A Molecular Dynamics Study of the Structure of an LiCl · 3 H_2O Solution

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The structure of an 18.5 molal aqueous LiCl solution has been investigated by MD simulation. The total radial distribution function from the simulation agrees reasonably well with that of an X-ray diffraction measurement. In the average each Li^+ is in contact with one Cl^-. Additionally, there are four water molecules in the first coordination sphere of Li^+ which occupy preferentially octahedral positions. The hydration shell of Cl^- is strongly disturbed by the formation of the contact ion pair. There is an almost complete breakdown of the water structure although the number of nearest neighbours is still four at the normal O–O distance in water. For the Cl^-–Cl^- radial distribution a strong discrepancy exists between a neutron diffraction study with chloride isotope substitution and the simulation. All results are compared in detail with recently published data from a simulation of a 13.9 molal LiCl solution.

I. Introduction

In the line of studies of the structure of highly concentrated electrolyte solutions, where less water molecules are available than needed to satisfy the hydration requirements of neither cations nor anions, recently the results of an MDF simulation of a 13.9 molal LiCl solution have been reported [1]. This work has been continued with the simulation of an 18.5 molal LiCl solution. The basic cube contained 43 ions of each kind and 129 water molecules. With an experimental density of 1.275 g/cm^3 a side length of the cube of 17.55 Å resulted. The simulation extended over 8000 time steps equivalent to a total elapsed time of 2 ps at an everage temperature of 305 K. The pair potentials employed and the details of the simulation were the same as described in [1].

The structure of the 18.5 molal LiCl solution is described on the basis of radial distribution functions and the orientation of water molecules in the hydration shell of the ions. The changes in the structural properties by the increase of the concentration from 13.9 to 18.5 molal are discussed. For the comparison with experimental data an X-ray measurement has been performed at the same concentration. Finally, the results are compared with a recent neutron diffraction study with Cl^- isotope substitution for a 14.9 molal LiCl solution [2].

II. Results and Discussion

a) Total Radial Distribution Function (RDF)

In order to check the pair potentials employed in the simulation an X-ray measurement of an 18.5 molal LiCl soluton has been performed. The resulting total $G(r)$ is compared in Fig. 1 with the one from the MD simulation. As in the case of the 13.9 molal solution [1] satisfactory agreement exists although in the experimental $G(r)$ the peaks are not as clearly resolved as in the one from the simulation.

The ion-oxygen, ion-hydrogen, and ion-ion RDFs for the 18.5 molal LiCl solution are shown separate-

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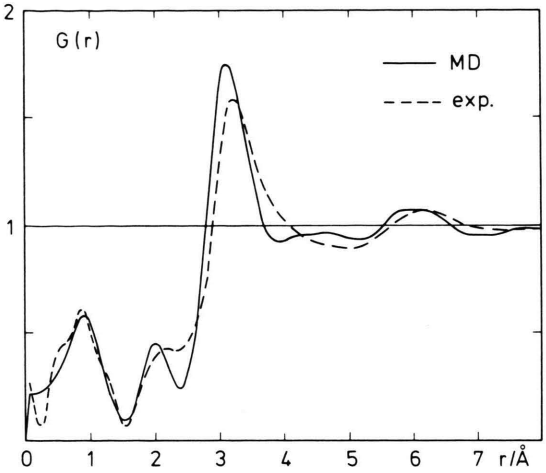

Fig. 1. X-ray weighted total radial distribution function for an 18.5 molal LiCl solution from the MD simultion (full) and from an experiment (dashed).

ly in Figs. 2, 4, and 6 together with the corresponding running integration numbers. In order to demonstrate the changes in the various RDFs with concentration the results for the 13.9 molal solution are drawn in these figures as dashed lines.

b) Hydration Shell of Li^+

The increase in concentration by 4.6 molal leads to only small changes in $g_{\mathrm{LiO}}(r)$ and $g_{\mathrm{LiH}}(r)$ as can be seen from Figure 2. The first peak in both RDFs becomes slightly lower and narrower. Because of the lower average number density of the water molecules at the higher concentration the hydration number of Li^+ reduces to four, a decrease by about one. The missing water molecule in the first hydration shell is replaced by a chloride ion. This formation of contact ion pairs can be read from the first peak in $g_{\mathrm{LiCl}}(r)$ and the corresponding running integration number as shown in Figure 6.

