The Second Hydration Shell of Li^+ in Aqueous LiI from X-Ray and MD Studies

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Indications from a molecular dynamics simulation of a 2.2 molal LiI solution of the existence of a second hydration shell of Li^+ have been checked by an x-ray investigation of the same solution. The scattering data are analysed via partial structure functions and radial distribution functions which have been obtained from a model fitted to the total structure function. Experiment and simulation agree on first neighbor ion-water distances. An octahedral arrangement of six water molecules in the first hydration shell of Li^+ and additional twelve water molecules in the second shell have been verified by the experiment.

I. Introduction

In the preceding paper [1] the structural properties of a 2.2 molal LiI solution are reported, derived from a molecular dynamics (MD) simulation. The MD results strongly indicate the existence of a well defined second hydration shell around the lithium ion. Monte Carlo (MC) calculations by Fromm, Clementi and Watts on the hydration of a Li^+-F^- pair [2] and by Mezei and Beveridge on a Li^+ surrounded by 215 water molecules [3] also support the existence of a second hydration shell. As the ST2 water model [4] was employed in the MD simulation and a water-water pair potential derived from ab initio calculations [5] was used in the MC simulations the formation of a second hydration shell around Li^+ seems to be real and not introduced artificially by the description of the water-water interactions in the computer simulations.

The only diffraction experiments on LiI solutions reported in the literature are the x-ray measurements by Lawrence and Kruh [6]. The problem connected with an x-ray investigation of a LiI solution is the relatively small contribution to the scattering from the Li^+-water interaction compared with the water-water and I^--water ones. Therefore, Lawrence and Kruh did not draw any conlusions on the hydration shell of the lithium ion from their experiments. X-ray measurements on LiBr solutions by Licheri, Piccaluga and Pinna [7] and on LiCl solutions by Pálinkás, Radnai and Hajdu [8] as well as neutron diffraction studies on LiCl solutions by Narten, Vaslow and Levy [9], Ohtomo and Arakawa [10] and Enderby and Neilson [11] did not lead to information on the existence of a second hydration shell of Li^+ for various reasons. Their conclusions are restricted to the first hydration shell, the structure of which has been discussed in a previous paper [12].

The indications of the existence of a second hydration shell of the lithium ion by the computer simulations has led us to reinvestigate this question by x-ray measurements of a LiI solution, in spite of the problems connected with the strongly different contributions to the scattering from the various interactions. In the analysis of the scattering data various models have been employed. The results of the x-ray measurements are compared in detail with the ones from the MD simulation on the basis of structure functions and radial distribution functions.

II. X-Ray Measurements

The x-ray measurements of the 2.2 molal LiI solution were performed at 25 °C using transmission geometry with a flat monochromator in the primary beam. The plane – parallel windows of the thermostated specimen holder had been prepared from 100 μm thick plates of a quartz single crystal placed at a distance of 1.4 mm. At this thickness of the liquid layer and due to the high attenuation

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factor of the iodide ion for MoKα radiation a relatively high absorption was exhibited by the solution. The measurements extended over the range $0 \leqq k \leqq 15$ Å^{-1} with a scattering variable $k = (4\pi/\lambda) \sin\vartheta$, where λ is the wavelength of the incident radiation and 2ϑ the scattering angle. The measured intensities were collected in equidistant steps with an increment $\Delta k = 0.1$ Å^{-1} and 10^5 impulses at each point. The resulting statistical error has led to a relatively poor quality of the data at the highest scattering angles. Therefore, the data above $k = 12$ Å^{-1} were omitted for the structural interpretation, although all measured points were used in the elaboration of the data. Due to the special distance spectrum in the solution this limitation did not affect the quality of the treatment significantly. The measured intensities were corrected for background, polarization, absorption, and Compton scattering. The Compton intensities needed for the corrections were calculated with analytical formulas developed by Hajdu for water and the iodide ion [13] and by Pálinkás and Radnai for Li^+ [14]. The absolute scale was established by the method of Krogh-Moe [15]. The details of data processing and the correction procedure are described elsewhere [16].

