Hydration Shell Structures in an $MgCl_2$ Solution from X-Ray and MD Studies

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Z. Naturforsch. **37a**, 1049—1060 (1982); received March 25, 1982

The results of a molecular dynamics simulation of a 1.1 molal aqueous $MgCl_2$ solution are compared with newly performed x-ray measurements. The structural properties of the solution are evaluated from the scattering data by a model fit to the experimental structure function. The comparison on the basis of fit parameters and partial structure functions shows an overall good agreement between experiment and simulation.

Detailed information on the structure of the hydration shells is deduced from the simulation and shown in form of density maps and angular distributions. It is demonstrated that the octahedral arrangement of the water molecules in the first hydration shell of Mg^{++} is strongly pronounced while it is only indicated in the case of Cl^-. A preferential arrangement in tetrahedral directions has been found for the nearest neighbor water molecules around a central water molecule with an asymmetry in respect to lone pair and hydrogen atom directions. In addition, the probability of finding water molecules at a given number of symmetry sites at the same time has been calculated.

I. Introduction

Structural information on aqueous $MgCl_2$ solution has been derived from diffraction measurements by Dorosh and Skryshevski [1], Albright [2] and Alves Marques and de Barros Marques [3]. The most recent x-ray investigations have been reported by Caminiti et al. [4]. For the evaluation of their scattering data they employed a model fitted to the structure function and derived from it the most detailed information on the structure of these solutions so far. In the preceding paper results of a molecular dynamics (MD) simulation of a 1.1 molal $MgCl_2$ solution are reported [5]. There is good agreement between experiment and simulation for all structural properties derivable from the x-ray data.

The detailed information on the structure of an aqueous electrolyte solution which can be calculated from an MD simulation goes significantly beyond that derived from x-ray measurements. The additional information is, of course, only reliable if the data which result unambiguously from the diffraction experiments are reproduced by the simulation. In order to perform this check to the most possible extent, new x-ray measurements on the $MgCl_2$ solution have been made and new, more sophisticated models have been employed in the analysis of the scattering data. Similar models have been used before in the investigation of an LiI solution [6].

In Sect. II measurements and simulation are compared on the basis of the structure functions and the total radial distribution functions. In Sect. III the model which has led to the best fit is introduced and the resulting fit parameters and partial structure functions are employed for a detailed comparison between x-ray measurement and simulation.

The deviation from the rigid geometry — assumed in the models for the analysis of x-ray scattering data — is for liquids only incompletely described by the root mean square deviations. Therefore, in Sect. IV the distortions of the anticipated symmetrical arrangements of the first hydration shells and the distribution of the water molecules around the symmetry positions have been calculated from the MD simulation. Finally, the probability of finding water molecules at a given number of symmetry sites at the same time has been calculated. From diffraction measurements only two particle correlations are accessible, there-

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fore information on such coincidence cannot be derived.

II. Structure Functions for the $MgCl_2$ Solution

A) X-Ray Measurements

The x-ray measurements of the 1.1 molal $MgCl_2$ solution were performed at 25 °C using transmission geometry with MoKα radiation. 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 data above $k = 12$ Å^{-1} were omitted for the structural interpretation, although all measured points were used in the elaboration of the data. Further details are given in a previously published paper [6].

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

$$H_{\exp}(k) = \left\{ I(k) - \sum_{\alpha} x_{\alpha} f_{\alpha}^{2}(k) \right\} \Big/ \left\{ \sum_{\alpha} x_{\alpha} f_{\alpha}(k) \right\}^{2}, \quad (1)$$

where $I(k)$ is the corrected absolute coherent intensity of the scattered beam and $f_{\alpha}(k)$ and x_{α} are the scattering amplitude for particle of type α and its mole fraction, respectively.

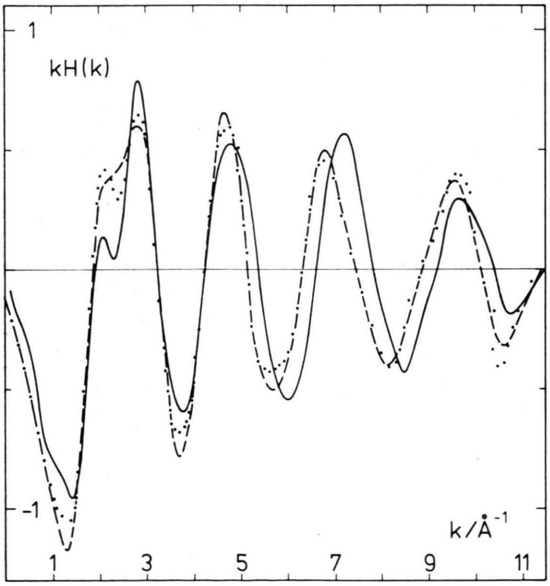

Fig. 1. Comparison of the total structure functions for a 1.1 molal $MgCl_2$ solution from experiment (dots), a model fit (dashed) and the MD simulation (full).

B) MD Simulation

The simulation of the 1.1 molal $MgCl_2$ solution — described in detail in the preceding paper [5] — on which the results reported here are based extended over 9100 time steps equivalent to a total elapsed time of about 2.3 ps. The average temperature of the solution was 308 K. The basic periodic cube contained 200 water molecules, 4 magnesium and 8 chloride ions. The Central Force (CF) model for water [7] was employed and the ion-water pair potentials have been determined from ab initio calculations.

The total structure function derived from the simulation is compared in Fig. 1 with the experimental one. The ion-water and water-water partial structure functions shown in Fig. 3 are calculated from the corresponding $g(r)$ by a Fourier transformation.