The ensemble and time averaged geometrical arrangement of the water molecules or chloride ions around an Li^+ can be calculated from the simulation by introducing a coordinate system where the Li^+ defines the origin, one of the neighboring oxygen atoms or ions the z-axis, and a second one the xz-plane. The positions of the six nearest neighbors (either oxygen atoms of water molecules or chloride ions) have been collected over several hundred different times steps spread over the whole simulation run. Their projections onto the xy-plane of this coordinate system are shown in Fig. 3 in the form of three-dimensional drawings for the 18.5 molal LiCl solution (above) and a 2.2 molal LiI solution (below) for comparison (see e.g. [3]). The arbitrary fixing of two neighbours in the z-axis and the xz-plane inevitably introduces some distortions resulting in an exaggerated height of the peaks in the center and along the positive x-direction as well as a difference in broadness between the peaks along the y-axis and the negative x-axis.

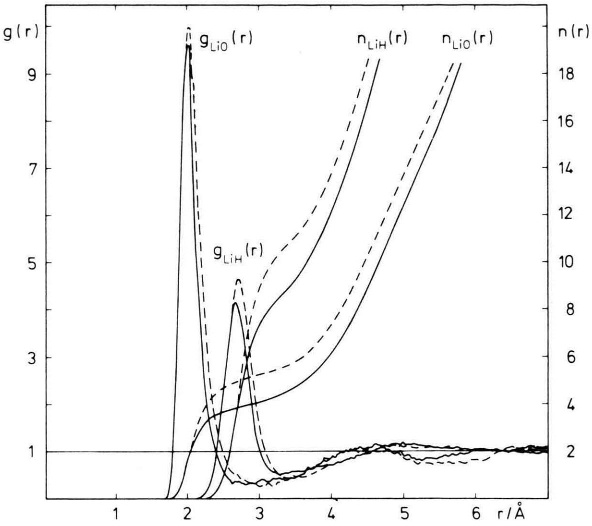

Fig. 2. Lithium-oxygen and lithium-hydrogen radial distribution functions and running integration numbers from MD simulations of 18.5 (full) and 13.9 (dashed) molal LiCl solutions.

In the 2.2 molal LiI solution the first coordination shell of Li^+ consists solely of water molecules while in the 18.5 molal LiCl solution each Li^+ is in the average in contact with one Cl^-. For producing the upper part of Fig. 3 all lithium ions have been selected which have at least one chloride ion in its first coordination sphere (about 70%) and this Cl^- has been employed for the definition of the positive z-axis. Therefore, the remaining nearest neighbors are mostly water molecules, only in some cases it is a Cl^-.

The comparison of the two drawings in Fig. 3 shows that the well defined octahedral arrangement of the water molecules around Li^+ in the dilute solution becomes strongly disturbed at the high concentration. But even in the 18.5 molal solution quite some preference for the occupation of the octa-

