Structural Properties of an Aqueous LiI Solution Derived from a Molecular Dynamics Simulation

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In the molecular dynamics simulation of the aqueous LiI solution the ST2 water model was employed and the ions were described as Lennard-Jones spheres with an elementary charge at the center. The basic periodic cube contained 200 water molecules and 8 ions of each kind equivalent to a 2.2 molal solution. The simulation extended over 10 ps with an average temperature of 305 K. The structure is discussed by means of ion-water, ion-ion and water-water radial pair distribution functions and the orientation of the water molecules. Potential energy relationships are reported and the heat of solution has been calculated and found in agreement with experimental values.

I. Introduction

In the literature only one investigation of the structure of an aqueous LiI solution has been reported. The x-ray measurements by Lawrence and Kruh [1] extended over different alkali iodide solutions at various concentrations. Because of the strongly different weight of the two ion-water contributions to the scattered intensity it is very difficult to deduce from x-ray measurements information on the structure of the hydration shells of both ions from the same solution.

Lawrence and Kruh, therefore, derived from their LiI investigation only properties of the hydration shell of the iodide ion. Further information on the hydration shell of I^- results from the x-ray measurements of a NH_4I solution by Narten [2] and of a NaI solution by Maeda and Ohtaki [3].

Numerous investigations of the hydration shell of Li^+ by x-ray and neutron diffraction with a number of different counterions have been reported in the literature. The recent most reliable measurements have been compiled in a short paper published recently [4] in which an octahedral arrangement of six nearest neighbor water molecules around Li^+ has been deduced from the same simulation on which the results reported here are based.

Preliminary results on the structural properties of a LiI solution from an MD simulation have been reported by us some time ago [5]. It was a very short run and the pair potential parameters – as far as the iodide ion is concerned – had been chosen so that e.g. wrong I^--0 distances resulted. The new data on the structure of the LiI solution reported here are based on a significantly longer run, an improved simulation technique and corrected potential parameters. The structure is discussed on the basis of ion-water, ion-ion and water-water radial distribution functions (RDF) and the orientation of the water molecules. Potential energy relationships are derived and the heat of solution has been calculated.

The combination of x-ray measurements and MD simulations has been shown to be a good way to elucidate structures of aqueous electrolyte solutions [6, 7]. Therefore, in a subsequent paper [8] new x-ray measurements on a LiI solution are reported and compared with the structural properties discussed here.

II. Details of the Simulation

In the MD simulation of the LiI solution the basic periodic cube contained 200 water molecules and 8 ions of each kind, equivalent to a 2.2 molal solution. The ST2 water model [9] was employed and the ions were modelled as $(6-12)$ Lennard-Jones (LJ) spheres with an elementary charge in the center. Compared with previously reported preliminary results of a simulation of the same solution [5] improved LJ parameters are used [6]. They are given in Table 1. With an experimental density of 1.19 g/cm^3 a sidelength of the basic cube of 18.68 Å results.

In the calculation of the Coulombic energy for the ion-ion interactions the Ewald method is employed. The ion-water and water-water interactions

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Table 1. Lennard-Jones parameters employed in the simulation of the aqueous LiI solution. σ is given in Å (first row) and ε in units of 10^{-16} erg.

	Li^+	I^-	H_2O
Li^+	2.37 24.8	4.30 13.5	2.77 37.2
I^-	— 	5.40 67.8	4.41 37.9
H_2O	—	—	3.10 52.6

are cut off at 9.34 Å (half of the sidelength of the basic cube) and the "shifted force potential" method is applied. Further details are given in [10]. With this technique the simulation extended over 46 000 time steps – equivalent to a total elapsed time of about 10 ps – without interference. Therefore, also the dynamical properties of the solution can be calculated with a high degree of reliability. They will be published separately. During the whole run the change in total energy $\Delta E/E$ was less than $5 \cdot 10^{-5}$ and the average temperature 305 K.

For comparison pure ST2 water was simulated with the same improved technique over about 5 ps. There seem to be no significant differences in the structural properties between our simulation and the one by Stillinger and Rahman [9].

III. Results and Discussion

A) Radial Distribution Functions

For the two ions of the alkali halide series extreme in size the ion-oxygen and ion-hydrogen RDFs are shown in Fig. 1 together with the corresponding running integration numbers, defined by

$$n_{xy}(r) = 4\,\pi\,\varrho_0 \int_0^r g_{xy}(r')\,r'^2\,\mathrm{d}r' ,$$

where ϱ_0 is the number density of the water molecules. Some characteristic values of the RDFs are given in Table 2. It is interesting to note that the second hydration shell of Li^+ is just as pronounced as the first shell of I^-.