The experimentel structure function, shown in Fig. 1, is given by

$$H_{\exp}(k) = \left[I(k) - \sum_{\alpha} x_a f_a^2(k)\right] \Big/ \left[\sum_{\alpha} x_a f_a(k)\right]^2, \qquad (1)$$

where $I(k)$ is the corrected absolute, coherent intensity of the scattered beam and $f_a(k)$ and x_a are the scattering amplitude for a particle of type α and its mole fraction, respectively. The scattering amplitudes were used in an analytical form, the parameters of which were taken from the literature [14, 17]. A correction of the scattering amplitude for anomalous dispersion was carried out for the iodide ion, where it is significant.

III. MD Simulation

The simulation of the 2.2 molal LiI solution – described in detail in the preceding paper [1] – extended over 46 000 time steps, equivalent to a total elapsed time of about 10 ps. The average temperature was 305 K. The basic periodic cube contained 200 water molecules and 8 ions of each kind. The ST2 model for water was employed [4] and the ions were modelled as Lennard-Jones spheres with an elementary charge at the center.

The ion-ion contributions to the total structure function are relatively small in the k-range which is of interest here and have therefore been neglected in the comparison with the experimental structure function. The partial structure functions.

$$h_{aw}(k) = 4\pi \varrho_0 \int_0^{\infty} (g_{aw}(r) - 1) r \frac{\sin k r}{k} \, \mathrm{d}r, \qquad (2)$$

where ϱ_0 is the average number density of the particles, are calculated from the radial distribution functions $g_{aw}(r)$ as given in [1] and reproduced for comparison in Figures 4 and 5. The weighted $h_{aw}(k)$ are compared in Fig. 3 with the ones determined from the model fitted to the experimental structure function. The resulting total structure function

$$H_{\mathrm{MD}}(k) = \sum_{\alpha=1}^{3} H_{aw}(k) = \sum_{\alpha=1}^{3} c_{aw}(k) h_{aw}(k), \qquad (3)$$

where the $c_{aw}(k)$ are calculated from the mole fractions x_a and the scattering amplitudes $f_a(k)$ by

$$c_{aw}(k) = (2 - \delta_{aw}) \cdot x_a x_w f_a(k) f_w(k) \Big/ \left[\sum_{\alpha=1}^{3} x_a f_a(k)\right]^2, \qquad (4)$$

is compared in Fig. 1 with the experimentally determined structure function $H_{\exp}(k)$ and the one resulting from the model $H_{\mathrm{ML}}(k)$ fitted to $H_{\exp}(k)$.

IV. Discussion

A) The Total Structure Function

The comparison of the structure function calculated from the MD simulation (full line) with the experimental one (dots) in Fig. 1 shows some discrepancies.

The first peak in $H_{\exp}(k)$ has a shoulder at k-values above that of the maximum – coinciding with the peak in $H_{\mathrm{MD}}(k)$ – contrary to the x-ray measurements on a LiCl solution at the same concentration [8] where a double peak is present, which results from long range water-water interactions [18]. This difference is connected with the change of the anion – nearest neighbor water distances in replacing Cl^- by I^-. The reason why there is no peak at $k = 2$ Å^{-1} in $H_{\mathrm{MD}}(k)$ becomes clear from Figure 3. The water-water and iodide-water interactions have similar weights in x-ray measurements on this solution, compared with the relatively small weight of the lithium-water interac-

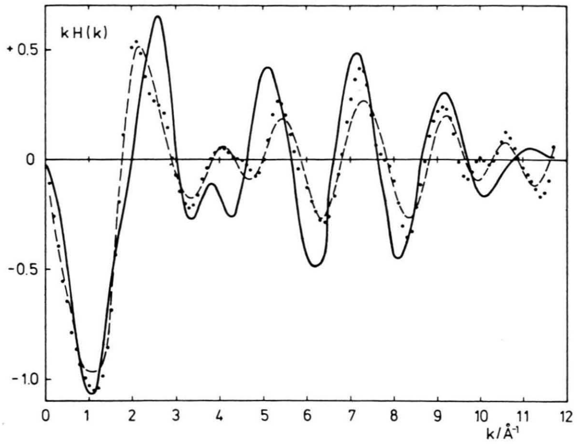

Fig. 1. Comparison of the total structure functions for a 2.2 molal LiI solution from experiment (dots), a model fit (dashed) and the MD simulation (full).

tions. As the ST2 model with its four point charges exaggerates the nearest neighbor water-water contributions, its negative part compensates the iodide-water part in the range in question.

