X-Ray Diffraction and Structural Properties of Aqueous Solutions of Divalent Metal-Chlorides

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X-ray diffraction data are reported for aqueous solutions of $CaCl_2$ (6.30 M), $CdCl_2$ (0.87 and 1.26 M) and $NiCl_2$ (1.96 and 3.88 M).

The highly concentrated $CaCl_2$ solution shows a medium range order resembling that of the corresponding hydrate crystal. The $CdCl_2$ solutions are characterized by the presence of complexes with chloride ions in the first coordination sphere of the cation. In $NiCl_2$ solutions, a first sphere Ni-Cl coordination can be excluded and the existence of six Ni-H_2O nearest neighbour contacts is clearly confirmed. In these solutions no evidence was found for the existence of highly ordered structures; hexa-aquo cations interact with external water molecules and, at the highest concentration, some outer sphere Ni-Cl correlation is possible as due to packing.

Introduction

Recently, increasing attention has been devoted to the structure of concentrated aqueous solutions of divalent metal halides, for which qualitative changes in local ordering at increasing concentration are thought to take place.

Our involvement in this field began with the study of two $NiCl_2$ aqueous solutions [1]. This choice arose from the fact that the structure of $NiCl_2$ concentrated aqueous solutions has been a point of discussions. Enderby and co-Workers [2–4], in neutron diffraction studies of $NiCl_2 \cdot D_2O$ solutions, attributed the presence of a small angle peak in the intensity curves, and its variation with concentration, to the existence of a correlation Ni^{2+}—Ni^{2+}, involving long range order due to a "quasi lattice" structure.

The question of long range order in $NiCl_2$ aqueous solutions and other II-I electrolyte solutions was investigated through measurements of viscosity [5], thermodynamic quantities [6] and Raman spectroscopy [7]. The results were interpreted in terms of collective modes in a solute-connected medium range lattice. As far as the nearest neighbours around the cation are concerned, it was found from neutron diffraction studies [8, 9] that Ni^{2+} has a coordination sphere of six water molecules, while Fontana et al. [7] suggested that, at concentrations higher than 1 M, about half of the Ni^{2+} ions are involved in $NiCl_4^{2-}$ complexes, which are correlated in an ordered structure. In our X-ray diffraction study it was shown that the environment of Ni^{2+} ions is basically aqueous, but no clear evidence was found of "quasi lattice" structures. This result is in good agreement with a recent EXAFS study by Sandstrom [10], in which no evidence was found for direct Ni-Cl bonding and for long range ordered structure. X-ray data, however, did not contradict a hypothesis of "outer-sphere ion pairing" [1], but an exhaustive description of the structure surrounding the $Ni(H_2O)_6^{2+}$ was not given.

Due to the great interest in these solutions, we thought it useful to check our previous findings on Ni^{2+} close hydration, and to search, mainly at the highest concentrations, for possible Ni^{2+}-Cl^- outer sphere correlations. To this end we collected new and more accurate diffraction data. In addition to the study of $NiCl_2$ solutions we investigated a very concentrated solution of $CaCl_2$ [11] (in practice liquid $CaCl_2 \cdot 6H_2O$) and two solutions of $CdCl_2$ (0.87 and 1.26 M).

The choice of these systems was based on the following considerations: $CaCl_2 \cdot 6H_2O$ melts near room temperature, which makes it possible to compare structural information about the fused phase with that obtained [12], under similar conditions, for $CaCl_2$ aqueous solutions at higher H_2O/salt ratios. This favours the observation of qualitative changes, if any, in local ordering around ions and the possible occurrence of order phenomena beyond first hydration shells. The goal was to

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clarify to what extent middle or long range ordering is revealable with X-ray diffraction.

$CdCl_2$ aqueous solutions are cases in which some ionic association exists. The interesting question regarding the presence of different complexes in equilibrium and their structure does not fall within the aim of the present discussion and will be approached elsewhere [13]. Here the emphasis is on the evidence, obtainable via X-ray diffraction, for the existence of inner-sphere $CdCl_n^{(2-n)+}$ aq. complexes, in opposition to Cd^{2+} aq. complexes. The choice of not too high concentrations corresponds to this purpose.

Experimental and Results

The concentration of the solutions and some data on the experimental conditions are listed in Table 1.