As far as the first hydration shell of the lithium ion is concerned it has been demonstrated in a preceding paper [4] that the MD results for the LiI solution – based on the simulation described in Sect. II – are in good agreement with x-ray and neutron diffraction data. Beyond this agreement it was concluded from the simulation that six water molecules in the first hydration shell are arranged octahedrally with a certain distribution around the octahedral positions as expected for a liquid. The existence of a second hydration shell of Li^+ with twelve water molecules (Fig. 1) has also been supported by x-ray measurements as reported in the subsequent paper [8].

The characteristic data of $g_{\mathrm{LiO}}(r)$ and $g_{\mathrm{LiH}}(r)$ agree in the limits of error with preliminary results published some time ago [5]. This shows that improvements in the simulation technique and a factor of ten in the simulation time do not alter significantly structural information derived from the simulation. A Monte Carlo study has been published recently by Mezei and Beveridge [11], where a single Li^+ is surrounded by 215 water molecules. These authors employed the pair potentials for ion-water and water-water interactions (MCY) derived by Clementi and coworkers from ab initio calcula-

Table 2. Characteristic values of the radial distribution functions $g_{xy}(r)$ for the 2.2 molal LiI solution and pure water (s and p denote solvent and pure water, respectively). R_i, $r_{\mathrm{M}i}$ and $r_{\mathrm{m}i}$ give the distances in Å where for the ith time $g_{xy}(r)$ is unity, has a maximum and a minimum, respectively. The uncertainties in all distances are smaller than ±0.02 Å, if not stated otherwise, and in the g values they are smaller than 3%.

xy	R_1	r_{M1}	$g_{xy}(r_{\mathrm{M1}})$	R_2	r_{m1}	$g_{xy}(r_{\mathrm{m1}})$	r_{M2}	$g_{xy}(r_{\mathrm{M2}})$	$n(r_{\mathrm{m1}})$
LiO	1.98	2.12	16.9	2.38	2.9 (1)	≈ 0	4.19 (3)	2.04	6.1 (1)
LiH	2.46	2.68	7.4	2.97	3.2 (1)	0.55	4.82 (4)	1.46	13.1 (2)
IO	3.44	3.68 (4)	2.28	4.20	4.4 (1)	0.90	5.2 (1)	1.27	8.7 (3)
IH	2.52	2.70	1.62	3.02	3.4 (1)	0.57	4.1 (1)	1.26	6.7 (2)
OO s	2.59	2.85	3.08	3.25	3.7 (1)	0.79	—	—	6.3 (6)
OO p	2.63	2.84	3.10	3.16	3.4 (1)	0.69	4.7 (2)	1.12	5.0 (3)
OH s	1.87	1.94	1.08	2.01	2.38 (4)	0.49	3.33 (5)	1.54	1.7 (1)
OH p	1.80	1.92	1.30	2.04	2.50 (4)	0.34	3.32 (4)	1.57	2.1 (1)
HH s	2.23	2.43 (3)	1.33	2.72	3.02 (4)	0.83	3.9 (1)	1.09	10.5 (4)
HH p	2.21	2.42	1.46	2.71	3.02 (6)	0.78	3.9 (1)	1.14	11.5 (7)

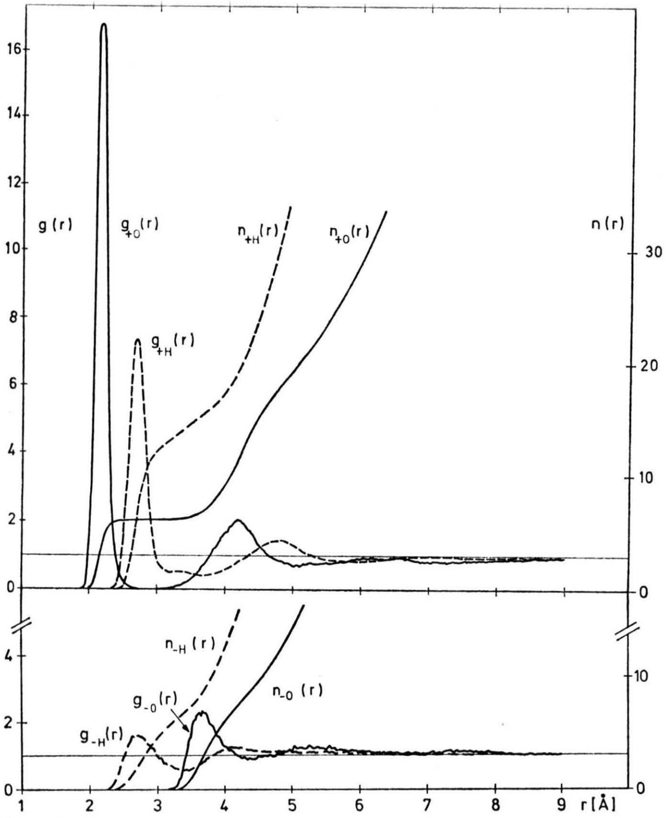

Fig. 1.