The discrepancies in the ranges $3.0-4.5$ and $10-12\,\text{Å}^{-1}$ result also from interferences of the iodide-water and water-water partial structure functions as shown in Fig. 3. These interferences are very sensitive to the weights of the two contributions.

Differences between the x-ray measurements and the MD simulation can be seen more clearly from the total radial distribution function $G(r)$ shown in Fig. 2 and derived by Fourier transformation from the total structure functions as given in Figure 1. The positions of the three main peaks representing ion-water and water-water nearest neighbor distances are in good agreement as are the heights of the ion-water peaks, while disagreement exists in the water-water case. The difference between the description of the water structure by the ST2 model and the measurements has been demonstrated before by Pálinkás, Kálmán and Kovács [19].

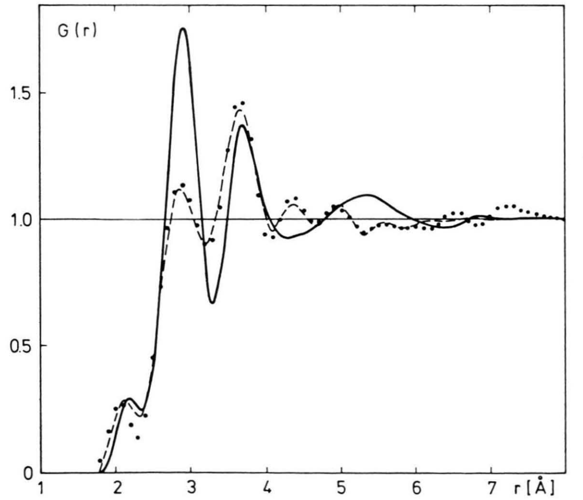

Fig. 2. Total radial distribution functions for a 2.2 molal LiI solution from experiment (dots), a model fit (dashed) and the MD simulation (full).

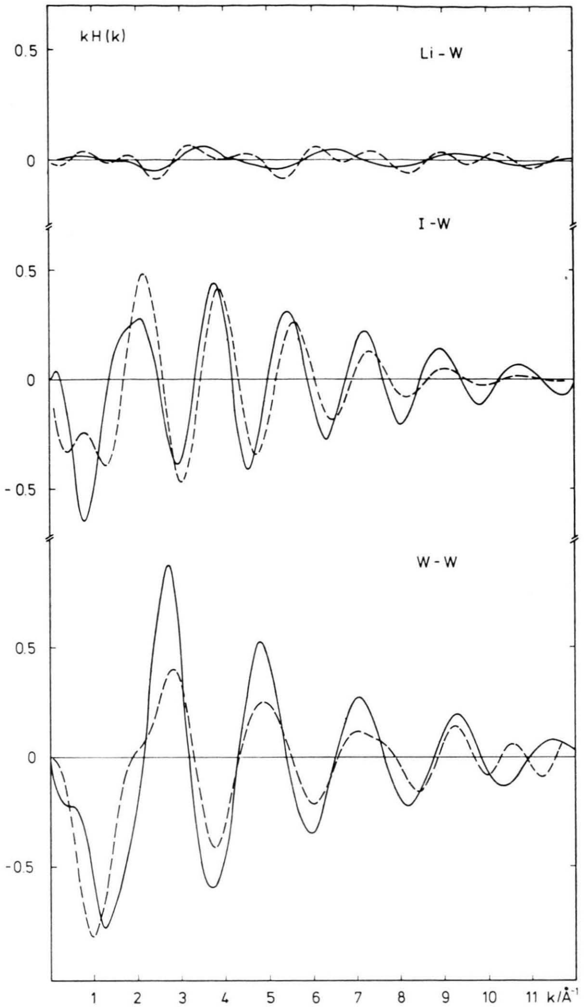

Fig. 3. Weighted partial structure functions for a 2.2 molal LiI solution from the MD simulation (full) and a model fitted to the experimental structure function (dashed).