The experimental procedure and the data treatment have been described in recent papers [1, 12]. Here we just wish to recall that the experimental intensity data were used in the evaluation of the correlation function according to

$$G(r) = 1 + (2\pi^2 \varrho_0 r)^{-1} \int_{s_{\min}}^{s_{\max}} si(s) \sin sr \, ds\,, \qquad (1)$$

where r is the interatomic distance, ϱ_0 the bulk density of the solutions and $s = 4\pi \sin \theta/\lambda \cdot 2\theta$ is the scattering angle, λ the wavelength of the radiation employed ($MoK\alpha$), and $s_{\min}$ and $s_{\max}$ are the lower and upper limit of the experimental data. $i(s)$ is the structure function defined as

$$i(s) = \left(I_{\text{e.u.}} - \sum_{i=1}^{m} x_i f_i^2\right) \Big/ \left(\sum_{i=1}^{m} x_i f_i\right)^2, \qquad (2)$$

where f_i are the scattering factors, x_i the stoichiometric coefficients in the structural unit containing m kinds of atoms, and $I_{\text{e.u.}}$ is the intensity in electron units.

Table 1. The molarity c, the molar fraction of the salt x the temperature T, the angular range $\theta_{\min} - \theta_{\max}$ used in collecting the scattered intensities and the upper limit $s_{\max}$ used in calculating the integral in (1) of the solutions under investigation.

Salt	c	x	T (°C)	$\theta_{\min} - \theta_{\max}$	$s_{\max}$ (Å^{-1})
$CaCl_2$	6.30	0.1241	28 ± 2	1−61	15.50
$CdCl_2$	0.87	0.0156	20 ± 1	2−56	14.68
$CdCl_2$	1.26	0.0277	21 ± 1	1.5−56	14.68
$NiCl_2$	3.88	0.0698	20 ± 1	2−60	15.28
$NiCl_2$	1.96	0.0356	20 ± 1	1.5−60	15.28

The values for the scattering factors were calculated by an analytical expression using the coefficients obtained by Hajdu [14] for the water molecule and by Cromer and Mann [15] for the other species. These values were then corrected for anomalous dispersion.

The first step of data analysis was based on the inspection of the $G(r)$ in order to obtain the direct information contained in them. For a more quantitative analysis a computer modelling technique was used. Structural models were tested against experimental data and systematically refined by least squares fitting synthetic structure functions to values derived from the measurements. The well-known formula proposed by Levy et al. [16] was used for the evaluation of these theoretical $si(s)$; the first term in this formula accounts for contributions from discrete interactions, while the second describes the transition to a uniform distribution of distances.

$CaCl_2$

In Fig. 1 we compare the correlation function obtained for the $CaCl_2$ melt (curve A, dots) with those already obtained [12] for two less concentrated solutions (curves B and C). Two main differences are evident: (i) in the distance range containing information on near-neighbour interactions, curve A shows three resolved peaks centered at about 2.40, 2.75 and 3.20 Å while curves B and C exhibit a first peak at about 2.40 Å, ascribed to sharp Ca^{2+}-H_2O interactions, a second peak at about 3.20 Å, due to weaker Cl^--H_2O interactions, and a deep minimum in the region 2.7 Å. (ii) curve A seems to indicate the existence of a longer "order range" due to the presence of a broad but significant peak in the region 6−6.5 Å, which is absent in the other curves.

It is therefore impossible to interpret the "structure" of the more concentrated solution in terms of a First Neighbour Model, in which the hydrated ions, with mean octahedral coordination geometry, are considered to be independent units [12].

The structure of the crystalline calcium chloride hexahydrate [17] might explain the three main peaks found. In fact, in these hexagonal crystals each cation is surrounded by three H_2O molecules