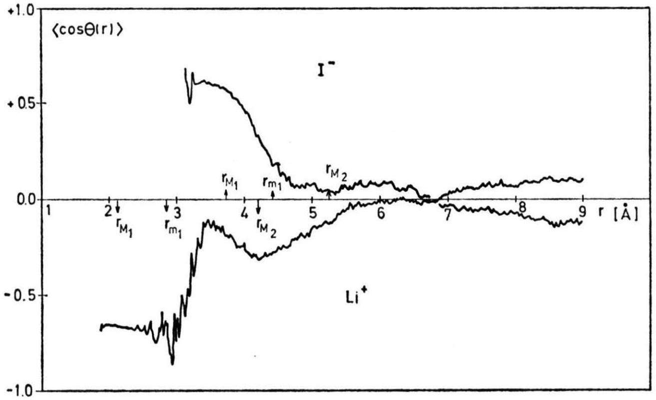

Fig. 4.

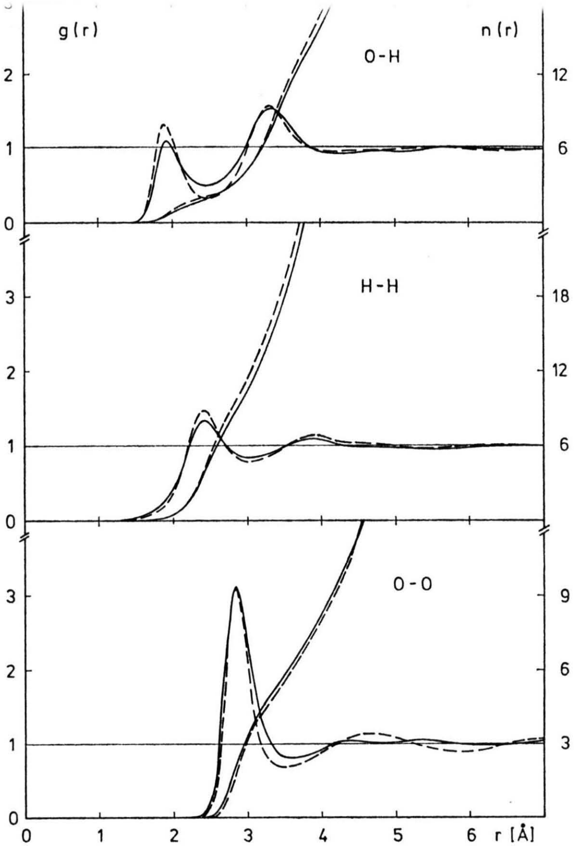

Fig. 3.

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

Fig. 3. Oxygen-oxygen, oxygen-hydrogen and hydrogen-hydrogen radial distribution functions and running integration numbers for the water molecules in a 2.2 molal LiI solution (full) and in pure water (dashed).

Fig. 4. Average value of cos θ as a function of distance from the iodide (upper part) and the lithium ion for the 2.2 molal LiI solution. θ is the angle between the dipole moment direction of the water molecule and the vector pointing from the oxygen atom towards the center of the ion. (For the definition of r_{Mi} an r_{mi} see caption of Table 2).

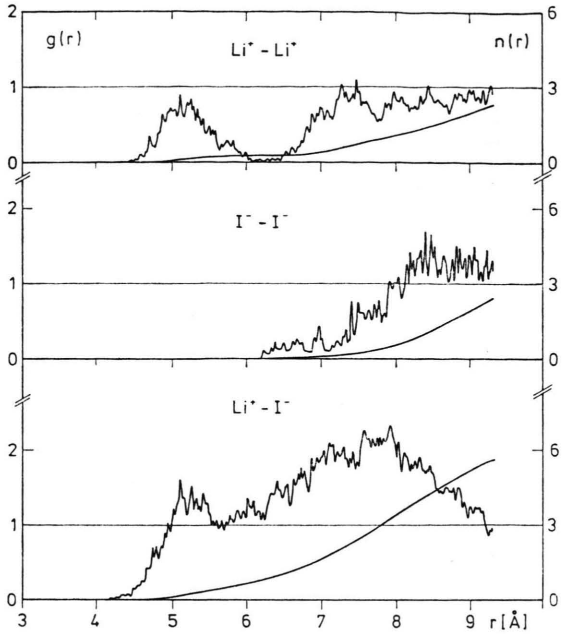

Fig. 2. Ion-ion radial distribution functions and running integration numbers for a 2.2 molal LiI solution.

tions [12, 13]. They find in agreement with the results from this simulation that the position of the first peak in $g_{\mathrm{LiO}}(r)$ is at $r = 2.10$ Å and that the hydration number is six. All other features of $g_{\mathrm{LiO}}(r)$ and $g_{\mathrm{LiH}}(r)$ – especially the well pronounced second hydration shell – seem to agree also as far as can be judged from their drawings; with one exception: The height of the first peak in $g_{\mathrm{LiO}}(r)$. The MCY potential leads to a less narrow Li^+-water first neighbor distribution ($g_{\mathrm{LiO}}(r_{\mathrm{M1}}) \approx 10$) than the ST2 model with its four tetrahedrally arranged point charges. A study of pure water with the MCY potential by Impey, Klein and McDonald [14] shows a less pronounced first peak in $g_{\mathrm{OO}}(r)$ than with the ST2 potential and is thus in better agreement with the experiments [15]. But for other properties the ST2 model leads to better results in comparison with experimental values [14]. Therefore, it remains open which of the two potentials gives a better overall description of water and aqueous solutions.