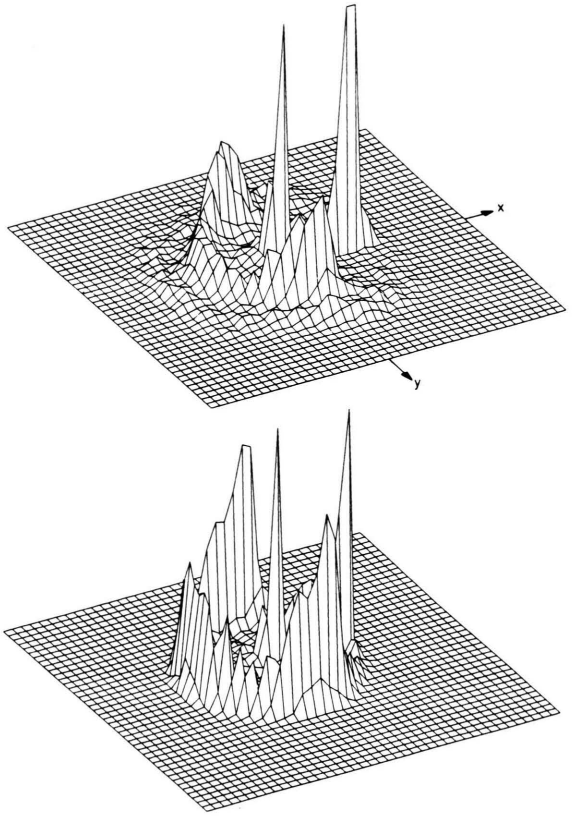

Fig. 3. Density of the projections of the six nearest neighbor oxygen atom or chloride ion positions around Li^+ onto the xy-plane of a coordinate system as defined in the text, calculated from an MD simulation of an 18.5 molal LiCl (above) and a 2.2 molal LiI solution (below).

hedral sites persists although the coordination number of Li^+ is reduced from six to five (four water molecules and one Cl^- in the average). The upper part of Fig. 3 shows also that the fifth water molecule or the second chloride ion can be found rather uniformly distributed at distances outside the first coordination sphere.

c) Hydration Shell of Cl^-

The $Cl^-{-}O$ and $Cl^-{-}H$ RDFs are drawn in Figure 4. The changes in the hydration shell of the chloride ion with increasing concentration are much stronger than those of the lithium ion. As the contact ion pair formation leaves the hydration shell of Li^+ almost unchanged – except for the replacement of a water molecule by a chloride ion – it has to be concluded that the Li^+ enters the hydration shell of the chloride ion with all but one of its first shell water molecules strongly attached. This means necessarily a huge disturbance of the rather soft hydration shell of Cl^-, resulting in a significant decrease in the heights of the first peaks in $g_{\mathrm{ClO}}(r)$ and $g_{\mathrm{ClH}}(r)$. This decrease in the case of $g_{\mathrm{ClH}}(r)$ is connected with a reduction in the number of hydrogen atoms in the first shell of about 1.5 in the average as a consequence of the excluded volume effect of the hydrated Li^+. The decrease in $g_{\mathrm{ClO}}(r)$ is compensated by a tail on the long distance side of the first peak, resulting in almost the same hydration number if $n(r)$ is taken at about 4.5 Å. This compensation is a consequence of the fact that part of the oxygen atoms of the first hydration shell of Li^+ belong by the ion pair formation at the same time to the hydration shell of Cl^-. The $Cl^-{-}O$ distances of these water molecules are in the average slightly larger than in the undisturbed case.

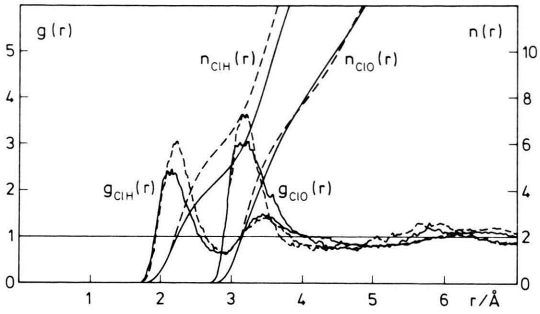

Fig. 4. Chloride-oxygen and chloride-hydrogen radial distribution functions and running integration numbers from MD simulations of 18.5 (full) and 13.9 (dashed) molal LiCl solutions.