The experimental $G(r)$ shows a small splitted maximum in the range $4-5$ Å which generally appears in aqueous solutions. In pure water it is not splitted. In general the discrepancies between simulation and experiment in $G(r)$ in the range $4-6$ Å are difficult to discuss. In this range contribute the second maxima and minima of the ion-water and water-water radial distribution functions. The complications arise because of the strongly different weights with which the $g_{\alpha w}(r)$ contribute to the total $G(r)$. In order to be able to compare simulation results and experiment in more detail, the total structure function is decomposed into partial structure functions with the help of a model, as it is usual in the analysis of scattering data. Finally the $g_{\alpha w}(r)$ calculated by Fourier transformation from the partial structure functions are compared with the MD results which are reported in the preceding paper [1].

B) Model

The partial structure functions $h_{\alpha w}$ can be derived from the x-ray measurements only by fitting a model to $H_{\exp}(k)$. The model which has led to the best fit, where the quality of the fit is measured by

$$\sigma^2 = \frac{1}{N-1} \sum_{i=1}^{N} [k_i H_{\exp}(k_i) - k_i H_{\mathrm{ML}}(k_i)]^2 , \qquad (5)$$

can be described in the following way:

1) Two hydration shells are assumed around the Li^+ with 6 water molecules in an octahedral arrangement in the first shell [12] and 12 in the second shell. To each of the inner water molecules w_1 two outer ones w_2 are correlated. The independent parameters used in the refinement are $r_{\mathrm{Li}w1}$, $r_{\mathrm{Li}w2}$, r_{w1w2}, r_{w2w2} and six root mean square deviations defined as $l_{\alpha w} = \langle (\langle r_{\alpha w} \rangle - r_{\alpha w})^2 \rangle^{1/2}$.
2) The hydration number $\mathrm{CN_I}$ of I^- is not fixed and consequently no symmetry is assumed for the hydration shell. The independent parameters are $r_{\mathrm{I}w}$, $l_{\mathrm{I}w}$ and $\mathrm{CN_I}$.
3) A tetrahedral arrangement is assumed for the solvent structure, in analogy to a previously employed First Neighbor Model (FNM2) [8, 20].
4) An additional continuum distribution is assumed for each of the three discrete contributions, with parameters $r^0_{\alpha w}$ and $l^0_{\alpha w}$.

Table 1. The number of water molecules in the first and second shell of Li^+ assumed in the four different models (A—D) employed in the analysis of the scattering data for the 2.2 molal LiI solution together with the quality of the best fit σ^2 as defined in (5).

model	1. shell	2. shell	$\sigma^2 \cdot 10^3$
A	6	12	3.07
B	4	8	4.18
C	6	0	5.33
D	4	0	5.70

Because of our special interest in the hydration of Li^+ three additional models (B, C, D) have been checked, the modifications being connected with the hydration of Li^+, and consequently with changes in the number of solvent aggregates. The descriptions of the models together with their σ^2 are given in Table 1. In the models B and D a tetrahedral arrangement is assumed for the four water molecules in the first hydration shell.

The parameters resulting from the best fit (model A) are given in Table 2. Model C and D, treating only the first neighbor hydration of Li^+, resulted in similar σ^2, while an intermediate value is found for model B. Obviously, the introduction of the second shell of Li^+ results in a significant improvement in the description of the structure. No significant variations were detected for the different models as far as the cation-water and anion-water distances are concerned.

The weighted partial structure functions derived from the x-ray measurement on the basis of model A are compared in Fig. 3 with the ones from the MD simulation. Differences are discussed below in connection with the radial distribution functions.

Table 2. Structural parameters in Å for the 2.2 molal LiI solution from the fit of model A to the experimental structure function. The value for $r_{w_1w_1}$ in parenthesis results from the octahedral geometry of the first hydration shell of Li^+ with $r_{\mathrm{Li}w_1} = 2.10$ Å.

α	$r_{\alpha w_1}$	$l_{\alpha w_1}$	$r_{\alpha w_2}$	$l_{\alpha w_2}$	$r^0_{\alpha w}$	$l^0_{\alpha w}$
Li	2.10 (2)	0.12 (4)	4.41 (4)	< 0.13	6.3 (1)	< 0.4
I	3.63 (2)	0.26 (4)	—	—	4.3 (1)	1.2 (2)
w_1	(2.97)	0.20 (2)	2.72 (2)	0.10 (2)	—	—
w_2	—	—	4.35 (3)	< 0.10	—	—

C) Radial Distribution Functions

From the partial structure functions – shown in Fig. 3 – $g_{\mathrm{Li}w}(r)$, $g_{\mathrm{I}w}(r)$ and $g_{ww}(r)$ are calculated by a Fourier transformation and compared in Figs. 4 and 5 with $g_{\mathrm{LiO}}(r)$, $g_{\mathrm{IO}}(r)$ and $g_{\mathrm{OO}}(r)$ from the MD simulation.