In the literatur no $g_{\mathrm{IO}}(r)$ and $g_{\mathrm{IH}}(r)$ – as shown in Fig. 1 (Table 1) – are reported which can be used for comparison, neither from diffraction measurements nor from computer simulations. (Preliminary results given in one of our previous papers [5] can not be used for comparison as the LJ parameters employed in the iodide ion-water pair potential proved to be inadequate). The iodide ion-water first neighbor distances determined from x-ray measurements on LiI [1], NH_4I [2] and NaI [3] solutions fall in the range 3.60 – 3.69 Å in agreement with the value of 3.68 Å calculated here. The measurements lead to hydration numbers between 6 and 8.8 while from the simulation a value of 8.7 results. A detailed comparison of $g_{\mathrm{IO}}(r)$ with newly performed x-ray measurements on a 2.2 molal LiI solution is given in the subsequent paper [8].

The length of the simulation of 10 ps provided for the first time the chance to calculate ion-ion RDFs with a certain degree of reliability. They are shown together with the running integration numbers in Figure 2. The curves are drawn from a histogram with an increment of 0.02 Å, therefore the relatively strong noise. The same increment has been used for the ion-oxygen and ion-hydrogen RDFs (Fig. 1) thus allowing a judgement on the relative statistical uncertainty. $g_{\mathrm{II}}(r)$ and $g_{\mathrm{LiI}}(r)$ start at distances where the two ions are linked by just one water molecule in a geometry – as discussed below – where a hydrogen atom is directed towards an anion and a cation is positioned in a lone pair direction. It can be calculated from $g_{\mathrm{LiLi}}(r)$ that the nearest approach (about 5 Å) of two Li^+ is somewhat less than the distance which results if they are separated by two water molecules in the proper geometry. The appearance of peaks in $g_{\mathrm{LiLi}}(r)$ and $g_{\mathrm{LiI}}(r)$ at slightly above 5 Å results from a configuration where two Li^+ are linked by one water each to the same I^-, and at the same time these two Li^+ are separated by two water molecules. This configuration existed in the simulation over the whole run of 10 ps. Obviously such an arrangement is rather stable, but one might expect that at significantly longer simulation times the two peaks and the following minima will disappear. From the running integration numbers it can be seen that in the average almost six out of the eight I^- in the basic cube are inside the inscribed sphere (about half of the volume of the cube) centered at a Li^+ and vice versa. In the case of the like ions there are in the average only 2.5 out of seven in the inscribed sphere. This is a not unreasonable distribution of the ions. It can be deduced from $n_{\mathrm{LiLi}}(r)$ and $n_{\mathrm{LiI}}(r)$ at about 6 Å that besides the configuration of one I^- and two Li^+ described above there are no further Li^+ nearer than 6.5 Å to each other, but that there are two more I^- – from the remaining seven – linked to a Li^+ by just one water molecule.

In Fig. 3 $g_{OO}(r)$, $g_{OH}(r)$ and $g_{HH}(r)$ for the water molecules in the 2.2 molal LiI solution are compared with the corresponding radial distribution functions from a simulation of pure water (Section II). The characteristic data are given in Table 1. Although the technique and details of our simulation are somewhat different from the pure water simulation of Stillinger and Rahman [9], the RDFs do not differ significantly.

The height of the first peak of $g_{OO}(r)$ in the LiI solution is in the limits of error the same as for pure water. This result is different from other alkali halide solutions investigated where $g_{OO}(r_{M1})$ is always lower than in pure water. The reason for this different behavior of the LiI solution might be explained in the following way. Although about half of the water molecules in the 2.2 molal LiI solution belong to the first hydration shells of the ions, their influence on water-water first neighbor distance is rather small. The iodide ion – because of its size – does not disturb the distribution of the water molecules significantly. On the other side the octahedral arrangement of the water molecules in the first hydration shell of Li^+ [4] leads to an O-O distance very near 3 Å, the range of the first peak in $g_{OO}(r)$. The enhancement of these O-O distances exceeds the reduction through the excluded volume effect of the ions [16] and leads to an increase of $g_{OO}(r)$ at the far distance side of the first peak. It results in a larger number of nearest neighbors in the solution than in pure water as can be seen from the difference in $n_{OO}(r)$.