C) Total Structure and Radial Distribution Functions

In Fig. 1 the total structure function from the x-ray measurement is compared with the one derived from the MD simulation. There is good agreement. Only one significant difference exists, the positions of the zeros of $kH(k)$ do not coincide in the range $k > 5$ Å^{-1}. The reason for this discrepancy can be understood on the basis of the total radial distribution functions (RDF), which have been calculated from the structure functions through:

$$G(r) = 1 + \frac{1}{2\pi^2 \varrho_0 r} \int k H(k) \sin k r \, dk. \quad (2)$$

The total RDFs from the experiment and the simulation are compared in Figure 2. They describe the distance spectrum of the solution investigated. On the basis of crystallographic radii the short range part ($r < 3.5$ Å) can be assigned to the nearest neighbor cation-water, water-water and anion-water distances, while the long range part has to be attributed to second and third neighbor distances. There seems to be good agreement between experiment and simulation in the first neighbor water-water and anion-water distances at about 2.85 Å and 3.18 Å, respectively. A small difference exists in the first neighbor Mg^{++}-water distance.

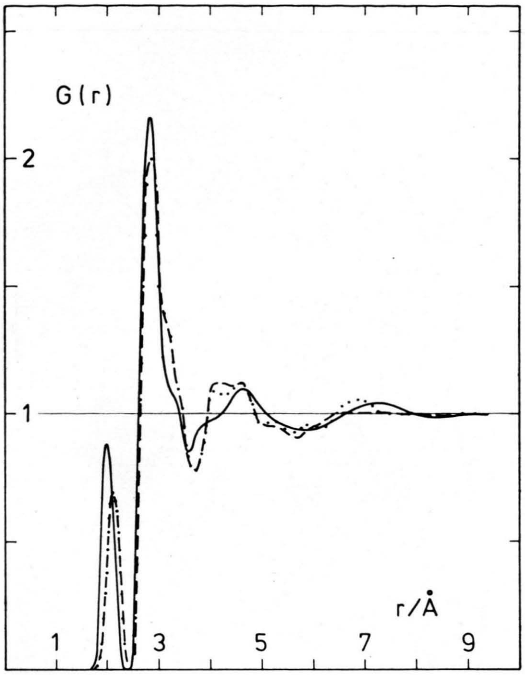

Fig. 2. Total radial distribution functions for a 1.1 molal $MgCl_2$ solution from experiment (dots), a model fit (dashed) and the MD simulation (full).

The differences in $G(r)$ in the range 4—5 Å seem to result mainly from differences in the second neighbor Mg^{++}-water distances, but a detailed analysis is not possible because first minima and second maxima of the various partial $g_{\alpha\beta}(r)$ contribute in this range.

In spite of the fact that the simulation provides the $g_{\alpha\beta}(r)$ a comparison has been made of the total RDFs, as on this level no approximations have to be introduced in the evaluation of the scattering data. In the following section models will be introduced which allow a more detailed analysis of the x-ray data as e.g. the evaluation of partial structure functions. The detailed information derived from the simulation then provides the possibility to check the models involved in this further analysis of the scattering data.

III. Geometrical Interpretation of the Total Structure Function

A) Models

In order to deduce further detailed information on the structural parameters separately for ion-water and wáter-water interactions in aqueous solutions, the total x-ray structure function has always to be decomposed with the help of models. This decomposition is achieved by fitting a model structure function $H_{\mathrm{mo}}(k)$ to the experimental one $H_{\mathrm{exp}}(k)$ by the variation of the parameters describing the various interactions. The quality of the fit is measured by

$$\sigma^2 = \frac{1}{N-1} \cdot \sum_{i=1}^{N} \{k_i H_{\mathrm{exp}}(k_i) - k_i H_{\mathrm{mo}}(k_i)\}^2 . \qquad (3)$$

The model which has led to the best fit in the case of the 1.1 molal $MgCl_2$ solution can be described in the following way:

1) Two hydration shells are assumed around the Mg^{++} with 6 water molecules in an octahedral arrangement in the first shell 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 are the distances $r_{\mathrm{Mgw_1}}$, $r_{\mathrm{Mgw_2}}$, $r_{\mathrm{w_1w_2}}$, $r_{\mathrm{w_2w_2}}$ and the corresponding four root mean square deviations $l_{\alpha\mathrm{w}}$ together with the $l^{(1)}_{\mathrm{w_1w_1}}$ and $l^{(2)}_{\mathrm{w_1w_1}}$ belonging to the distances $r^{(1)}_{\mathrm{w_1w_1}} = \sqrt{2}\, r_{\mathrm{Mgw_1}}$ and $r^{(2)}_{\mathrm{w_1w_1}} = 2 r_{\mathrm{Mgw_1}}$ as a consequence of the geometry of the model.

2) Six water molecules in an octahedral arrangement are assumed for the hydration shell of Cl^-. The independent parameters are r_{Clw}, l_{Clw} and the two l_{ww}.

3) A tetrahedral arrangement is assumed for the structure of the remaining water molecules with r_{ww} and the two l_{ww} as independent parameters.

4) For each of the three discrete contributions an additional continuum distribution is assumed with the parameters $r^0_{\alpha\mathrm{w}}$ and $l^0_{\alpha\mathrm{w}}$ ($\alpha = $ Mg, Cl, w).

In every model simplifications are incorporated which introduce features on which the resulting set of parameters may depend. In order to check some of the a priori introduced features of model A, three additional models (B, C, D) have been investigated. The description of the models together with their σ^2 values are given in Table 1.

The assumption of eight water molecules with a hexahedral symmetry in the first hydration shell of Cl^- without any other changes (model B) leads to a decrease of the quality of the fit by about 10%.

Table 1. The number of water molecules in the hydration shells of Mg^{++} and Cl^- assumed in the four different models (A–D) employed in the analysis of the scattering data for the 1.1 molal $MgCl_2$ solution together with the quality of the best fit σ^2 as defined by (3). The value in parenthesis gives σ^2 for the fit of model A to the structure function derived from the MD simulation.

Model	Mg^{++}		Cl^-	
	1. shell	2. shell	1. shell	$\sigma^2 \cdot 10^3$
A	6	12	6	4.6 (4.3)
B	6	12	8	5.2
C	6	12	N	6.0
D	6	0	6	5.6

In model C the hydration number of Cl was a free parameter and no symmetry was assumed for the hydration shell. Although the resulting hydration number was 5.9, this model has led to the worst fit indicating the necessity of symmetry assumptions. (Section III). Finally, in model D the assumption of a second hydration shell of Mg^{++} has been dropped. This leads to a decrease of the quality of the fit by about 20%. It should be mentioned that in the case of the LiI solution the assumption of a second hydration shell of Li^+ has led to an improvement of about 75% [6]. The model structure function and the resulting $G(r)$ are shown together with the experimental and MD ones for comparison in Figs. 1–2 as dashed lines.

