 5.32 molal NaCl solution
(Fig. 3 of [19]) one finds that the peak positions
are in good agreement as expected from Table 3
while the relative peak heights differ. Here the first
peak ($Cl^-$-H) is almost twice as high as the second
peak ($Cl^-$-O) while both peaks are of similar height
for the NaCl solution. Of course, the curves could
be rescaled for concentration, but the changes of the
$g(r)$ with concentration and counterions are not
known [22]. Therefore, part of the difference in the
relative peak heights may be attributed to the
different size of the counterions, where the larger
$K^+$ is expected to disturb the water structure less
than the $Na^+$, thus allowing the formation of a more
pronounced first hydration shell around $Cl^-$. It
should be mentioned here that the MD simulations
show generally a dependence of $g_{ClO}(r)$ and $g_{ClH}(r)$
on the counterions, while it has been concluded
from the NDIS measurements that the hydration
shell of $Cl^-$ is not influenced by changes in con­
centration and counterions [19]. This discrepancy
may have to be attributed to accuracy problems
connected with the difficulty of this kind of mea­
surements.

The ion-ion RDFs are shown in Figure 5. The
curves were drawn with the same binning as in
Fig. 1, thus allowing a judgement on the relative
statistical uncertainty. The noise results from the
small number of ions in the basic cell. No signifi­
cant structure seems to be present in $g_{CC}(r)$ and
$g_{KK}(r)$. Experimentally, the ion-ion RDFs can be
determined from neutron diffraction measurements
by the second order difference method. $g_{ClCl}(r)$ has
been reported from measurements of 4.35 molal NiCl$_2$ and 14.9 molal LiCl solutions [19]. Although a direct comparison with the results of this simulation is not justified because of the different concentrations and counterions, there is a striking difference between simulation and experiment. The surprisingly sharp peaks in the experimental $g_{\text{ClCl}}(r)$ are rather unexpected for an aqueous electrolyte solution [19, 23].

The $g_{\text{KCl}}(r)$ RDF, although noisy, exhibits some structure and a large peak seems to be present around 6 Å. This result would exclude ion pairing between K$^+$ and Cl$^-$, and it suggests that a certain number of ions are separated by just one water molecule.

Finally, in Fig. 6 the X-ray weighted total structure function calculated from this simulation is compared with the results of an X-ray measurement on a 2 molal KCl solution [20]. The simulation does not reproduce the first double peak. This is a shortcoming of the ST2 model for water and has to do with the long range water-water interaction as has been demonstrated before [24]. Otherwise there is very good agreement between simulation and experiment, which again confirms the reliability of the RDFs calculated from the simulation.
b) Hydration Shell Structures

The ensemble and time averaged geometrical arrangement of the water molecules in the hydration shells of ions can be calculated from the simulation by introducing a cartesian coordinate system with the ion in the origin, one oxygen atom of the hydration shell water molecules in the \(z\)-axis and a second one in the \(xz\)-plane with \(y > 0\). The oxygen atom positions of the eight nearest neighbor water molecules around \(K^+\) and \(Cl^-\) in this ion-centered coordinate system have been collected at 300 different times spread over the whole simulation run and projected onto the \(xy\)-plane. In Fig. 7 the projections for the half plane \(x > 0\), which are not characteristic for the hydration shell of the ions but rather connected with the fixation of the two oxygen atoms [25], have been replaced by the reflected image of those for the projections for the half plane \(x < 0\). Evidently the hydration shells of \(K^+\) and \(Cl^-\) show no traces of a polygonal structure. \(K^+\) and \(Cl^-\) differ only in respect to the ion-water first neighbor distances. The same result has been found for \(Cl^-\) before while the picture for \(K^+\) fits nicely into the alkali ion series [26].

c) Orientation of the Water Molecules

The orientation of a water molecule in respect to an ion can be described by the cosine of the angle \(\theta\) between the water dipole moment and the vector pointing from the oxygen to the ion. Information relevant to this orientation is summarized in Figs. 8 and 9. The average dipole moment direction of
water molecules, \( \langle \cos \theta \rangle \), vs. the distance of the water oxygen atom is shown in Figure 8. For \( \text{Cl}^- \) \( \langle \cos \theta(r) \rangle \) decreases over the first hydration shell of \( g_{\text{ClO}}(r) \) from the initial value 0.61 to 0.45. As for \( \text{NaCl} \) and \( \text{MgCl}_2 \) [6], one can see here too that in the vicinity of a halide ion a linear hydrogen bonding to water molecules is preferred, in agreement with experimental indications [19, 22]. The initial plateau is, however, shorter than for \( \text{F}^- \). For \( \text{K}^+ \), the \( \langle \cos \theta(r) \rangle \) increases over the first peak of \( g_{\text{KO}}(r) \) from \(-0.66\) to \(-0.50\). This behaviour is slower than for \( \text{Cs}^+ \).

Further, a second region of preferential water orientation is evident, which corresponds to the second peak of \( g_{\text{KO}}(r) \).

The distributions of \( \cos \theta \) over the first hydration shell of the ions are drawn in Figure 9. For \( \text{Cl}^- \) the \( \cos \theta \) distribution shows a peak at \( \cos \theta = 0.6 \) corresponding to a preferentially linear hydrogen bonding as pointed out above. The distribution is, however, more widely spread than for \( \text{F}^- \), and for a significant fraction of water molecules \( \cos \theta \) is negative.

For \( \text{K}^+ \) the \( \cos \theta \) distribution shows a peak at \( \cos \theta = -0.7 \), which corresponds to the orientation of water lone pair toward the cation. This result is consistent with previous MD simulations of alkali solutions using ST2 [7], MCY [12] and TIPS4P [13] water models.

d) Pair Interaction Energy Distribution

The distributions of the potential energies for the water molecules with respect to a central ion, as drawn in Figure 10, reflect the more or less pronounced first hydration shells of \( \text{K}^+ \) and \( \text{Cl}^- \), respectively, with relative maxima at \(-1.15 \times 10^{-12} \) erg for \( \text{K}^+ \) and \(-0.89 \times 10^{-12} \) erg for \( \text{Cl}^- \). The general features of the peaks corresponding to the first shells, which become smaller and broader with increasing ion size, are consistent with results of previous simulations of alkali halide solutions. In particular, the \( \text{K}^+ \) peak has a position and width intermediate between the analogous values for \( \text{Na}^+ \) and for \( \text{Cs}^+ \) ions [3, 7]. The same conclusion can be drawn comparing the \( \text{Cl}^- \) case with the \( \text{F}^- \) and \( \text{I}^- \) cases [3, 7].

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Fig. 9. Distribution of $\cos \theta$ in the first hydration shells of $K^+$ and $Cl^-$ for a 2.2 molal KCl solution. The distributions are normalized and given in arbitrary units.

Fig. 10. Pair interaction energy distribution for $K^+$-water (full line) and $Cl^-$-water (dashed line) in a 2.2 molal KCl solution. $P(V_{ionw})$ is given in arbitrary units.
