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 dyamics 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/cm^3. 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 2.18×10^{-16} s and the simulation extended over 2×10^4 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 3×10^{-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, $g_{\mathrm{IO}}(r)$, and ion-hydrogen, $g_{\mathrm{IH}}(r)$, radial distribution functions (RDF) for K^+ and Cl^- are shown in Fig. 1 together with the corresponding running integration numbers, which are given by

$$n_{xy}(r) = 4\pi\varrho \int_0^r g_{xy}(r')\, r'^2\, \mathrm{d}r',$$

where ϱ 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 $g_{\mathrm{KO}}(r)$ and $g_{\mathrm{KH}}(r)$ 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. σ (first row) is given in Å and ε (second row) is expressed in units of 10^{-16} erg.

	K^+	Cl^-	H_2O
K^+	3.36 186.0	4.08 67.7	3.25 94.32
Cl^-		4.86 27.87	4.02 30.83
H_2O			3.1 52.61

Table 2. Characterstic 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}	$g_{xy}(r_{\mathrm{M1}})$	r_{m1}	$g_{xy}(r_{\mathrm{m1}})$	r_{M2}	$g_{xy}(r_{\mathrm{M2}})$	$n_{xy}(r_{\mathrm{m1}})$
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
2.71	3.19	6.3	3.25	2.25	8.4	MC	[11]
2.76	3.35	7.5	3.29	2.35	7.2	MD	[12]
2.86	3.32	7.6	3.23	3.29	5.9	MD	[13]
–	–	–	3.20	2.26	5.7	NDIS [a]	[19]
2.80	–	8.1	3.14	–	6	X-ray	[20]

[a] Data from measurements of NaCl and RbCl solutions.

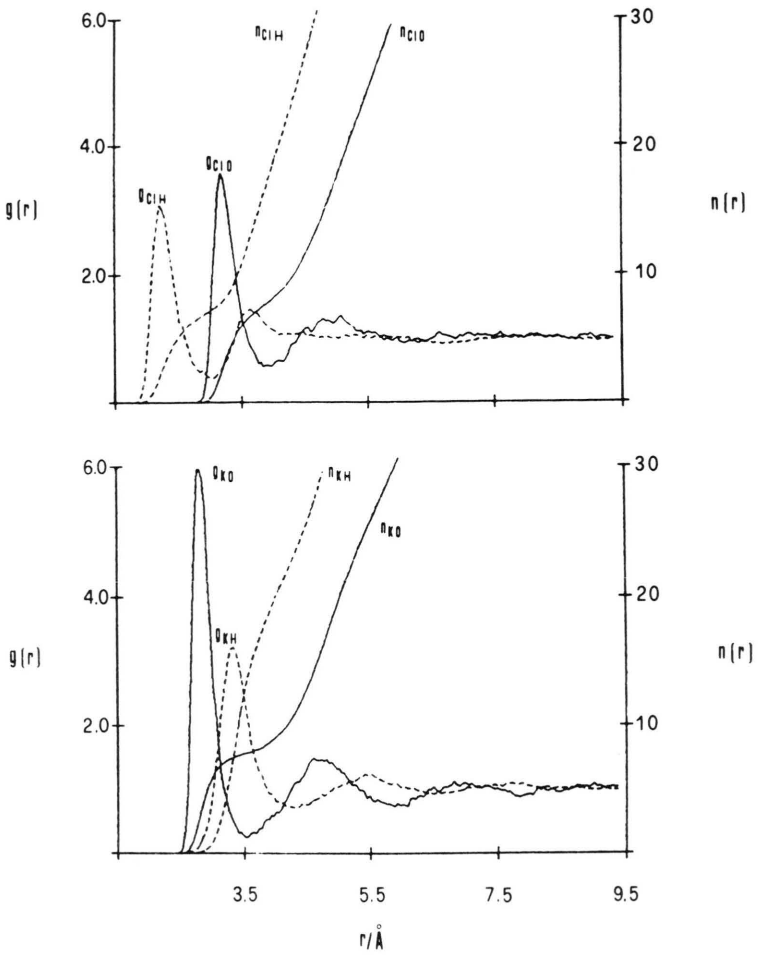

Fig. 1. Ion-oxygen (full) and ion-hydrogen (dashed) radial distribution functions and running integration numbers for a 2.2 molal KCl solution.