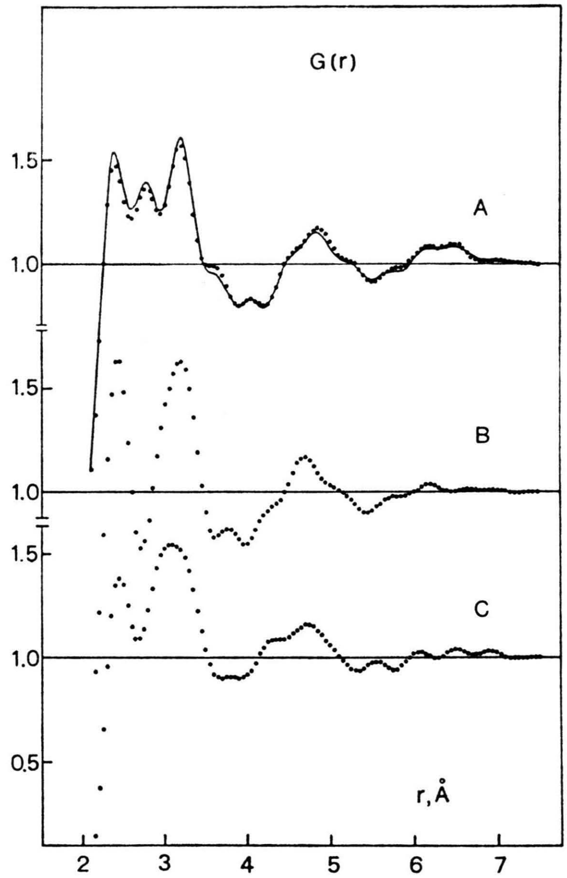

Fig. 1. Correlation functions for $CaCl_2$ solutions. A: 6.30 M, B: 4 M, C: 2 M. Dots: experimental curve; full line: model curve.

at the nearest distance of about 2.4 Å in the plane containing the Ca atom and perpendicular to the c axis, while six other water molecules are at a greater distance of about 2.7 Å in the positions $\frac{1}{2}$ and $\frac{\bar{1}}{2}$ along the *c* axis. The chloride ions, being interposed between parallel Ca-H_2O-Ca chains developing along the *c* axis, see six water molecules at distances near 3.2 Å and three others at about 3.6 Å.

The existence of water-mediated Ca-Ca chains, with Ca-Ca distance of about 4 Å, may also explain the presence, in the liquid, of some sort of medium range order, which disappears when the concentration is lower. The crystal lattice of $CaCl_2 \cdot 6H_2O$ was therefore used as a model in order to obtain in the liquid the distances spectrum around each atom.

The chains along the c axis were described using three distances as independent parameters: i) a distance r_{c_1} between each Ca atom and the three nearest neighbour water molecules, ii) a distance r_{c_2} between each Ca atom and the six next nearest water molecules, iii) a distance r_{cc} representing the shortest Ca-Ca distance. A large number of tentative calculations were made in order to choose an order range around each atomic species in the solution, starting from the case involving only nearest neighbour interactions. The result was that no convergence could be reached without including in the model a rather large number of medium range distances. Then, considering that deviations from a uniform distribution of distances are evident in the correlation function up to about 6.5 Å, all the distances shorter than 7 Å among atoms in the same chain were included in the model as discrete distances. As the shortest Ca-Ca distance in the layers normal to the c axis in the hydrated crystal is about 8 Å, we did not consider any positional correlation between atoms of different chains.

From the anion-water interactions, we considered only two distances r_{A_1} and r_{A_2}, shorter than 4 Å and involving six and three Cl^--H_2O contacts, respectively.

This model proved to be consistent with experimental data as shown in Fig. 1 where the correlation function obtained from the model appears to be in very good agreement with the experimental one. In Table 2 the final values of the significant parameters are reported.

Table 2. Mean distances r(Å) and root mean square deviations σ(Å) obtained from the least-squares refinement for the cation-water (c_1; c_2), cation-cation (cc) and anion-water (A_1, A_2) interactions, for the $CaCl_2$ solutions. Standard errors are given in parentheses.

r_{c_1}	σ_{c_1}	r_{c_2}	σ_{c_2}	r_{cc}	σ_{cc}	r_{A_1}	r_{A_2}	$\sigma_{A_1} = \sigma_{A_2}$
2.355 (3)	0.088 (3)	2.698 (7)	0.29 (2)	3.993 (8)	0.31 (1)	3.215 (4)	3.638 (9)	0.212 (4)

$CdCl_2$

In Fig. 2 we report the correlation functions obtained for the two $CdCl_2$ solutions. In both curves the first peak is by far the most important one; the position of its maximum is at about 2.55—2.60 Å, a distance frequently observed for Cd^{2+}-Cl^- contacts in crystalline $CdCl_2$ hydrates [18—20]. The broadness of this peak indicates that also other interactions contribute to it, in particular Cd^{2+}-H_2O distances at about 2.30—2.35 Å, as observed in hydrated crystals [18—20] and in aqueous solutions [21—22], and the usual H_2O-H_2O distances at about 2.80—2.85 Å [23, 12]. This fact makes a direct evaluation of the mean number of cation-anion contacts impossible. It is however worth noting that the radial curves clearly show the presence of chloride ions in the first cationic coordination sphere.