B) Partial Structure Functions

On the basis of the parameters resulting from model A the model structure function has been decomposed into the cation-water, anion-water and water-water partial structure functions. They are compared in Fig. 3 with the ones calculated from the MD simulation by Fourier transformation of the RDFs, g_{MgO}, g_{ClO} and g_{OO} shown in the preceding paper [5]. The comparison of the partial structure functions together with the calculated fit parameters leads to more detailed information about the differences in the total structure functions than can be deduced from the total RDFs only. The origins of the differences can be localized more exactly and their relative contributions can be better determined. To provide a basis of comparison, model A was fitted to the MD total structure function as well as to the experimental one (Figure 1). The resulting parameters are given in Table 2.

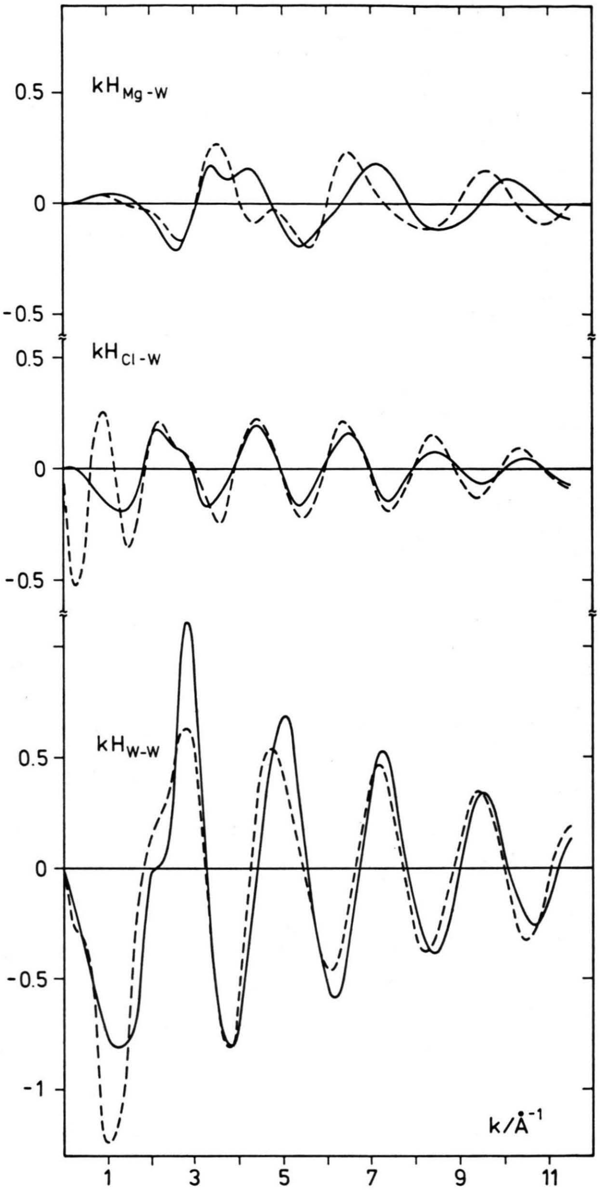

Fig. 3. Weighted partial structure functions for a 1.1 molal $MgCl_2$ solution from the MD simulation (full) and a model fitted to the experimental structure function (dashed).

The discrepancies between simulation and experiment in the Mg^{++}-water partial structure function result from small differences in the Mg^{++}-water distances for the first and second hydration shell. For the first neighbor distance the MD value of 2.00 Å is shorter than the experimental value of

Table 2. Structural parameters describing the hydration shells of the ions in a 1.1 molal $MgCl_2$ solution from the fit of model A to the experimental and the MD structure function. The values for r_{w1w1} in parenthesis result from the geometries assumed for the first hydration shells and the corresponding $r_{\alpha \mathrm{w}_1}$. Forthe parameters describing the water-water interactions [$r_{\mathrm{ww}} = 2.87(2)$, $l_{\mathrm{ww}} < 0.1$ and $l_{\mathrm{w_1w_1}} = 0.3(1)$] agreement has been found between experiment and MD in the limits of error.

α		$r_{\alpha \mathrm{w}_1}$	$l_{\alpha \mathrm{w}_1}$	$r_{\alpha \mathrm{w}_2}$	$l_{\alpha \mathrm{w}_2}$	$r_{\mathrm{w_1w_1}}$	$l_{\mathrm{w_1w_1}}$
Mg	Exp.	2.12 (1)	0.04 (1)	4.1 (1)	< 0.5	(3.00)	0.15 (2)
	MD	2.00 (1)	0.07 (1)	4.47 (5)	0.7 (1)	(2.82)	0.12 (3)
Cl	Exp.	3.16 (3)	0.15 (3)	—	—	(4.47)	0.32 (3)
	MD	3.10 (2)	0.27 (5)	—	—	(4.37)	0.40 (2)
w_2	Exp.	2.79 (3)	< 0.02	4.65 (5)	< 0.4	—	—
	MD	2.70 (2)	0.04 (3)	4.76 (5)	0.20 (5)	—	—

2.12 Å (Table 1). The second neighbor distance from MD is 4.47 Å compared to 4.1 Å from x-ray scattering. It must be added, however, that the g_{MgO} shows a broad unsymmetrical second shell peak whereas the model gives a relatively narrow symmetrical peak. This limitation of the model may suggest a greater difference in the partial structure functions from the fit parameters than actually occurs.

There is very good agreement between the simulated and the experimental Cl^--water partial structure function except for the peak at a k-value of about 1 $Å^{-1}$. This agreement is not to be expected if we compare the fit parameters which give values of 3.16 Å (x-ray) and 3.10 Å (MD). But g_{ClO} — as the basis of the MD partial structure function — shows a first neighbor peak at 3.18 Å in accordance to the x-ray value.