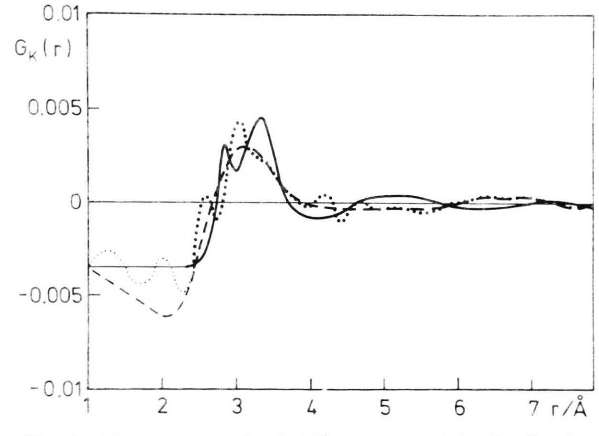

Fig. 2. Neutron weighted K^+-water radial distribution function in barn from the simulation of the 2.2 molal KCl solution (rescaled for 4 molal, full) and from a neutron diffraction measurement with isotopic substitution (dots, dashed).

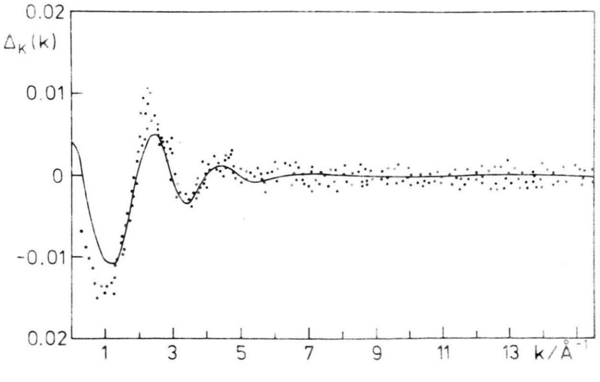

Fig. 3. Difference structure functions for a 4 molal KCl solution from neutron diffraction measurements with potassium isotope substitution (dots) and rescaled results from the simulation of a 2.2 molal KCl solution (full).

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 experimental 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 unresolved 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 simulation 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 significantly 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 reasonable 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 $G_{Cl}(r)$ 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 one (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 concentration and counterions [19]. This discrepancy may have to be attributed to accuracy problems connected with the difficulty of this kind of measurements.

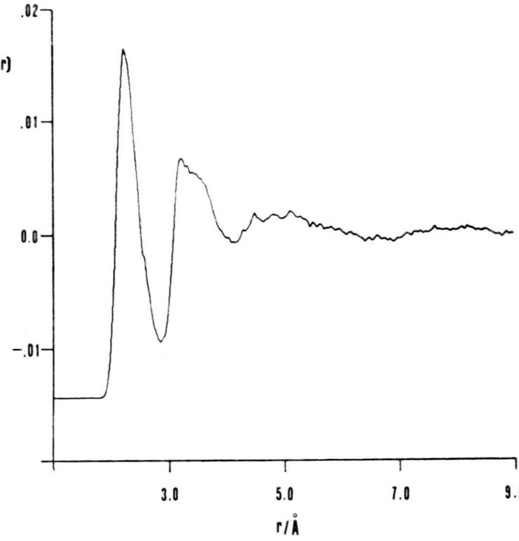

Fig. 4. Neutron weighted Cl^--water radial distribution function in barn from the simulation of a 2.2 molal KCl solution.

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 significant structure seems to be present in $g_{ClCl}(r)$ 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