In spite of the small weight of the Li-w interactions in x-ray measurements, the assumption of a second hydration shell in model A not only leads to the best fit (Table 2), but in many details there is agreement between the MD simulation and the experiment as can be seen from Figure 4. The positions of the two maxima in $g_{\mathrm{Li}w}(r)$:

	Exp	MD
r_{M1}	2.10 (2)	2.12 (2)
r_{M2}	4.41 (4)	4.19 (3)

coincide in the limits of error as far as r_{M1} is concerned and deviate only by 0.2Å in the position of the second maximum. The octahedral arrangement of the six water molecules in the first hydration shell – demonstrated in a previous paper [12] – has been confirmed. Even the number of water molecules in the second hydration shell are the same as can be seen from $n_{\mathrm{Li}w}(r)$ at $r = 5$ Å. The strongly different heights of the second peak and the discrepancy in the range 4.5 – 6.5 Å result from a limitation of the model. This difference also leads to the relative poor agreement in the partial structure functions where the double maxima are not reproduced by the MD simulation. It is interesting to note that the distances between the water molecules in the first and second hydration shell of 2.72 Å (Table 2) are very similar to the ones in aqueous solutions of Mg^{2+}, Al^{3+} and Cr^{3+} where the existence of a second hydration shell has been established by x-ray measurements [21 – 23]. It has been proposed [24] that these short water-water distances exist when $s > 0.4$ with s defined as z/CN, where z is the charge and CN the number of the water molecules in the first hydration shell of the ion. This simple relationship is not confirmed here as in this case $s = 0.17$. From the distances r_{w1w2} and r_{w2w2} the average value of the angle $\widehat{w_2 w_1 w_2}$ can be calculated to be 106°, compatible with the formation of linear hydrogen bonds between the water molecules in the first and second hydration shell.

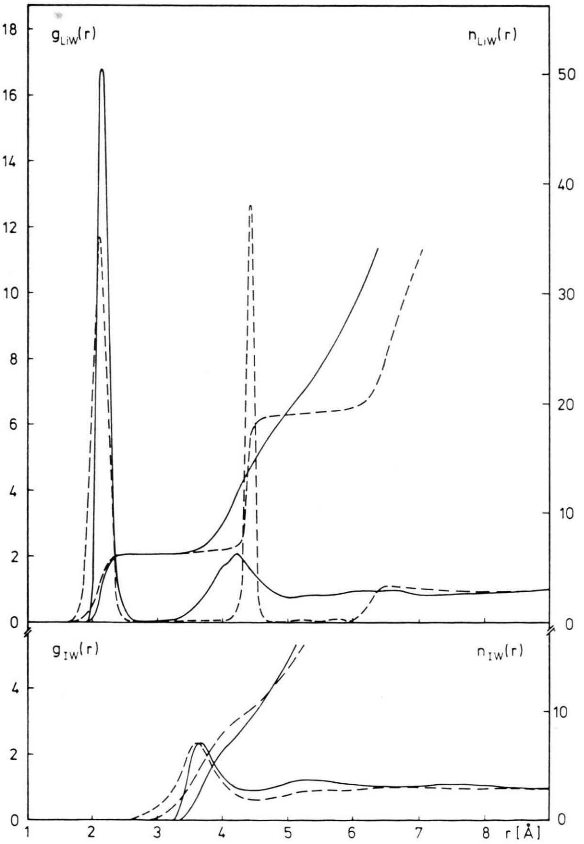

Fig. 4. Ion-water radial distribution functions and running integration numbers for a 2.2 molal LiI solution from the MD simulation (full) and a model fitted to the experimental structure function (dashed).