The discrepancy in the range of $k \approx 1$ $Å^{-1}$ has to be attributed to limitations of the model. It seems to result from deficiencies in the description of the water-water interactions, which lead to the strongly negative peak in kH_{ww} at $k = 1$ $Å^{-1}$. In order to achieve agreement with the experimental total structure function the model introduces this short peak in the Cl^--water partial structure function for compensation.

There is again good agreement between experiment and simulation in the water-water partial structure function except for the strong negative peak at $k = 1$ $Å^{-1}$ discussed in the preceding paragraph. Small differences in the positions where $kH_{\mathrm{ww}}(k)$ is zero result from differences in the water-water nearest neighbor distances, so small that they can hardly be seen in the total RDFs.

In the water-water partial structure function we have contributions from bulk water and from hydration shell water of the ions. Because it is difficult to assign the differences to the fit parameter of Table 2, we discuss only the mean values. From the MD g_{OO} we get a first neighbor distance of 2.82 Å whereas the structure functions suggest a slightly greater experimental value between 2.85 Å and 2.90 Å.

The discussion of the partial structure functions shows that the discrepancies between simulation and experiment in the total structure function (Fig. 1) in the range $k > 5$ $Å^{-1}$ result mainly from small differences in the Mg^{++}-water first and second neighbor and water-water nearest neighbor distances.

The parameters found in this work from the fit of model A to the experimental structure function of the 1.1 molal $MgCl_2$ solution are in very good agreement with the results of Caminiti et al., although they used a different experimental technique and a different model for the evaluation of their x-ray scattering data. Therefore, the small differences found here between experiment and simulation have to be attributed to insufficiencies in the ion-water and water-water pair potentials employed in the simulation. But the overall good agreement confirms strongly the reliability of the conclusion drawn from the MD calculations on the symmetries of the hydration shells in the following section; results which cannot be deduced so far from experimental investigations.

C) Properties of the Mg^{++}-Hydration Shells

The parameters from the x-ray experiment indicate a shorter mean distance $r_{\mathrm{w_1w_2}}$ of the water molecules in the first and second hydration shell of Mg^{++} than the mean water-water distance r_{ww} outside the hydration shells (Table 2). The same

	α	$r_{\alpha w_1}$	$l_{\alpha w_1}$	$l_{w_1 w_1}$	$r_{\alpha w_2}$	$l_{\alpha w_2}$	$l_{w_2 w_2}$
Exp.	Mg	2.12 (1)	0.04 (1)	0.15 (2)	4.1 (1)	< 0.5	< 0.4
	Li	2.10 (2)	0.12 (4)	0.20 (2)	4.41 (4)	< 0.13	< 0.1
MD	Mg	2.00 (1)	0.07 (1)	0.12 (3)	4.47 (5)	0.7 (1)	0.20 (5)
	Li	2.12 (2)	0.14 (4)	0.19 (3)	4.19 (3)	0.14 (5)	< 0.1

Table 3. Comparison of the parameters in Å describing the first and second hydration shell of Mg^{++} in a 1.1 molal $MgCl_2$ solution and of Li^+ in a 2.2 molal LiI solution from x-ray measurements and MD simulations.

result is obtained from the MD simulation together with a more detailed information about the distribution of the distances.

In Fig. 4 the radial distribution function g_{OO} from the MD simulation is shown. The second RDF g^*_{OO} (dashed curve) gives in the range shown in Fig. 4 the contribution of $w_1 - w_2$ to g_{OO}. From g^*_{OO} an average number of two w_2-neighbors of w_1 within a distance of 3.0 Å is calculated. The distance $r_{w_1 w_2}$ from g^*_{OO} is 2.72 Å, that is 0.1 Å shorter than the mean water-water distance of 2.82 from g_{OO}. There is good agreement with the distance $r_{w_1 w_2}$ from model A, whereas the distribution is more spread in g^*_{OO} than indicated by $l_{w_1 w_2}$.

Such shortened hydrogen bonds have been found also in aqueous solutions with Li^+ and other manifold charged cations by x-ray investigations and — in the case of Li^+ — by MD simulation [4, 6, 8, 9, 10]. The reason for this short water-water distance is not quite clear. It is surely connected with the charge of the cation. But a simple description only by the charge of the ion and the number of water molecules in the first hydration shell as proposed in literature [11] fails in the case of $MgCl_2$, as it did in the case of LiI [6].

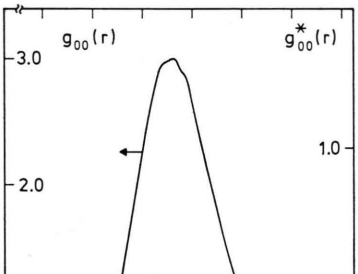

Fig. 4. Oxygen-oxygen radial distribution function $g_{OO}(r)$ (full) for all water molecules in the 1.1 molal $MgCl_2$ solution from the MD calculation. $g^*_{OO}(r)$ (dashed) is the contribution to $g_{OO}(r)$ for the special case where only distances are taken into account if one water molecule belongs to the first and the other to the second hydration shell of Mg^{++}.

It is interesting to compare the parameters for the first and second hydration shell of Mg^{++} with Li^+. They are given in Table 3. The values for Li^+ are taken from a previously published paper, where the ST2 model for water was employed in the simulation [12]. The $l_{\alpha w_1}$ and $l_{w_1 w_1}$ from experiment and simulation show undoubtedly that the octahedral arrangement of the water molecules in the first hydration of Mg^{++} is significantly less disturbed than that of Li^+, while the ion-water first neighbor distances are the same in the limits of error for both ions. This simply results from the two-fold charge of Mg^{++}. In the case of the second hydration shell it is the other way around. It is more pronounced for Li^+ than for Mg^{++}. This seems to be an effect of the counterions. The parameters describing the hydration shell of Cl^- and I^- are given in Table 4. The best fit in the case of the LiI solution had been found for the model where no symmetry had been assumed for the hydration shell of I^- and consequently instead of $l_{w_1 w_1}$ the hydration number N becomes a free parameter [6]. For comparison the parameters for Cl^- have been taken from the fit of model B (Table 1).