In Fig. 5 the neutron weighted chloride-water RDFs, as defined in the legend of this figure, are shown from the simulation of a 13.9 and 18.5 and a neutron diffraction study with isotopic substitution [2] of a 14.9 molal LiCl solution. The position of the first hydrogen peak from the simulation of the 13.9 molal solution agrees in the limits of uncertainty with the experimental result for the 14.9 molal solution, being 2.20 Å and 2.24 Å, respectively. For the 18.5 molal solution this peak is shifted to a shorter distance by about 0.1 Å. This may be an effect of concentration where the stronger Coulomb interactions because of the larger number of ions squeeze the water molecules closer to the Cl^-. In the second peak the contributions of the $Cl^-{-}O$ and $Cl^-{-}H$ interactions overlap, while even at the high concentration the $Li^+{-}Cl^-$ and $Cl^-{-}Cl$ contributions are quite small, below about 4 Å.

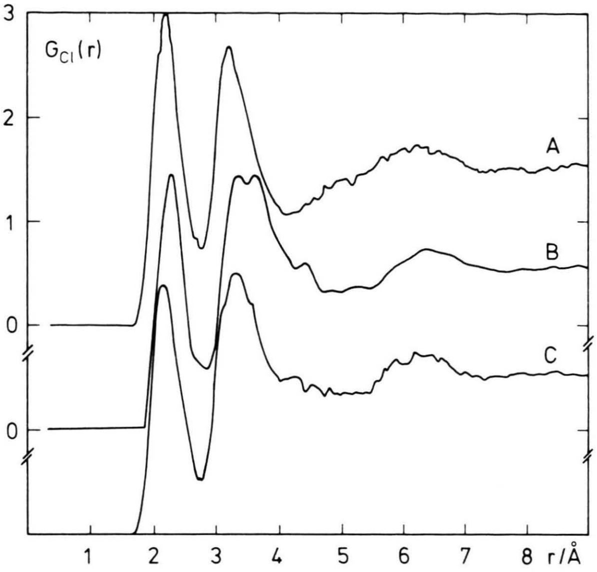

Fig. 5. Neutron weighted chloride-water radial distribution functions from an experiment of a 14.9 (B) and from MD simulations of 13.9 (A) and 18.5 (C) molal LiCl solutions. $G(r) = (\tilde{G}(r) + E)/B$ where $\tilde{G}(r) = A(g_{\mathrm{ClO}} - 1) + B(g_{\mathrm{ClH}} - 1) + C(g_{\mathrm{ClLi}}(r) - 1) + D(g_{\mathrm{ClCl}} - 1)$ and $E = -(A+B+C+D)$.

Because of this overlay it is difficult to analyze the differences between the three curves in the range of the second peak. It might be a consequence of concentration dependent orientation of the water molecules in the hydration shell of Cl^-.

The investigation of the geometrical arrangement of the water molecules around Cl^- in the same way as presented in Fig. 3 for Li^+ shows a uniform distribution similar to what has been found in dilute solutions (see e.g. [3]). Therefore, this figure is not presented here.

d) Ion-Ion Radial Distribution Functions

The ion-ion RDFs are shown in Figure 6. The first peak in $g_{\mathrm{LiLi}}(r)$ – positioned slightly above 3 Å – corresponds to a configuration where two Li^+ are coordinated to the same water molecule. With increasing concentration its position remains practically unchanged while its height decreases. As the average number density is increased at the higher concentration, the same $n(r)$ results at distances below 4 Å. The first minimum becomes significantly shallower indicating a tendency to a more uniform distribution of the lithium ions with increasing concentration. Experimental information on $g_{\mathrm{LiLi}}(r)$ is not available in the literature.