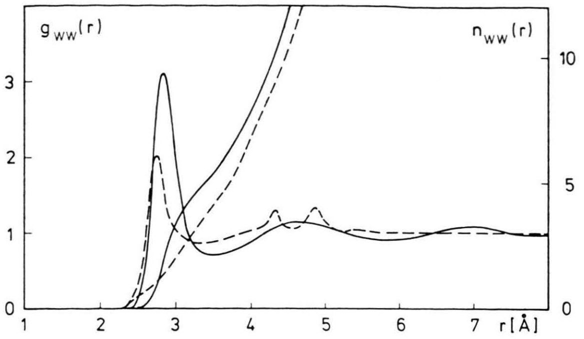

Fig. 5. Water-water radial distribution functions and running integration numbers for a 2.2 molal LiI solution from the MD simulation (full) and a model fitted to the experimental structure function (dashed).

There is good agreement between experiment and simulation for $g_{\mathrm{I}w}(r)$ as shown in Figure 4. Only a small difference exists in the position of the first maximum (3.63 as compared with 3.68 Å) and in the range 4 – 6.5 Å. Both differences result from the small discrepancies in range of the first peak and the positions of the zeros in the partial structure functions (Figure 3). The quality of the fit improved significantly when the symmetry in the hydration shell of I^- was given up in agreement with the MD simulation where no hydration shell structure could be detected [12]. The fit resulted in a hydration number of 6.9 compared with 8.7 from the simulation, but the beginning of the continuum distribution near to the first peak ($r^0_{Iw} = 4.3$; Table 2) compensates this lack of water molecules in the discrete part and at a distance of $r = 5$ Å the running integration numbers $n_{Iw}(r)$ are the same as can be seen from Figure 4. This behavior of I^- is strongly different from what has been found for Cl^- where $r^0_{Clw} = 6.0$ [18] and indicates more loosely bound water molecules in the hydration shell of I^- as expected from the different size of the two ions. Residence times and self-diffusion coefficients calculated from the MD simulations confirm this finding [25].

The differences in $g_{ww}(r)$ – shown in Fig. 5 – in the first peak and in the amplitudes of the partial structure function (Fig. 3) seem to result from limitations of the ST2 model as discussed above in connection with the total structure function. For a discussion of the solvent structure the parameters from all four models can be employed. They are given in Table 3. It is obvious from these numbers that in the solution two distinct nearest neighbor water distances exist outside the first hydration shells of the ions. A short one between the first and second hydration shell of Li^+ with $r_{w1w2} \approx 2.70$ Å and a longer one for the water aggregates in the remaining solvent with r_{ww} between 2.91 and 2.99 Å (as for the hydration shell of I^- no symmetry is assumed; the water-water distances there do not appear as adjustable parameter). In the models C and D, where no second hydration shell of Li^+ is assumed there remains only the parameter r_{ww} as nearest neighbor distance, and necessarily an averaged distance results for the increased amount of solvent water which is significantly smaller than r_{ww} in models A and B. The smaller value for σ^2 in the case of models A and B therefore indicates the existence of the two nearest neighbor solvent distances in the solution.

Table 3. Model parameters characterising the nearest neighbor distances of water molecules. ww refers to the tetrahedrally arranged solvent aggregates and M_w denotes their molal concentrations, while w_1 and w_2 refer to the water molecules in the first and second hydration shell of Li^+. The differences in the models A–D are given in Table 2.

Model	r_{ww}	l_{ww}	$r_{w_1w_2}$	$l_{w_1w_2}$	M_w
A	2.99 (2)	< 0.1	2.72 (2)	0.10 (1)	3.1
B	2.91 (2)	0.11 (5)	2.69 (2)	0.09 (1)	5.8
C	2.80 (2)	0.18 (3)	—	—	8.4
D	2.78 (2)	0.12 (3)	—	—	9.3

D) Concluding Remarks

The existence of a second hydration shell around the lithium ion, which was concluded from an MD simulation has been verified by x-ray measurements for a 2.2 molal LiI solution. Agreement between experiment and simulation has been found also for the distances of the first and second shell from Li^+ and the number of water molecules in the two hydration shells. The iodide ion – water radial distribution function from the MD simulation has been verified by the x-ray measurements. Some discrepancies exist in respect to $g_{ww}(r)$ which are attributed to limitations of the ST2 model.

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