At the concentrations investigated the second hydration shells of the cations may overlap partly with the first hydration shells of the anion. The smaller Cl^- with its significantly better defined hydration shell seems to disturb the second hydration shell of Mg^{++} more than the larger I^- does in the case of Li^+ in spite of the higher concentration.

α	$r_{\alpha w}$	$l_{\alpha w}$	N_α
Cl	3.15 (2)	0.14 (3)	5.9
I	3.63 (2)	0.26 (4)	6.9

Table 4. Comparison of the hydration numbers N and the parameters in Å describing the first hydration shell of Cl^- in a 1.1 molal $MgCl_2$ solution and of I^- in a 2.2 molal LiI solution from x-ray measurements.

IV. Symmetries in the Hydration Shells

A) Projections on Reference Planes

The models employed in the evaluation of x-ray scattering of aqueous electrolyte solutions generally assume a symmetrical arrangement of the water molecules in the hydration shells. The quality of the fit decides which symmetry is the most probable. In the case of the 1.1 $MgCl_2$ solution an octahedral arrangement of the nearest neighbor water molecules resulted for Mg^{++} and Cl^- and a tetrahedral one for bulk water. Once it is decided upon the symmetry the root mean square deviations $l_{\alpha W}$ are a measure of the distribution of the water molecules around the symmetry positions. $l_{\alpha W_1}$ measures the distribution of the central particle — nearest neighbor distances, while $l_{W_1 W_1}$ indicates the deviation from the symmetrical arrangement of the first hydration shell. Inherent in the models is the assumption of a symmetrical distribution of the distances around the mean distance. Because of this assumption and the fact that the structure of the hydration shells of various ions — especially the larger ions — has contributions from different symmetry elements the geometrical interpretation of the root mean square deviations is often difficult.

The MD simulation provides the position of all particles as a function of time. In order to deduce from it the geometrical arrangement of the water molecules in the first hydration shells of Mg^{++} and Cl^- from a particle and time average, a coordinate system was introduced in the following way: The oxygen atom of the water molecule nearest to the ion is placed in the positive z-direction with the Mg^{++} or Cl^- forming the center of the coordinate system. Then the whole hydration shell is rotated around the z-axis until the oxygen atom of the water molecule second nearest to the ion is in the xz-plane in the positive x-direction. For both ions the six nearest neighbor water molecules are regarded as forming the first hydration shell. These numbers are based on the ion-oxygen RDFs shown in the preceding paper [5]. In order to reduce some

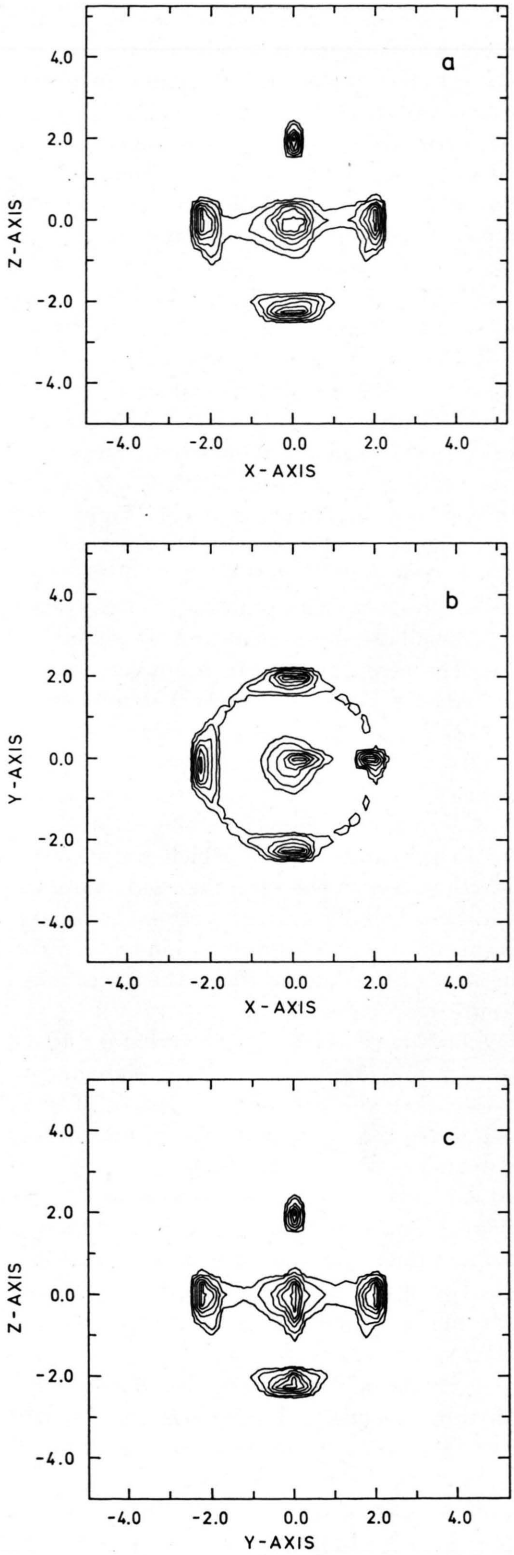

Fig. 5. Density maps of the projections of the oxygen atom position distributions of the six nearest neighbor water molecules around Mg^{++} onto the three planes of an ion centered coordinate system as defined in the text, from the MD simulation of a 1.1 molal $MgCl_2$ solution. The normalized contour lines increase in the sequence 0.01, 0.02, 0.04, 0.06, 0.08 and $\geqq 0.1$.

of the arbitrariness introduced by the coordinate system chosen the same procedure has been repeated six times by placing all water molecules once in the positive z-direction.

The registration of the water positions in the ion centered coordinate systems at 300 different times spread over the whole simulation run provides the three dimensional water distribution in the hydration shells. The projections onto the three planes of this coordinate system are shown for Mg^{++} in the form of density maps in Figure 5. The density profile of the water molecule positioned on the positive z-axes by the construction of the coordinate system reflects only the distribution of Mg^{++}-water distances (Figs. 5a and 5c). Similarly for the second water molecule, needed to establish the xz-plane, no variation in y-direction can occur (Figure 5b).