Some other details are observable in the $G(r)$ curves: a small peak at about 3.25 Å appearing as a shoulder in the more dilute solution, and a quite pronunced peak at about 4.5 Å. The first one may contain contributions from Cl^--H_2O interactions, which usually [24] have equilibrium distances near 3.2 Å, and from interatomic distances in the $CdCl_n$ aq. complexes as well. The large peak at about 4.5 Å comes from overlapping of many different contributions, which makes a direct interpretation impossible.

Different models were tested for the two $CdCl_2$ solutions in the attempt to get information on percentages, compositions and geometries of the different chloro-complexes probably existing in these solutions. This analysis, which shows the impossibility of a clear discrimination between different situations, is reported elsewhere [13]. However, the complexation of the anions in the first coordination sphere of the cation was clearly confirmed, the mean number of Cd^{2+}-Cl^- contacts being equal to two. Here we report as an example the results obtained with a model involving pseudo-octahedral $CdCl_2(H_2O)_4$ complexes, with the Cl atomsin trans position. Each Cl atom and each H_2O molecule interact with three and two external water molecules, respectively.

The final correlation functions obtained with this model are compared with the experimental ones in Figure 2. The best fit values of the distances and root mean squares deviations of the Cd^{2+}-Cl^- and Cd^{2+}-H_2O pairs are given in Table 3.

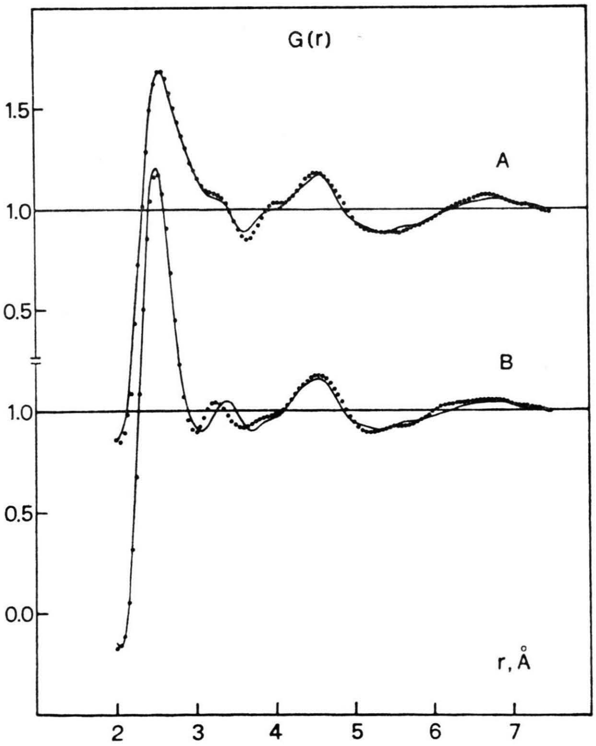

Fig. 2. Correlation functions for $CdCl_2$ solutions. A: 0,87 M, B: 1.25 M. Dots: experimental curve; full line: model curve.

Table 3. Mean distances r(Å) and root mean square deviations σ(Å) obtained from least squares refinement for $Cd^{2+}-Cl^-$ and $Cd^{2+}-H_2O$ interactions in $CdCl_2$ solutions. Standard errors are given in parentheses.

	0.87 M	1.26 M
$^rCd^{2+}-H_2O$	2.366 (6)	2.373 (5)
$^\sigma Cd^{2+}-H_2O$	0.166 (6)	0.134 (4)
$^rCd^{2+}-Cl^-$	2.569 (4)	2.570 (3)
$^\sigma Cd^{2+}-Cl^-$	0.151 (3)	0.140 (3)

$NiCl_2$

The experimental correlation functions, reported in Fig. 3, show three main peaks. The first peak is very sharp and symmetric, and the position of its maximum is at about 2.00—2.10 Å, a distance very close to the sum of the ionic radii of Ni^{2+} and the water molecule. The interpretation of this peak as due to cation-water interactions is thus confirmed.