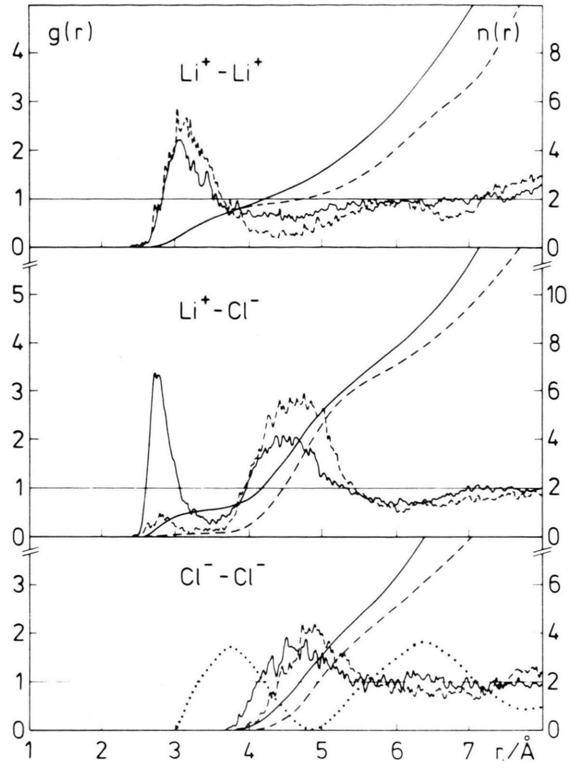

Fig. 6. Ion-ion radial distribution functions and running integration numbers from MD simulations of 18.5 (full) and 13.9 (dashed) molal LiCl solutions. The dotted curve gives the result of a neutron diffraction study of a 14.9 molal LiCl solution with chloride isotope subsitution [2].

It can be seen from the first peak in $g_{\mathrm{LiCl}}(r)$ at 2.8 Å and from $n_{\mathrm{LiCl}}(r)$ in Fig. 6 that the contact ion pair formation increases strongly with increasing concentration at the expense of the water molecule separated ion pairs. In the 18.5 molal LiCl solution each ion is in contact with about one counterion, while it is only one out of ten in the 13.9 molal solution. This result is in keeping with the measurements by Ichikawa et al. [4]. They investigated a 27.5 molal LiCl solution at 130 °C by neutron diffraction measurements with lithium isotope substitution and found that in the average each Li^+ is in contact with 1.5 Cl^-.

The geometrical arrangement of the chloride ions around Li^+ is shown in Figure 7. Different from Fig. 3, only the seven nearest Cl^- are included in the statistics, i.e. all Cl^- up to a distance of about 5.7 Å from the Li^+. It can be seen from Fig. 6 that in this way all Cl^- are included which are separated from

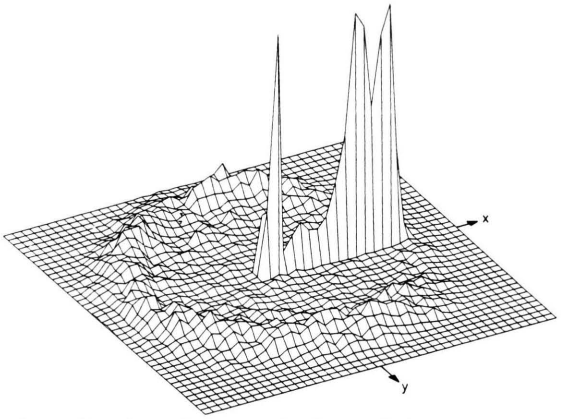

Fig. 7. Density of the projections of the seven nearest neighbor chloride ion positions around a Li^+ onto the xy-plane of a coordinate system as defined in the text, calculated from an MD simulation of an 18.5 molal LiCl solution.

an Li^+ by one water molecule. As the Cl^- in contact with Li^+ has been employed for the definition of the z-axis, it can be seen from Fig. 7 that the Cl^- separated from Li^+ by one water molecule are distributed rather uniformly around Li^+.

In Fig. 6 the maximum of the first peak in $g_{ClCl}(r)$ shifts from about 4.9 Å in the 13.9 molal solution to about 4.5 Å in 18.5 molal one and broadens. While there seems to be a preference for the configurations where two Cl^- are linked by linear hydrogen bonds to the same water molecule at the lower concentration there is with increasing concentration a tendency to a more uniform distribution of the chloride ions, similar to what has been concluded from $g_{LiLi}(r)$. The short distance end of $g_{ClCl}(r)$ approaches 3.6 Å, the distance of contact ion pair formation.