Figure 5 shows unambiguously that the six water molecules in the first hydration shell of Mg^{++} are arranged octahedrally with practically no distortion and only a small distribution around the octahedral positions. The comparison with a similar analysis for the hydration shell of Li^{+} [13] demonstrates that the octahedral arrangement of the water molecules around Mg^{++} is significantly more rigid. The ionic radii of Mg^{++} and Li^{+} are very similar and lead to water-water distances in the octahedrally arranged first hydration shell which are near the ones in pure water. In this case the rigidness of the first hydration shell depends not only on the charge of the central ion but also on the ion-oxygen distance because of the volume which the water molecules occupy.

The evaluation of the x-ray scattering data lead to Li^{+}-water and Mg^{++}-water first neighbor distances which are the same in the limits of error (Table 3), while the MD simulation results in ion-oxygen distances which differ by 0.1 Å. Therefore, the rigidness of the octahedron in the case of Mg^{++} might be slightly exaggerated. According to our experience with the simulation of NaCl solutions [14] the employment of the ST2 model in the LiI and of the CF model in the $MgCl_2$ solution should not lead to differences in this respect.

The density maps of Fig. 5 are reproduced in the form of three-dimensional drawings in the first column of Fig. 6 for comparison with the structure of the hydration shell of the chloride ion (second column). The peaks connected with the fixation of an oxygen atom in the positive z-direction are reduced. The octahedral arrangement of the water molecules in the hydration shell of Cl^{-} is significantly less pronounced than in the case of Mg^{++}. This difference can also be seen from the parameters $l_{\mathrm{Mgw_1}}$, $l_{\mathrm{Clw_1}}$ and $l_{\mathrm{w_1w_1}}$ as given in Table 2. But the preference for this geometry is still clearly indicated and becomes obvious if Fig. 6 is compared with the result of a similar analysis of the hydration shell of the iodide ion [13], where no definite structure could be detected. Also the x-ray measurements give an indication of a preference for octahedral geometry. The quality of the fit of model A to the experimental structure function is higher by about 10% compared to model B, where a hexahedral arrangement of the eight nearest neighbor water molecules was assumed (Table 1). The asymmetries resulting from the coordinate system are much more pronounced in the case of Cl^{-} because of the less well defined geometry.

The choice of the coordinate system for the evaluation of the geometrical arrangement of the four nearest neighbor water molecules around a central water molecule involves much less arbitrariness than in the case of the spherically symmetric ions. It was chosen in such a way that the plane of the central water molecule coincides with yz-plane of the coordinate system, the center of mass is positioned at the origin and the oxygen atom in the positive z-direction (insertion in Figure 7). The projections of the oxygen atom positions onto the three planes of this coordinate system are shown in Fig. 7 again as three-dimensional drawings. A preference for the occupation of tetrahedral positions is obvious. The existence of an asymmetry between the x- and y-directions can be recognized clearly. It means that the distribution of the neighboring oxygen atoms is significantly broader in the lone pair directions of the central water molecule than in the hydrogen atom directions.

B) Angular Distributions

The qualitative picture of the averaged spatial arrangement of the six nearest neighbor water molecules around an ion and four around a central water molecule shown in Figs. 6 and 7 can be quantified by the calculation of the angular distributions of their oxygen atom positions in the coordinate systems defined in the preceding chapter. The resulting probability densities for the azimuth

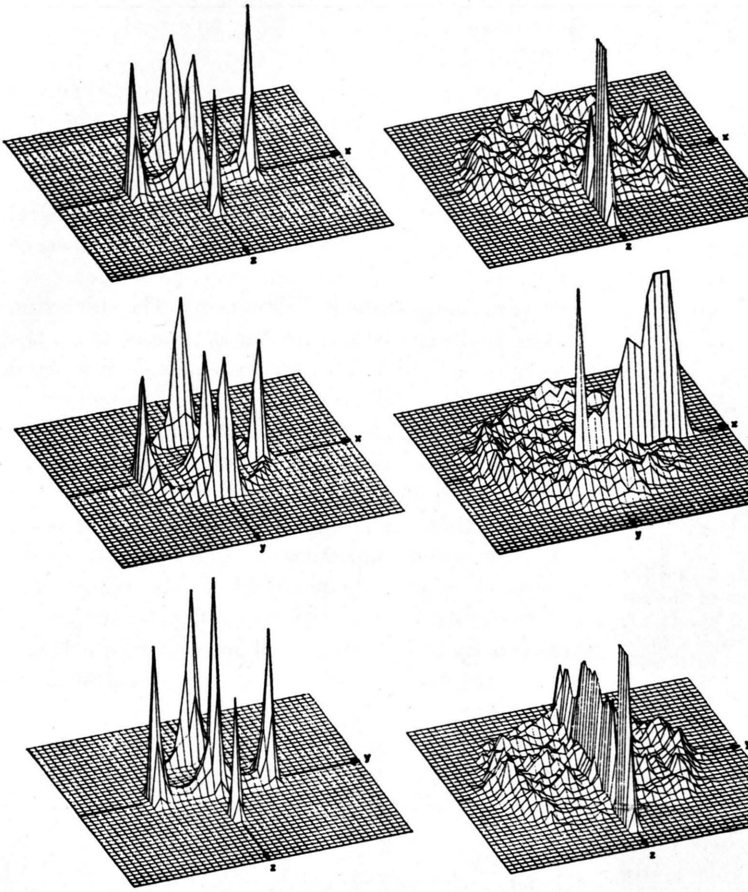

Fig. 6. Three-dimensional drawings of the projections of the oxygen atom position distributions of the six nearest neighbor water molecules around a magnesium (first column) and a chloride ion onto the three planes of a coordinate rystem as defined in the text, calculated from the MD simulation of a 1.1 molal $MgCl_2$ solution.