In $g_{OH}(r)$ the first peak in the case of the solution is strongly reduced compared with pure water. It can be expected that in the hydration water of I^- the first neighbor O-H distances will not be effected significantly by the ion as either an H-atom or the dipol moment vector is directed towards I^- and the lone pair orbitals are free to form hydrogen bonds with other water molecules. In the case of Li^+ the water molecules in the first hydration shell are strongly oriented with a lone pair orbital directed towards the ion. For geometric reasons, therefore, only one hydrogen bond can be formed and the contribution of the hydration water of Li^+ to $g_{OH}(r_{M1})$ is reduced to half. This can be seen directly from $n_{OH}(r_{M1})$. The reduction of this number from 2.1 in pure water to 1.7 in the solution (Table 1) is simply and almost quantitatively a consequence of the fact that nearly one out of four water molecules belongs to the first hydration shell of Li^+. As the relative height of the first peak in $g_{OH}(r)$ is obviously a consequence of an excluded volume effect it does not really lead to information about the water structure in the hydration shell of the ion and should, therefore, not be used as a measure of its increase or decrease [17]. The investigation of dynamical properties of the hydration shell water – as discussed for the LiI solution in a separate paper [18] – seems to be a better way to discuss these questions.

The difference in the height of the first peaks in $g_{HH}(r)$ between pure water and water in the solution is much less significant than in the case of $g_{OH}(r)$, as for geometrical reasons the excluded volume effect of the ions is much smaller.

B) Orientation of the Water Molecules

The average orientation of the water molecules in the hydration shells of the ions could be deduced from the relative distances of the first peaks in the ion-oxygen and ion-hydrogen RDFs (Fig. 1), in the same way as it is being done in the analysis of neutron diffraction data [19]. But the information from the MD simulation allows a direct calculation of the average orientation of the water molecules as a function of distance from the ion. The average value of $\cos\theta$ is shown in Fig. 4 for the lithium and the iodide ion. θ is defined as the angle between the dipole moment direction of the water molecule and the vector pointing from the oxygen atom towards the center of the ion.

In the case of lithium, $\langle\cos\theta\rangle$ is constant over the whole range of the first peak in $g_{LiO}(r)$ at -0.66 or $\theta = 131°$. Not only the average value is constant but also the distribution of $\cos\theta$ is very narrow for the water molecules in the first hydration shell of Li^+ as can be seen from Fig. 5, where the distributions of $\cos\theta$ for the water molecules in the first hydration shells of both ions are shown. The six nearest neighbor water molecules of Li^+ have a strong preference for a lone pair orientation towards the ion which is in the average only about six degrees off the linearity. This result is in good agreement with the neutron diffraction measurements by Enderby and Neilson [19].

In the case of the iodide ion, $\langle\cos\theta\rangle$ decreases from 0.60 to 0.17 over the range of the first peak

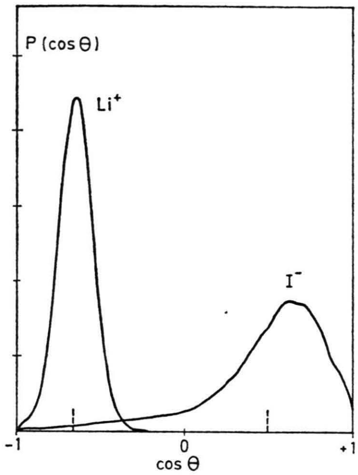

Fig. 5. Distribution of the orientation of the water dipoles in the first hydration shells of the lithium and the iodide ion for the 2.2 molal LiI solution. The dashed marks indicate the mean value of cos θ. The distributions are normalized and given in arbitrary units. The definition of θ is given in the caption of Figure 4.

in $g_{\mathrm{IO}}(r)$. Only the water molecules very near to the ion form a linear hydrogen bond. The distribution of $\cos\theta$ shows (Fig. 5) that even in the first hydration shell of I^- a number of water molecules have a very unfavorable orientation (negative values of $\cos\theta$) from an energetic point of view. This results most probably from the competitive influence of a Li^+ and an I^- on the orientation of a water molecule which belongs to the first hydration shell of both ions at the same time.

The preferential orientation of the water molecules decreases beyond the first hydration sphere rapidly for both ions except for the range of the second hydration shell of Li^+ where again a pronounced preferential orientation exists. It should be mentioned that $\langle\cos\theta(r)\rangle$ changes its sign for both ions at a distance of about 7 Å, a result which is significantly different from the preliminary data published previously [5]. This effect could be artificial, i. e. caused by the "shifted force potential" employed in this simulation. It reduces the ion-water forces to zero at the cut-off distance thus allowing neighboring water molecules to govern the orientation leading to an unfavorable orientation relative to the central ion.