A direct attribution of the other peaks is more difficult. The one around 3 Å is doubly composed,

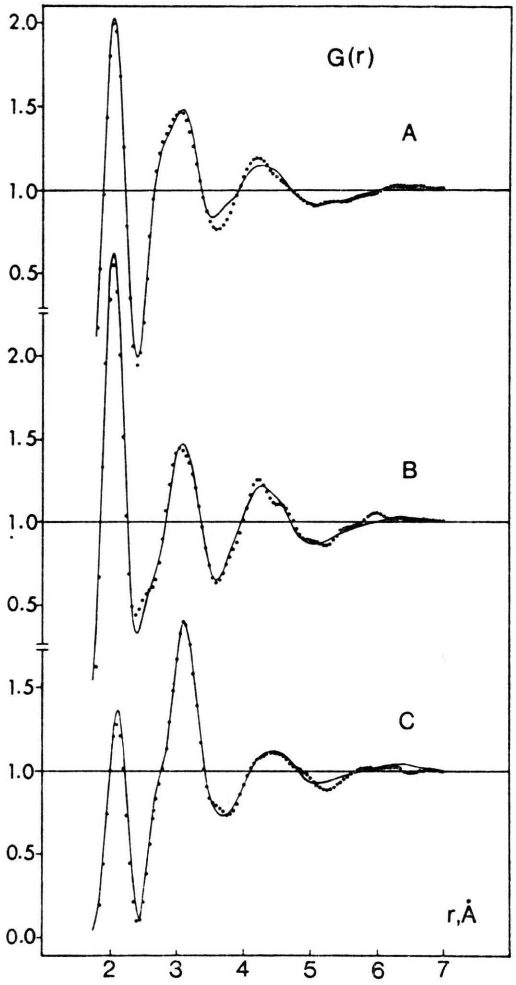

Fig. 3. Correlation functions for $NiCl_2$ solutions. (A: 2 M, B: 4 M) and a 4 M $MgCl_2$ solution (C). Dots: experimental curve; full line: model curve.

(Figure 3A). One component at about 2.85—2.90 Å is characteristic of H_2O-H_2O distances — nearest-neighbour H_2O-H_2O interactions and H_2O-H_2O cis distances inside the cation hydration complexes —, the other one at about 3.15—3.20 Å corresponds to nearest-neighbour Cl^--H_2O distances frequently observed in Cl^- aqueous solutions [24]. The peak at about 4.10—4.20 Å may result from H_2O-H_2O distances inside ionic coordination shells as well as from interactions between Ni^{2+} and second neighbour water molecules. In both solutions examined, peaks from longer intermolecular distances are not discernible in the radial curves.

In the study on $NiCl_2$ concentrated aqueous solutions mentioned before [1] we showed that a First Neighbour Model (with hexa-coordinated ions considered as independent and non correlated units) described the general behaviour of the structure and correlation functions but did not yield model functions in complete agreement with the experimental ones. More satisfactory agreement was reached by adding next nearest neighbour contacts (12 for the 2M and 6 for the 4M solution) between the hydration water of Ni^{2+} and "external" water molecules. These findings are confirmed here. In Fig. 3A the model correlation function of the 2M solution is compared with the corresponding experimental curve. The model employed here is the same as the one used successfully for the interpretion of X-ray diffraction data from 1M and 2M solutions of $MgCl_2$ [25].

In a 4M solution the amount of water available allows unilayer anionic hydration and bilayer cationic hydration to be formed only if some water molecules are shared by coordination shells of neighbouring ions. In this way some sort of outer-sphere ionic association may form through hydrogen bonds among anions and water molecules of hexaaquo cations. To investigate better such a hypothesis, alternative models were tentatively tested against diffraction data for the 4M solution with $Ni^{2+}(H_2O)_6 \ldots Cl^-$ contributions explicitly included in the structure function.

A first model was derived from the one proposed by Dorosh and Sykryshevskii [26]. The Cl^- ions were placed in "holes" at two opposing faces of the octahedron formed by the hydration water of the cation. They have six nearest neighbour water molecules, and their geometry depends upon the cation-water and cation-cation distances, which are assumed to be independent parameters. This model, however, did not result in any reasonable fit, probably because of the great distortion imposed on the anion coordination shell by the geometry used.

Following this indication a model not involving rigid geometry for Ni^{2+}-Cl^- interactions was tried by simply adding to the ion-water (r_{+w_1}, r_{-w}) and water-water distances inside the first coordination shells of the ions a variable number of Ni^{2+}-Cl^-(r_{+-}), Ni^{2+}-external water (r_{+w_2}) and hydration water-external water ($r_{w_1w_2}$) distances. The idea was, that by lowering the H_2O/salt ratio, some water of the first coordination shell could be shared between neighbouring cations and anions without substan-

Table 4. Mean distances r(Å), root mean square deviations σ(Å) and coordination numbers n, obtained from least squares refinement for the main interaction in the $NiCl_2$ and $MgCl_2$ solutions. Standard errors of refined parameters are given in parentheses.