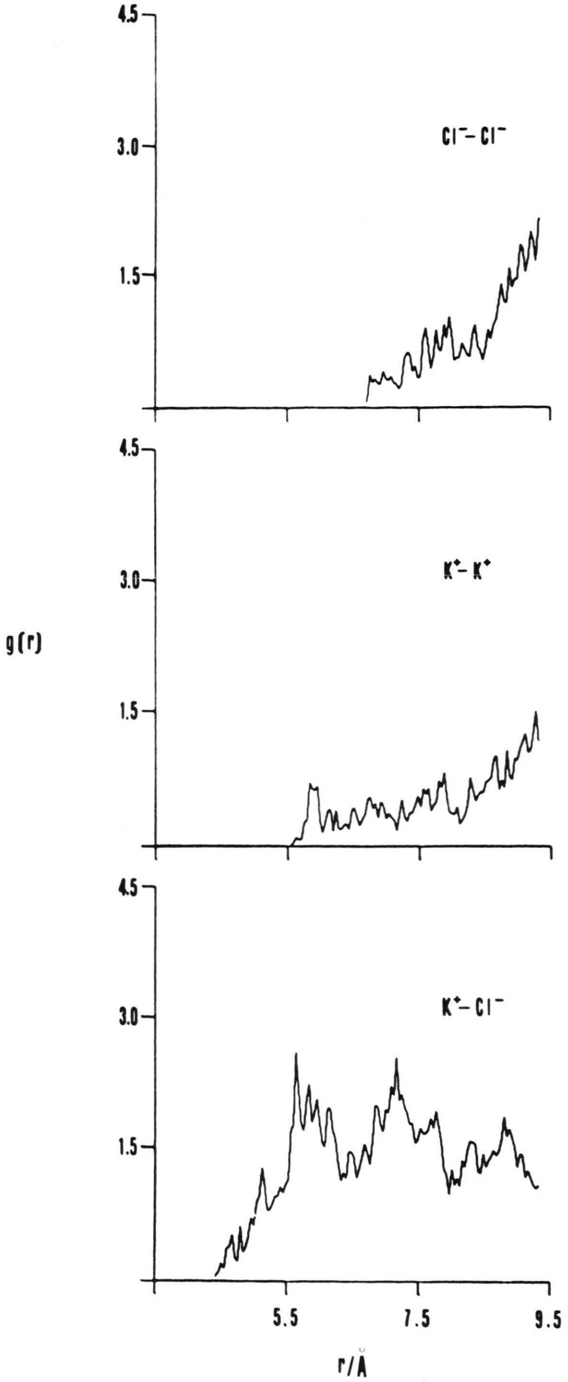

Fig. 5. Ion-ion radial distribution functions for a 2.2 molal KCl solution.

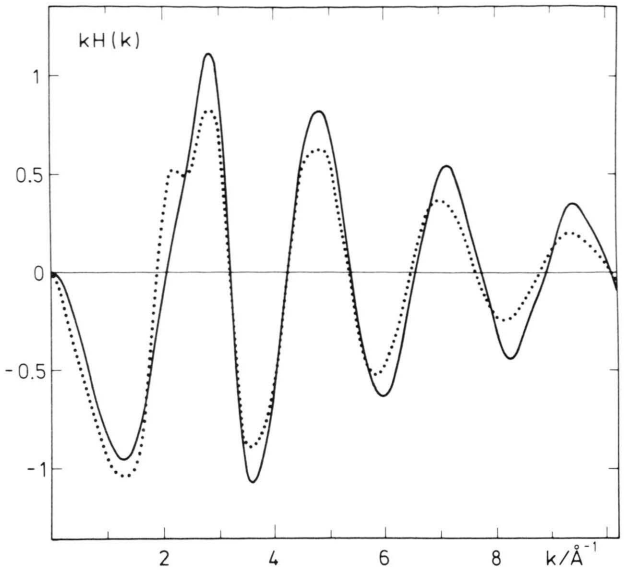

Fig. 6. Total X-ray structure function for a 2.2 molal KCl solution from an experiment (dots) and from the MD simulation (full).

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 $g_{\mathrm{ClCl}}(r)$ are rather unexpected for an aqueous electrolyte solution [19, 23].

The $g_{\mathrm{KCl}}(r)$ 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.