The average value of the cosine of the angle θ_{ww} between the dipole moment directions of two water molecules in the 2.2 molal LiI solution and in pure water is shown in Fig. 6 as a function of distance between the two oxygen atoms. For the LiI solution $\langle\cos\theta_{\mathrm{ww}}(r)\rangle$ is different from pure water only in the range 3 – 7 Å. Both curves start at small distances at a value of 0.5 and show a sharp decrease over the range of the first peak in $g_{\mathrm{OO}}(r)$. Above 7 Å, $\langle\cos\theta_{\mathrm{ww}}(r)\rangle$ is slightly negative in both cases. From the range where LiI solution and pure water differ it can be deduced that in pure water the directional dipole moment correlation ranges significantly further than in the solution where the ions disturb the correlation.

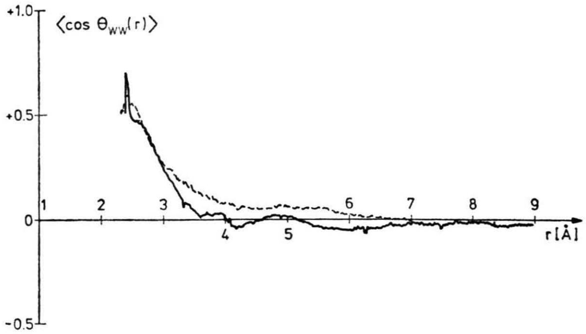

Fig. 6. Average value of the cosine of the angle θ_{ww} between the dipole moment vectors of two water molecules in the 2.2 molal LiI solution (full) and in pure water (dashed) as a function of distance between the two oxygen atoms.

In Fig. 7 the distribution $P(\cos\theta_{\mathrm{ww}})$ is given for the nearest neighbor water molecules (O-O distance $\leqq 3.6$ Å). The distribution is smeared out in the whole range of $\cos\theta_{\mathrm{ww}}$, the parallel orientation of the dipoles being the most probable orientation. In pure water, the mean value of θ_{ww} is 72° and increases slightly to 78° for the LiI solution. As $-1 \leqq \cos\theta_{\mathrm{ww}} \leqq 0.33$ is not compatible with a linear

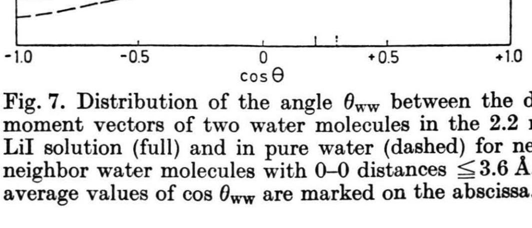

Fig. 7. Distribution of the angle θ_{ww} between the dipole moment vectors of two water molecules in the 2.2 molal LiI solution (full) and in pure water (dashed) for nearest neighbor water molecules with O–O distances $\leqq 3.6$ Å. The average values of cos θ_{ww} are marked on the abscissa.

hydrogen bond, the 45% increase of the probability in this range indicates increased bending of hydrogen bonds in the solution.

From the relative orientation of water dipoles one cannot conclude that the ST2 water model gives a too pronounced structure of nearest neighbors, although the height of the first peak of $g_{\mathrm{OO}}(r)$ indicates it. The broad distribution of the relative orientation (Fig. 7) corresponds to a less pronounced structure of $g_{\mathrm{OH}}(r)$ and $g_{\mathrm{HH}}(r)$ (Fig. 2) in comparison to the experimental atomic RDF's of pure water [15]. Probably, the increased number of first neighbor water molecules in the MD calculations compared with the experiment is responsible for the broader distribution of relative orientation.

C) Average Potential Energy and Pair Interaction Energy Distribution

The average potential energy of a water molecule in the field of a lithium and an iodide ion are shown in Fig. 8 as a function of ion-oxygen distance. The $\langle V_{\mathrm{Iw}}(r)\rangle$ curve is significantly different from a previously reported one [5] because of an improvement in the Lennard-Jones parameters for I^- leading to a larger ion-oxygen nearest neighbor distance. Consequently the depth of the minimum is less pronounced. The position of the minimum coincides with the maximum in $g_{\mathrm{Iw}}(r)$ (Fig. 1) as has been found for all alkali halide solutions. The potential energy distribution $P_{\mathrm{Iw}}(V)$ – shown in Fig. 9 – reflects this minimum, resulting in a narrow relative maximum at about $-0.5\cdot 10^{-12}$ erg.