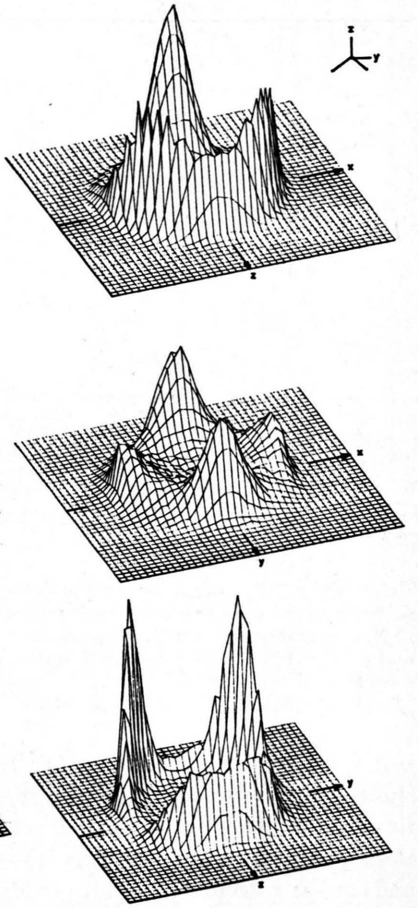

Fig. 7. Three-dimensional drawings of the projections of the oxygen atom position distributions of the four nearest neighbor water molecules around a central water molecule onto the three planes of a coordinate system as shown in the insertion, calculated from the MD simulation of a 1.1 molal $MgCl_2$ solution.

angle φ and polar angle ϑ — denoted by $P_{\alpha w}(\varphi)$ and $P_{\alpha w}(\cos \vartheta)$ — are given in Figure 8. The dashed lines indicate uniform distribution.

In the coordinate system introduced for the investigation of the hydration shell structure of the ions one of the water molecules defines the positive z-direction. As for its oxygen atom position $\vartheta = 0$ by definition, it is not included in the calculation of the $\cos \vartheta$ distribution. Simply by its size this water molecule causes an exclusion of certain ϑ values. The angle of exclusion depends on the ion-water distance and amounts (see Fig. 8) to 66° and 33° for Mg^{++} and Cl^-, respectively. Figure 8 shows that the distribution of four water molecules is centered at $\vartheta = 90°$ while the fifth molecule is positioned around $\vartheta = 180°$. In the case of Mg^{++} the distributions are rather sharp and they are much less pronounced for Cl^-.

To the oxygen atom of the water molecule which defines the positive z-direction, no φ-value can be attributed. Therefore, it is not considered in the calculation of $P_{\mathrm{Mgw}}(\varphi)$ and $P_{\mathrm{Clw}}(\varphi)$. Also the second molecule, whose oxygen atom position determines the xz-plane, is left out as its φ-value is equal to zero by definition. From the remaining four water molecules the oxygen atoms of three are located near the xy-plane and the distributions are centered around φ-values of 90°, 180° and 270°. The fourth

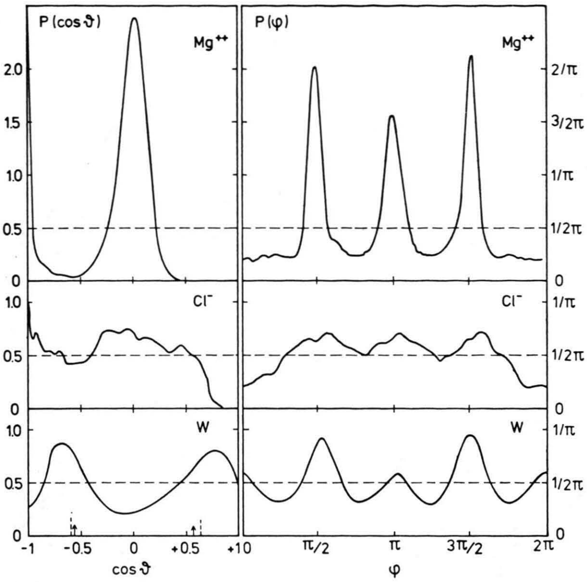

Fig. 8. Probability densities for the polar angle ϑ and the azimuth angle φ of the oxygen atom positions of the six nearest neighbor water molecules around an Mg^{++} and a Cl^- and for the four nearest neighbor water molecules around a central one in the coordinate systems defined in the text. The dashed lines indicate uniform distributions.

water molecule, located near the negative z-axis, shows as expected no preference in φ and is therefore responsible for the φ-independent contribution. The peak at 180° in $P_{\mathrm{Mgw}}(\varphi)$ is slightly lower and broader than the other two, as this water molecule is opposite to the fixed one and therefore less restricted in its position in the imposed coordinate system.

Figure 8 confirms, of course, that there exists a well pronounced octahedral arrangement of the water molecules in the first hydration shell of Mg^{++}. For Cl^- a preference for an octahedral structure still exists but this structure is significantly less pronounced than in the case of Mg^{++}. The construction of the coordinate system for the evaluation of the hydration shell structure of the ions necessarily introduces some distortion in the probability densities.

For the investigation of the angular distribution of the oxygen atoms of the nearest neighbor water molecules around a central one, a molecule fixed coordinate system is employed (insertion in Figure 7). As none of the neighboring water molecules has to be fixed, no restrictions exist as in the case of the ions. $P_{\mathrm{ww}}(\cos\vartheta)$ and $P_{\mathrm{ww}}(\varphi)$ are shown in the bottom part of Figure 8. In the coordinate system chosen the hydrogen atom (lone pair) directions have values $\vartheta > 90°$ ($\vartheta < 90°$) and φ values of 90° and 270° (about 0° and 180°). In $P_{\mathrm{ww}}(\varphi)$ the peaks appear at positions which are expected for tetrahedral structure. The distributions are significantly sharper in the hydrogen atom directions than in the lone pair directions. On the abscissa of the cosine distribution the tetrahedral directions are marked by an arrow and the average values by a dashed line. The maxima do not coincide with the tetrahedral directions. The deviation in the hydrogen atom directions results from the average angle of the water molecule — not fixed in the model — which has been found to be 98° for the 1.1 molal $MgCl_2$ solution. In the lone pair directions the CF model has no charges and therefore a preferential direction is less pronounced. Figure 8 confirms that the oxygen atoms of the nearest neighbor water molecules around a central one occupy preferentially positions at the edges of a distorted tetrahedron with a significant asymmetry between hydrogen atom and lone pair directions. In $P_{\mathrm{ww}}(\varphi)$ the maxima at $\varphi = 0°$ and 180° corresponding to the lone pair direction are only slightly higher than for a uniform distribution and in $P_{\mathrm{ww}}(\cos\vartheta)$ the peak is significantly broader than the one for hydrogen atom directions.