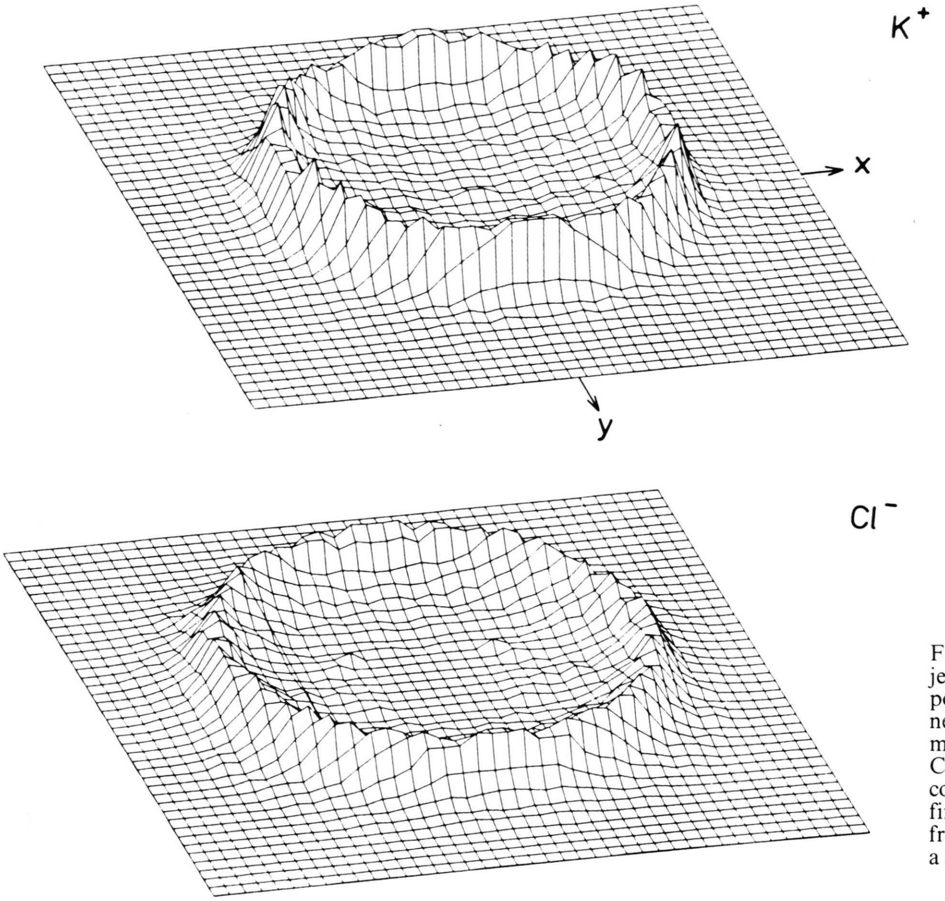

Fig. 7. Density of the projections of the oxygen atom positions of the eight nearest neighbor water molecules around K^+ and Cl^- onto the xy-plane of a coordinate system as defined in the text, calculated from an MD simulation of a 2.2 molal KCl solution.

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 $x > 0$. 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 (θ) 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

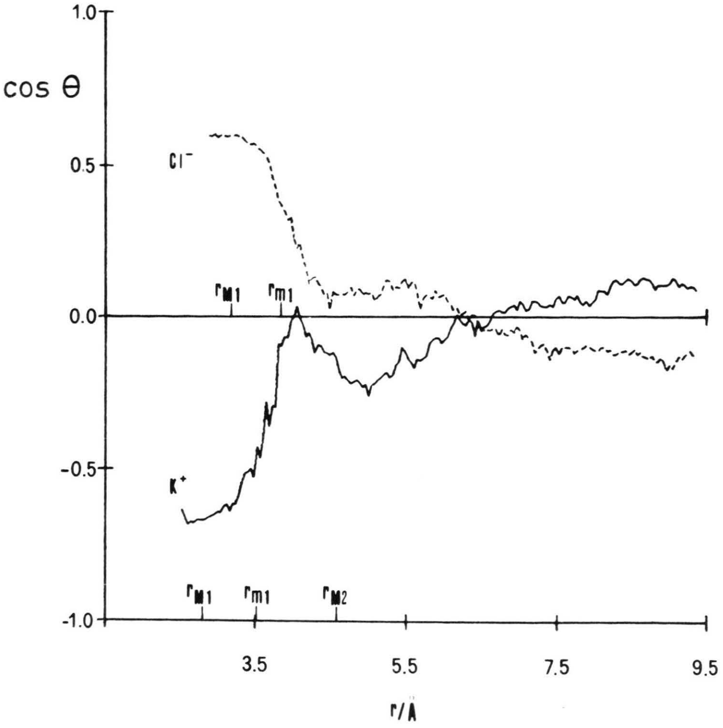

Fig. 8. Average value of cos θ as a function of distance from the potassium (full line) and the chloride (dashed line) ions for the 2.2 molal KCl solution. θ is the angle between the water dipole moment and the vector pointing from the oxygen atom towards the center of the ion (for the definition of r_{M1} and r_{m1} see captions of Table 2).