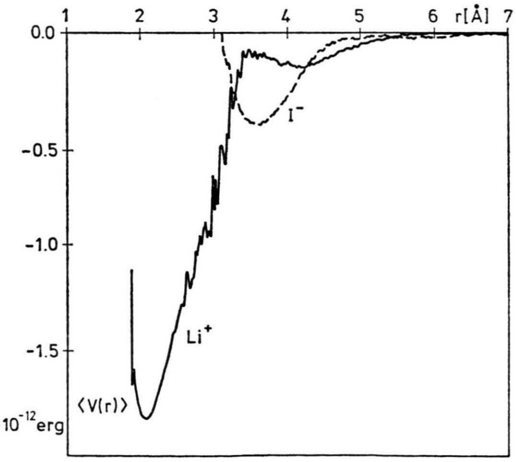

Fig. 8. Average potential energy of a water molecule in the field of the lithium ion (full) and the iodide ion (dashed) as a function of ion-oxygen distance in a 2.2 molal LiI solution.

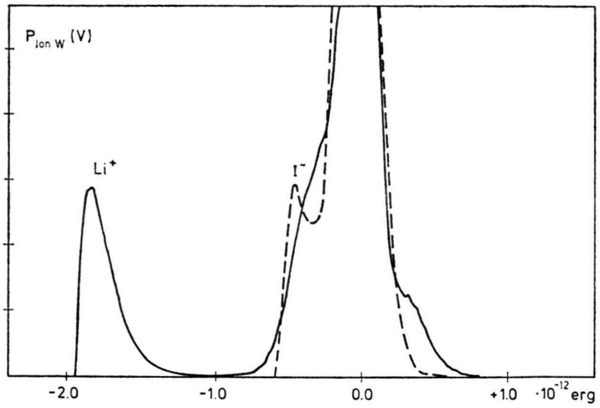

Fig. 9. Pair interaction energy distribution for Li^+-water (full) and I^--water (dashed) in a 2.2 molal LiI solution. $P(V)$ is given in arbitrary units.

In the potential energy distribution $P_{\mathrm{Liw}}(V)$ (Fig. 9) the maximum at $-1.8\cdot 10^{-12}$ erg is well separated and corresponds to the first hydration shell of Li^+. The small probability to find pair interaction energies between -1.4 and $-0.7\cdot 10^{-12}$ erg is a consequence of the very pronounced first minimum in $g_{\mathrm{LiO}}(r)$. The formation of the second maximum in $g_{\mathrm{LiO}}(r)$ is connected with a preferential orientation of the water molecules in this range (Fig. 5) which in turn results in a second minimum in the average potential energy as can be seen from Figure 8. In the potential energy distribution (Fig. 9) the shoulder at the negative energy side of the main maximum at the origin corresponds to the second maximum of $g_{\mathrm{LiO}}(r)$. But at the positive energy side of $P_{\mathrm{Liw}}(r)$ there appears also a shoulder, the corresponding energy values being nearly the same as the absolute values of the left side shoulder. This implies that there exist some unfavorably oriented water molecules at a distance at about 4 Å from Li^+. This unfavorable orientation to Li^+ is forced by the influence of their nearest neighbors. The positive energy shoulder can partially result from the two Li^+ near to each other as can be seen from the peak above 5 Å in $g_{\mathrm{LiLi}}(r)$ and discussed above (Figure 2). This means that water molecules in the second hydration shell of one Li^+ belong at the same time to the first hydration shell of the second Li^+ and this results, of course, in a unfavorable orientation relative to the first Li^+. The existence of positive and negative potential energies in the range of the second hydration shell can also explain the rather small average potential energy in this range (Figure 8).

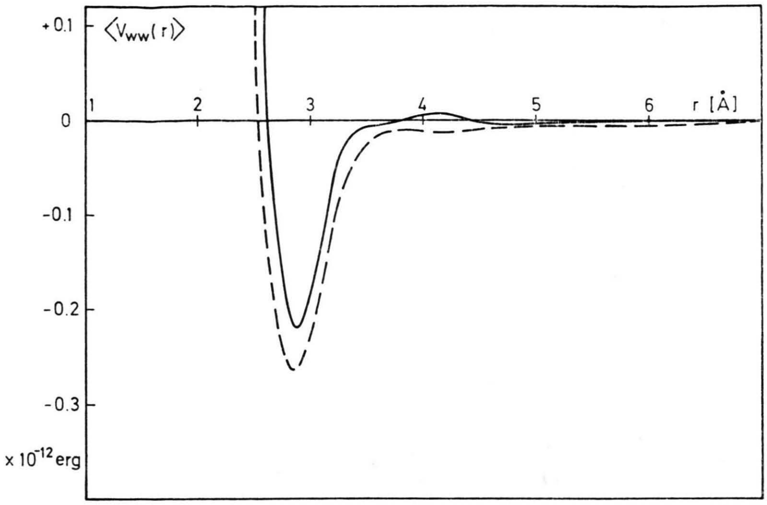

Fig. 10. Average potential energy of the water molecules as a function of oxygen-oxygen distance in a 2.2 molal LiI solution (full) and in pure water (dashed).