The $Cl^- - Cl^-$ RDF in the 14.9 molal LiCl solution has been determined through the second order difference method from neutron diffraction studies with chloride isotope substitution by Copestake, Neilson and Enderby and is drawn as dotted line in Fig. 6 additionally [2]. Simulation and experiment differ completely. We have no explanation for this discrepancy. It seems to us very much surprising that the experiment shows a well defined first neighbor shell and a very far ranging pronounced order of the chlorid ions in the solution. But it is very satisfying to see that in spite of the discrepancy in $g_{ClCl}(r)$ there is good agreement between experiment and simulation in the number of nearest neighbors if counted up to the first minimum in the experimental RDF at 4.9 Å. While it has been concluded from the experiment that in the average 2.3 $Cl^- - Cl^-$ contact ion pairs exist in the 14.9 molal solution, the simulations result in 1.9 and 2.6 nearest neighbors for the 13.9 and the 18.5 molal solutions, respectively, located mainly at larger distances ranging from contact ion pair formation to water molecule separated ion pairs.

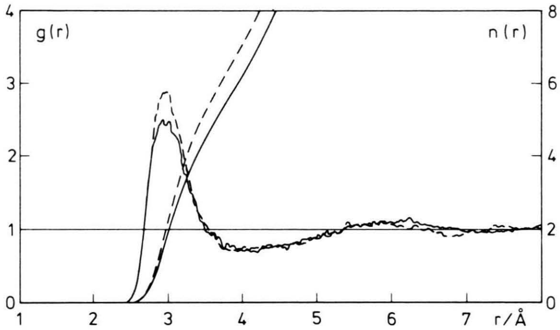

Fig. 8. Oxygen-oxygen radial distribution functions and running integration numbers from MD simulations of 18.5 (full) and 13.9 (dashed) molal LiCl solutions.

e) Water Structure

On the basis of $g_{OH}(r)$ and $g_{HH}(r)$ it was concluded from the simulation that in the 13.9 molal solution hydrogen bonding between water molecules is scarce. As obviously a further breakdown of the water structure cannot occur there is no significant difference between the two concentrations for $g_{OH}(r)$ and $g_{HH}(r)$ and therefore they are not depicted here. The decrease in the density of water with increasing concentration is reflected in the $g_{OO}(r)$ shown in Fig. 8 for the 13.9 and the 18.5 molal solutions. The smaller density does not lead to a change in the nearest neighbor distance but the number of nearest neighbors decreases significantly by about one.

The choice of the coordinate system for the evaluation of the geometrical arrangement of the water molecules around a central water molecule involves much less arbitrariness than in the case of the spherically symmetric ions. Figure 9 shows for the 18.5 molal LiCl solution (above) and pure water [5] (below) the projections of the positions of the oxygen atoms of the four nearest neighbor water molecules around a central one onto the xy-plane of a coordinate system defined by the central water molecule, its center of mass being placed in the

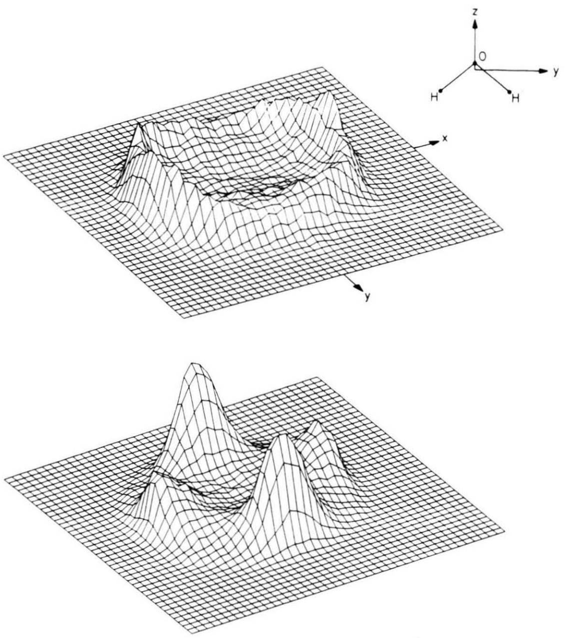

Fig. 9. Density of the projections of the oxygen atom positions of the four nearest neighbor water molecules around a central water molecule onto the xy-plane of a coordinate system as defined in the insertion, calculated from MD simulations of an 18.5 molal LiCl solution and of pure water.