water molecules, $\langle\cos\theta\rangle$, vs. the distance of the water oxygen atom is shown in Figure 8. For Cl^- $\langle\cos\theta(r)\rangle$ decreases over the first hydration shell of $g_{ClO}(r)$ from the initial value 0.61 to 0.45. As for NaCl and $MgCl_2$ [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 F^-. For K^+, the $\langle\cos\theta(r)\rangle$ increases over the first peak of $g_{KO}(r)$ from -0.66 to -0.50. This behaviour is slower than for Cs^+. Further, a second region of preferential water orientation is evident, which corresponds to the second peak of $g_{KO}(r)$.

The distributions of cos θ over the first hydration shell of the ions are drawn in Figure 9. For Cl^- the cos θ 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 F^-, and for a significant fraction of water molecules cos θ is negative.

For K^+ the cos θ 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 Fig. 10, reflect the more or less pronounced first hydration shells of K^+ and Cl^-, respectively, with relative maxima at -1.15×10^{-12} erg for K^+ and -0.89×10^{-12} erg for 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 K^+ peak has a position and width intermediate between the analogous values for Na^+ and for Cs^+ ions [3, 7]. The same conclusion can be drawn comparing the Cl^- case with the F^- and I^- cases [3, 7].

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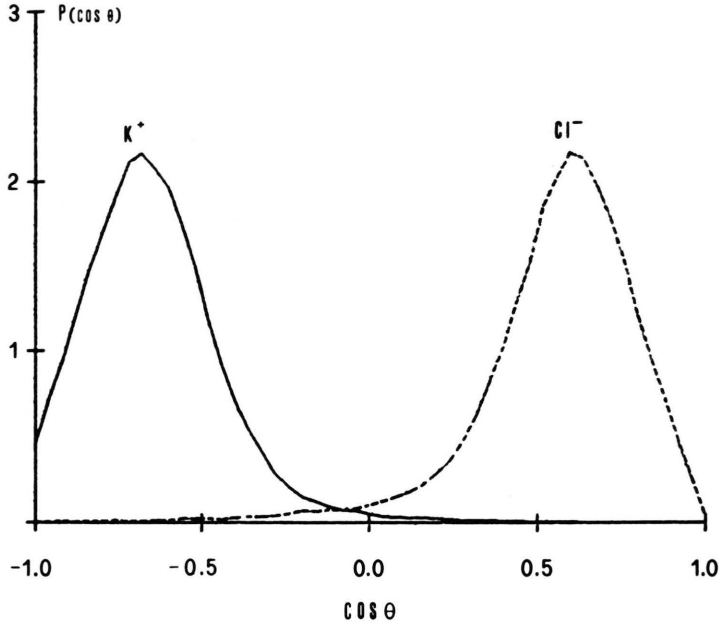

Fig. 9. Distribution of $\cos\theta$ in the first hydration shells of K^+ and Cl^- for a 2.2 molal KCl solution. The distributions are normalized and given in arbitrary units.

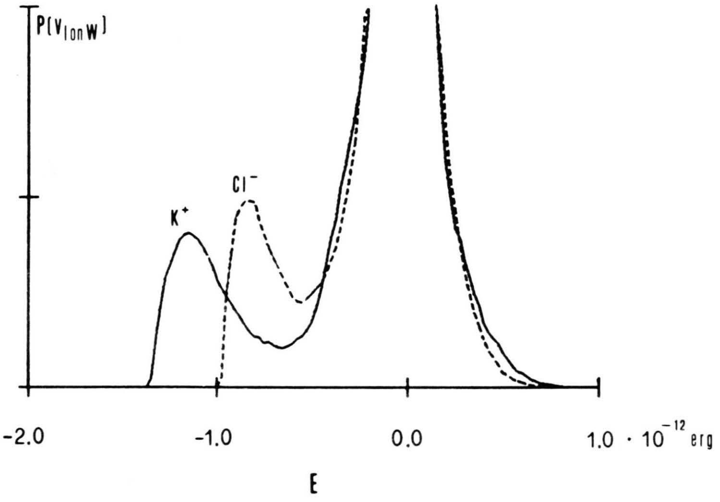

Fig. 10. Pair interaction energy distribution for K^+-water (full line) and Cl^--water (dashed line) in a 2.2 molal KCl solution. $P(V_{\text{ion W}})$ is given in arbitrary units.