The average potential energy of two water molecules as a function of distance $\langle V_{\mathrm{ww}}(r)\rangle$ in the 2.2 molal LiI solution is compared with the one for pure water in Fig. 10, and the corresponding pair interaction energy distributions $P_{\mathrm{ww}}(r)$ are shown in Figure 11. Obviously the ions force the water molecules into orientations relative to each other which are energetically less favorable. This can be seen from $\langle V_{\mathrm{ww}}(r)\rangle$ where the minimum is less pronounced than in pure water and positive energies appear at about 4 Å. In $P_{\mathrm{ww}}(r)$ there exists a positive shoulder – almost a second peak – which has also been found before in other alkali halide solutions [5]. Its energy value of about $+2.8\cdot 10^{-13}$ erg indicates that there exist nearest neighbor water molecules with an energetically extremely unfavorable orientation. At the negative energy side of Fig. 11 the maximum for the solution is slightly shifted to less negative energies when compared with pure water, in accordance with the less pronounced minimum in $\langle V_{\mathrm{ww}}(r)\rangle$ (Figure 10). The decrease in the relative height of the maximum and the minimum in the case of the solution indicates the disturbance of the nearest neighbor water structure by the ions.

D) Heat of Solution

The integrated energies of hydration, defined by

$$V_{\alpha}^{\mathrm{h}}(r) = 4\pi\varrho_0\int_0^r g_{\alpha\mathrm{w}}(r')\,\langle V_{\alpha\mathrm{w}}(r')\rangle\, r'^2\,\mathrm{d}r'\,,$$

are drawn in Fig. 12 as a function of distance. There is a significant difference (almost a factor of two) in

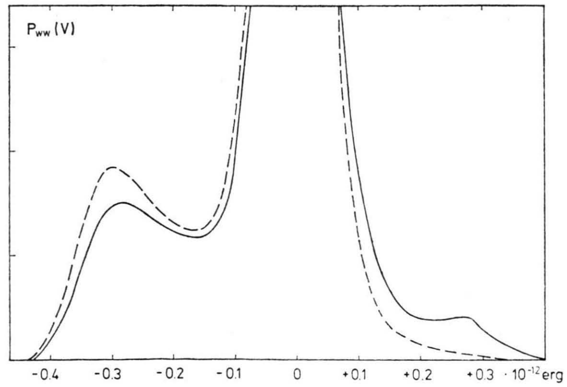

Fig. 11. Pair interaction energy distribution for water-water in a 2.2 molal LiI solution (full) and in pure water (dashed). $P(V)$ is given in arbitrary units.

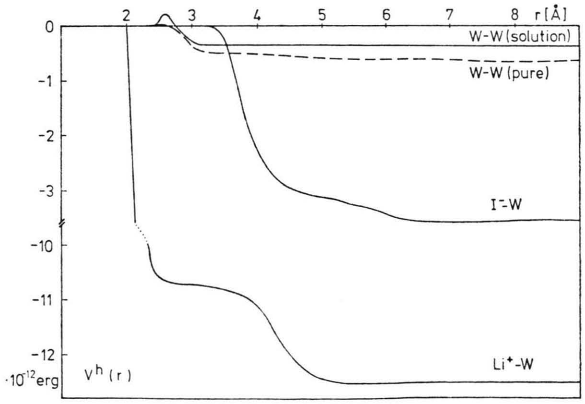

Fig. 12. Integrated energy of hydration for ion-water and water-water interactions in the 2.2 molal LiI solution (full) and in pure water (dashed) as a function of ion-oxygen or oxygen-oxygen distances.

the hydration energy between the water in the solution and pure water. This difference results partly from an excluded volume effect of the ion and partly from the fact that the ions force the water molecules into energetically rather unfavorable orientations relative to each other, leading even to positive energies at small distances. The second hydration shell of Li^+ contributes only about 15% to the total hydration energy and there is no further contribution beyond 5.5 Å. In the case of I^- the first hydration shell ends at about 4.5 Å with again about 85% of the total hydration energy. In the range 4.5 – 6.5 Å, $g_{IO}(r)$ is slightly above one, the average orientation (Fig. 4) is energetically favorable and even in $\langle V_{Iw}(r) \rangle$ a negative contribution is recognizable accounting for the remaining 15%.

The potential energies resulting from the simulation for the subsystems provide the possibility to calculate the heat of solution. The following values (kcal/Mol) have been found for the 2.2 molal LiI solution and pure water:

	Ions	Li^+-water	I^--water	Solvent	Pure water
$-E_{pot}$	76.0	178.5	51.1	133.6	246.3

Together with the lattice energy of LiI of – 176 kcal/Mol, a heat of solution of – 16.9 kcal/Mol results from the simulation, which has to be compared with an experimental value of – 14.3 kcal/Mol [20]. The result from the MD simulation is a small difference of two big numbers and it can not be excluded that the good agreement with the experimental value is partly fortuitous.

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