	$NiCl_2$ 2 M	$MgCl_2$ 2 M	$NiCl_2$ 4 M	$MgCl_2$ 4 M
r_{+w_1}	2.063 (2)	2.099 (2)	2.068 (3)	2.111 (3)
σ_{+w_1}	0.120 (2)	0.100 (3)	0.128 (2)	0.124 (5)
r_{-w}	3.122 (5)	3.144 (3)	3.188 (6)	3.159 (5)
σ_{-w}	0.178 (5)	0.207 (2)	0.184 (6)	0.208 (4)
r_{+-}	—	—	4.27 (2)	4.27 (8)
σ_{+-}	—	—	0.30 (2)	0.38 (2)
$r_{w_1w_2}$	2.717 (5)	2.752 (3)	2.68 (3)	2.69 (2)
$\sigma_{w_1w_2}$	0.056 (8)	0.051 (2)	0.18 (1)	0.07 (3)
r_{+w_2}	3.99 (3)	4.23 (9)	4.05 (2)	3.99 (4)
σ_{+w_2}	0.56 (2)	0.61 (4)	0.32 (2)	0.37 (3)
n_{+-}	—	—	1.8 (2)	1.6 (5)
n_{+w_2}	12	12	6.2 (3)	5.2 (9)

tial perturbation of their hydration shells. In the fitting procedure, the number of the contacts Ni^{2+}-Cl^-(n_{+-}) and Ni^{2+}-w_2(n_{+w_2}) was varied to obtain the best fit. The model correlation function shows good agreement with the experimental data (Figure 3B).

A question arises here: is this result characteristic of $NiCl_2$ solutions or does it simply come out because of the packing due to the concentration of the solution? In order to obtain indications on this point we used X-ray diffraction data previously obtained [25] for a 4M $MgCl_2$ solution, whose structure function is not completely described by the First Neighbour Model in analogy to the $NiCl_2$ solution at the same concentration. Good agreement between model and experimental curves (Fig. 3C) was obtained by using the same model and the same fitting procedure as for $NiCl_2$. In Tab. 4, best fit values of the most significant parameters for $NiCl_2$ solutions are compared with those obtained for $MgCl_2$ solutions of the same concentration. Striking analogies in the structural behaviour of these solutions can be observed.

Conclusions

The structure of aqueous $CaCl_2$ solutions in the concentration range 1—4M appear to be essentially dominated by nearest-neighbour interactions inside the octahedral coordination shells of both the ions. When the H_2O/salt ratio approaches that of the corresponding solid hydrate the nearest neighbour structures change significantly and medium range correlations appear.

$CdCl_2$ aqueous solutions of concentrations around 1M appear to be characterized clearly by the entry of two halide ions in the first coordination sphere of the cation.

These two results are helpful for the understanding of the structural behaviour of $NiCl_2$ solutions, which was the main point of our study.

Up the concentration 4M, Ni^{2+} is found to be sixfold coordinated at about 2.07 Å in an octahedral geometry. No evidence was found for Cl^- in the first coordination sphere of Ni^{2+} as suggested for the II-I transition metal solutions by Fontana et al. [7] and confirmed here for $CdCl_2$ solutions. This result is in agreement with those obtained from neutron diffraction studies [8, 9] and with EXAFS measurements by Sandstrom [10]. Even a more recent EXAFS study by Lagarde et al. [27] gave no evidence for inner shell halogen coordination in $NiCl_2$ and $NiBr_2$ solutions, contrary to what they observed for $CuCl_2$, $CuBr_2$ and $ZnBr_2$ solutions. Recently, Weingärtner et al. [28, 29] determined from NMR measurements in a 1 molal solution of $NiCl_2$, the mean number of Cl^- ions in the first coordination sphere of Ni^{2+} to be 0.14. This value is well beyond the detection capability of the technique used here.

No evidence for highly ordered long range structures is found in our diffraction data. As far as an order beyond the first coordination shell is concerned, we found that in the 2M solutions interactions between hexahydrated cations and a second shell of about 12 water molecules are important for a good description of the complete behaviour of the structure function. In a 4M solution, some evidence for outer sphere Ni^{2+}-Cl^- correlations appears to be essentially due to packing. Some evidence for Ni^{2+}-Cl^- outer sphere correlations has been obtained by Sandstrom [10] in his EXAFS study, but the Ni^{2+}-Cl^- distance he reports (3.1 Å) is, in our opinion, too short and would involve very short Cl^--H_2O distances which are not consistent with our data.

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