origin and its hydrogens in the yz-plane with equal distances from the z-axis (see insert). In the case of pure water (lower part of Fig. 9) there is a strong preference for the occupation of tetrahedral sites. The peaks are narrower in the H-atom directions when compared with the lone pair directions because of the less well localized lone pair orbitals. The breakdown of the hydrogen bond structure in the 18.5 molal LiCl solution, which has been concluded above from $g_{\mathrm{OH}}(r)$ and $g_{\mathrm{HH}}(r)$ becomes obvious from the comparison of the two drawings in Figure 9. The preference for the occupation of the tetrahedral sites has practically disappeared. The distribution of the water molecules around a central one becomes almost uniform.

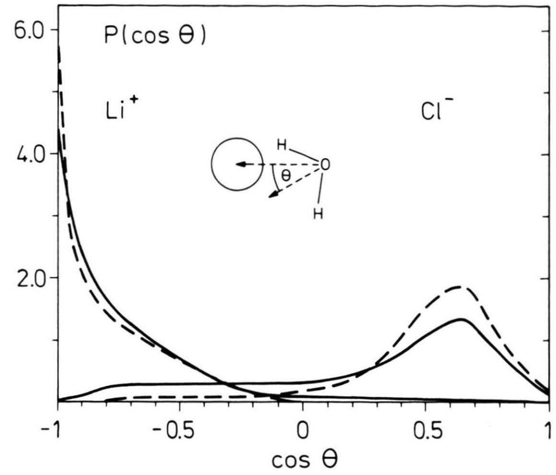

Fig. 10. Distribution of cos Θ for the water molecules in the first hydration shells of Li^+ and Cl^- calculated from an MD simulation of an 18.5 molal (full) and a 13.9 molal (dashed) LiCl solution. Θ is defined in the insertion.

f) Orientation of the Water Molecules

The distribution of cos Θ – where Θ is defined as the angle between the dipole moment direction of a water molecule and the vector pointing from the oxygen atom toward the center of the ion – in the hydration shells of Li^+ and Cl^- is shown in Fig. 10 for the 18.5 (full) and the 13.9 (dashed) molal LiCl solutions. In the hydration shell of Li^+ the preference for trigonal orientation remains with increasing concentration but it becomes slightly less pronounced. The preference for the formation of linear hydrogen bonds with Cl^- is significantly reduced at the higher concentration with a strong tendency towards a uniform distribution of cos Θ.

g) Other Properties

There are no significant differences between the 18.5 and the 13.9 molal LiCl solutions as far as the water molecule geometry, the average potential energies, and the pair interaction energy distributions are concerned. Therefore, these results are not presented here.

Acknowledgement

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[1] P. Bopp, I. Okada, H. Ohtaki, and K. Heinzinger, Z. Naturforsch. **40a,** 116 (1985).
[2] A. P. Copestake, G. W. Neilson, and J. E. Enderby, J. Phys. C: Solid State Phys. **18,** 4211 (1985).
[3] K. Heinzinger, Pure Appl. Chem. **57,** 1031 (1985).
[4] K. Ichikawa, Y. Kameda, T. Matsumoto, and M. Misawa, J. Phys. C: Solid State Phys. **17,** L 725 (1984).
[5] G. Pálinkás, P. Bopp, G. Jancsó, and K. Heinzinger, Z. Naturforsch. **39a,** 179 (1984).