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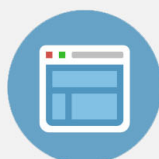
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Composition of the first coordination sphere of Ni^{2+} in concentrated aqueous NiBr_2 solutions by x-ray diffraction

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Two concentrated solutions of NiBr_2 have been examined by x-ray diffraction. The Fourier transformed scattering data indicate inner complex formation between Ni^{2+} and Br^- ions. Average numbers of bonded bromide ions per nickel atom have been determined for each solution and the reliability of the complexation numbers as well as of the other structural parameters has been critically examined.

INTRODUCTION

The study of the interactions between Ni^{2+} and halide ions has received considerable attention in the past few years. Solutions of NiCl_2 in particular have been investigated by several workers, who, among other things, have studied by various techniques the composition of the first cationic coordination shell in different conditions of concentration and composition.

In concentrated solutions of NiCl_2 , where $\text{Cl}^-/\text{Ni}^{2+}$ atomic ratios greater than 2 were obtained through the addition of LiCl or HCl , x-ray diffraction¹ (XRD) and EXAFS spectroscopy² have clearly demonstrated the formation of chloro complexes. Coordination parameters estimated in these two studies were in excellent agreement as far as $\text{Ni}^{2+}-\text{H}_2\text{O}$ and $\text{Ni}^{2+}-\text{Cl}^-$ direct distances are concerned, and in good agreement as regards the average number of $\text{Ni}^{2+}-\text{Cl}^-$ contacts, n_{Cl^-} .

Going to stoichiometric solutions of NiCl_2 ($\text{Cl}^-/\text{Ni}^{2+}$ ratio = 2), the situation is less clear, at least apparently. In fact: (a) EXAFS investigations at the metal K edge^{3,4} seem to indicate absence of Cl^- ions in the first coordination sphere of Ni^{2+} ; (b) studies by neutron diffraction with isotopic substitutions (NDIS)^{5,6} support the full hydration of Ni^{2+} ions; (c) XRD data analysis⁷ suggests the existence of a considerable percentage (~50%) of the complex $\text{Ni}(\text{H}_2\text{O})_5\text{Cl}^+$ at concentrations $> 3\text{M}$ ⁸; (d) studies of proton, deuteron, and chlorine relaxation rates (NMR)^{9,10} support the presence of $\text{Ni}^{2+}-\text{Cl}^-$ direct bonds and propose a linear dependence of n_{Cl^-} on the concentration, according to which the number of Cl^- nearest neighbor to the cation is about 0.5 at the saturation concentration; (e) Raman spectroscopy investigations^{11,12} show evidence of $\text{Ni}^{2+}-\text{Cl}^-$ contacts and put forth the hypothesis that these contacts take place in NiCl_4^{2-} units.

Actually the situation is less chaotic than it appears. In fact, if we neglect the Raman results, as the existence of NiCl_4^{2-} units is a mere speculation in complete disagreement with XRD, EXAFS, NMR, and NDIS studies, the discre-

pancies between results from XRD and NMR and those from EXAFS and NDIS narrow dramatically so that they are likely reflecting the different sensitivity of these techniques to minority interactions. As discussed by one of the authors,⁷ in a 50% mixture of $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ni}(\text{H}_2\text{O})_5\text{Cl}^+$, the average number of $\text{Ni}^{2+}-\text{Cl}^-$ contacts is only 8.3%. It is probable that such small percentage goes unnoticed or does not reveal itself in some observations, even if it involves a great amount of halo complexes.¹³ On the other hand, this fact draws a serious limit to the ability of the mentioned techniques to reveal halo complexes in solution.

To clear up this matter, the investigation of NiBr_2 solutions should be a very good choice. In fact, there are several reasons why $\text{Ni}^{2+}-\text{Br}^-$ contacts should be better identifiable than the $\text{Ni}^{2+}-\text{Cl}^-$ ones in a structural investigation. First, the $\text{Ni}^{2+}-\text{Br}^-$ distance is longer than the $\text{Ni}^{2+}-\text{Cl}^-$ one; therefore, whichever be the technique used, it should come easier to separate $\text{Ni}^{2+}-\text{H}_2\text{O}$ from $\text{Ni}^{2+}-\text{Br}^-$ interactions. In EXAFS the advantages should come from the very large backscattering amplitudes and from the different behavior of the phase function for a Br scatterer, as well as from the easier accessibility of the energy range of the anion K edge to the experiments. Finally, in XRD, since the Br^- scattering factor is much larger than the Cl^- one, $\text{Ni}^{2+}-\text{halogen}$ pairs should give a heavier contribution to the total scattering, so that even a small number of contacts might be revealed and characterized.