C) Simultaneous Occupation of Symmetry Sites

The angular distributions of the oxygen atom positions in the hydration shells of the ions and around a central water molecule shown in the preceding chapter give a picture of the hydration shells averaged over particles and time. A more sophisticated question — connected with many particle correlations — which can be answered only by the MD simulation is, how often does it occur that at the same time the six water molecules in the neighborhood of a Mg^{++} or a Cl^- and the four water molecules near a central one occupy octahedral and tetrahedral positions, respectively. In order to derive this information from the simulation, solid angles have to be defined on the basis of which it is decided if the oxygen atom of a given water molecule is positioned in an octahedral or tetrahedral direction. In the choice of these angles there is, of course, some arbitrariness involved. It was decided to choose a solid angle of 0.12π centered at the octahedral and tetrahedral direction for the ion-water and water-water configurations, respectively. These solid angles correspond to 40° aperture angle of each cone. The result is shown in Figure 9. It gives the probability in percent of finding a given number of octahedral or tetrahedral directions occupied in coincidence.

The strongly different histograms for Mg^{++} and Cl^- result from the different ion-water distances and the width of their distributions, which is in turn, of course, a consequence of the ion size and the strength of the ion-water interaction. Once a water molecule occupies an octahedral position in the hydration shell of Mg^{++} — this is true for at least one water molecule because of the definition of the coordinate system — the remaining space leads to a high probability for the occupation of all octahedral positions (60%). In the case of Cl^- the larger ion-water distance (3.18 Å) together with the broader radial distribution causes a decrease of the probability for higher coincidences because of the larger available volume for the six hydration shell water molecules. The relatively high probability for two octahedral positions occupied results again from the definition of the coordinate system as a second water molecule is fixed at $\varphi = 0°$ and only in ϑ it can be outside the given solid angle.

In the investigation of the arrangement of the four nearest water molecules around a central one the definition of the coordinate system does not involve the fixation of an oxygen atom and therefore it occurs that none of the water molecules occupies one of the tetrahedral directions. The very low percentage of the water molecules with a complete tetrahedral environment is no surprise as for pure ST2 water only 10% have been found. In the $MgCl_2$ solution a significant decrease can be expected as the water structure is further disturbed by ions. The same arguments which have been employed for the explanation of Fig. 8 — very broad angular distribution in the lone pair directions and an average angle of the water molecule of 98° deviating significantly from a tetrahedral angle — contribute also to the understanding of the low coincidence rate and explain the relatively high probabilities to find only one or two neighbors in tetrahedral directions.

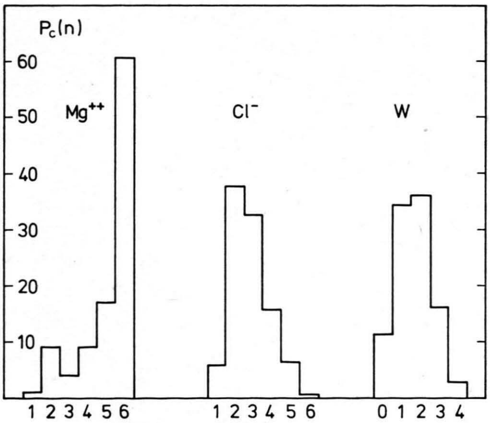

Fig. 9. The probability in percent that given numbers of hydration shell water molecules occupy octahedral (Mg^{++} and Cl^-) or tetrahedral (w) directions in coincidence.

V. Summary

The result of a molecular dynamics simulation and an x-ray investigation of a 1.1 molal $MgCl_2$ solution are compared on the basis of the total structure functions, the total radial distribution functions and the partial structure functions which have been deduced from the diffraction data by the employment of a first neighbor model. Good agreement has been found between simulation and experiment. Therefore additional detailed information on the structure of the solution — information which goes significantly beyond that what can be deduced from diffraction studies — can be calculated from the simulation with a high degree of reliability.

Detailed structural information on the hydration shells of Mg^{++} and Cl^- and on the spatial arrangement of the water molecules around a central one have been derived from the simulation by the calculation of the oxygen atom positions of the six and four nearest neighbor water molecules around the ions and a central water molecule, respectively. Hydrated ion- and water-fixed coordinate systems have been introduced in order to perform the particle and time averages. The results are presented in the form of density maps for the projections of the oxygen atom position distributions of the water molecules onto the three planes of the given coordinate systems (Figures 5—7). In addition the angular distributions of the hydration shell water molecules are shown as a function of φ and $\cos\vartheta$ in Figure 8. It can be concluded from the drawings that a very pronounced octahedral structure of the hydration shell of Mg^{++} exists, while in the case of Cl^- the octahedral structure is still indicated but strongly disturbed. The tetrahedral arrangement of the water molecules around a central one is strongly asymmetric in the sense that the distribution of the neighboring oxygen atoms is rather narrow in the hydrogen atom directions and very broad in the lone pair directions.

The probability has been calculated of finding the oxygen atom positions of all six nearest neighbor water molecules around a given ion and of all four around a given water molecule at the same time in octahedral and tetrahedral directions, respectively (Figure 9). The result is that for Mg in more then 60% of all cases all octahedral positions are occupied in coincidence, while this occurs only in 1% for Cl^-. A similarly low coincidence rate of 2.9% has been found for the tetrahedral arrangement around a water molecule.

Acknowledgement

Financial support by Deutsche Forschungsgemeinschaft and the Department of International Relations of the Hungarian Academy of Sciences are gratefully acknowledged.

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