[1] a) R. W. Gurney, Ionic Processes in Solutions. McGraw-Hill, New York 1953; b) T. Erdey-Gruz, Transport Phenomena in Aqueous Solutions. Hilger, London 1974.

[2] a) R. M. Glaeser and B. K. Jap, Biophys. J. **45,** 95 (1984); b) S. L. Fornili, M. Migliore, D. P. Vercauteren, and E. Clementi, J. Physique **45,** C7-219 (1984).

[3] G. Pálinkás, W. O. Riede, and K. Heinzinger, Z. Naturforsch. **32 a,** 1137 (1977).

[4] Gy. I. Szász and K. Heinzinger, Z. Naturforsch. **34 a,** 840 (1979).

[5] T. Radnai, G. Pálinkás, Gy. I. Szász, and K. Heinzinger, Z. Naturforsch. **36 a,** 1076 (1981).

[6] W. Dietz, W. O. Riede, and K. Heinzinger, Z. Naturforsch. **37 a,** 1038 (1982).

[7] Gy. I. Szász and K. Heinzinger, Z. Naturforsch. **38 a,** 214 (1983).

[8] P. Bopp, I. Okada, H. Ohtaki, and K. Heinzinger, Z. Naturforsch. **40 a,** 116 (1985).

[9] M. M. Probst, T. Radnai, K. Heinzinger, P. Bopp, and B. M. Rode, J. Phys. Chem. **89,** 753 (1985).

[10] E. Clementi and R. Barsotti, Chem. Phys. Lett. **59,** 21 (1978).

[11] M. Mezei and D. L. Beveridge, J. Chem. Phys. **74,** 6902 (1981).

[12] R. W. Impey, P. A. Madden, and I. R. McDonald, J. Phys. Chem. **87,** 5071 (1983).

[13] D. G. Bounds, Mol. Phys. **54,** 1335 (1985).

[14] a) D. L. Beveridge, M. Mezei, S. Swaminathan, and J. W. Harrison, in: Computer Modeling of Matter, ed.

P. G. Lykos, Amer. Chem. Soc., Washington, D.C. 1978; b) K. Heinzinger, Physica **131 B,** 196 (1985).
[15] G. W. Neilson and N. Skipper, Chem. Phys. Lett. **114,** 35 (1985).
[16] S. Cummings, J. E. Enderby, G. W. Neilson, R. A. Howe, W. S. Howells, and A. K. Soper, Nature London **287,** 714 (1980).
[17] F. H. Stillinger and A. Rahman, J. Chem. Phys. **60,** 1545 (1974).
[18] C. L. Kong, J. Chem. Phys. **59,** 2464 (1973).
[19] G. W. Neilson, J. Physique **45,** C 7-119 (1984).
[20] G. Pálinkás, T. Radnai, and F. Hajdu, Z. Naturforsch. **35 a,** 107 (1980).
[21] W. Dietz and K. Heinzinger, Ber. Bunsenges. Phys. Chem. **89,** 968 (1985).
[22] G. I. Szász, W. Dietz, K. Heinzinger, G. Pálinkás, and T. Radnai, Chem. Phys. Lett. **92,** 388 (1982).
[23] A. P. Copestake, G. W. Neilson, and J. Enderby, J. Phys. C: Solid State Phys. **18,** 4211 (1985).
[24] P. Bopp. W. Dietz, and K. Heinzinger, Z. Naturforsch. **34 a,** 1424 (1979).
[25] G. Pálinkás, T. Radnai, W. Dietz, Gy. I. Szász, and K. Heinzinger, Z. Naturforsch. **37 a,** 1049 (1982).
[26] K. Heinzinger, Pure Appl. Chem. **57,** 1031 (1985).