As extensively discussed in the Discussion, Cl^- and Br^- ions show similar tendency to bind Ni^{2+} ions. Results on NiBr_2 solutions should be therefore a valuable help also to clarify the ambiguities mentioned about NiCl_2 solutions. In the light of these considerations we thought it convenient to extend our x-ray diffraction investigations to two NiBr_2 solutions (2 and 4 M) at room temperature ($T = 20 \pm 1^\circ\text{C}$).

Looking at the literature, with surprise we took notice that, in two recent XRD studies^{14,15} on NiBr_2 solutions, very different evaluations of the bromo complexation were given. This seems to wipe out the hope that clearer results can be obtained from the study of the chosen system. However, a comparison of the reduced intensity data published in the papers quoted above clearly shows that important differences exist between the two sets of experimental data. There-

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TABLE I. Compositions in mol/l, atomic ratios and densities in g/cm³ are given for the solutions investigated.

Solutions	Ni ²⁺	Br ⁻ /Ni ²⁺	H ₂ O/Ni ²⁺	<i>d</i>
NiBr ₂ 2M	2.102	2	24.7	1.396
NiBr ₂ 4M	4.071	2	11.9	1.761

fore, the differences in the final results are unlikely to be a consequence of the ambiguity of the analysis, but they must follow from some inaccuracy in one of the two experiments. A further objective of our work is therefore also the understanding of these controversial results.

EXPERIMENTAL AND DATA TREATMENT

The solutions of NiBr₂ were prepared from Carlo Erba reagent grade NiBr₂ · 6H₂O. Nickel and bromide ion concentrations in the solutions were determined by EDTA and argentometric titrations, respectively. The two methods agreed within less than 1%. The densities of the samples were obtained by a digital precision densimeter. Density values obtained by us are in good agreement with those estimated by Wakita *et al.*,¹⁵ while the value proposed by Caminiti *et al.*¹⁴ for the 2M solution they examined is slightly smaller. The compositions of the solutions and their reference symbols are given in Table I.

X-ray apparatus and data normalization procedures have been described elsewhere.^{16,17} Diffraction intensities (at least 100 000 counts per point) were recorded in the angular range $\theta = 1. - 70^\circ$, using a Mo x-ray tube ($\lambda = 0.7107 \text{ \AA}$), corresponding to an s range from $s_{\min} 0.3$ to $s_{\max} 16.6 \text{ \AA}^{-1}$, where s is $4\pi \sin \theta / \lambda$. The observed intensities were corrected for background, absorption, and polarization. Most of the incoherent scattered radiation was eliminated by using a quartz monochromator on the diffracted beam. The data normalization was carried out using standard methods.¹⁶⁻¹⁸ A correction for spurious ripples below 1.0 \AA was also applied.¹⁹

From the normalized intensities $I_{e.u.}$ the structure functions were obtained according to

$$i(s) = I_{e.u.} - \sum_{i=1}^m n_i f_i^2(s) \quad (1)$$

and the radial distribution functions $D(r)$ were then evaluated by a Fourier transformation:

$$D(r) = 4\pi r^2 \rho_0 + 2r/\pi \int_{s_{\min}}^{s_{\max}} s i(s) M(s) \sin rs ds. \quad (2)$$

In Eqs. (1) and (2), n_i 's are the stoichiometric coefficients of the assumed unit, containing m kinds of atoms; f_i 's are the scattering factors of the species; ρ_0 is the average electronic bulk density; $M(s)$ is a modification function of the form

$$\{ [\sum n_i f_i(0)]^2 / [\sum n_i f_i(s)]^2 \} \exp(-ks^2),$$

with $k = 0.005$.

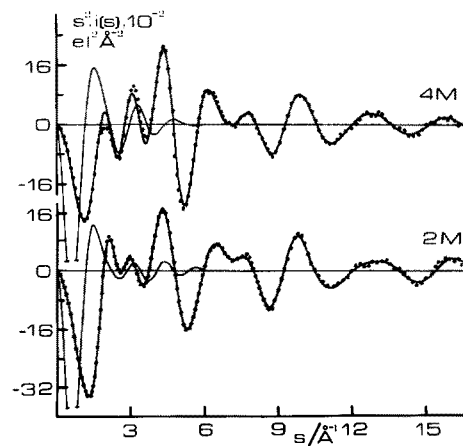


FIG. 1. Experimental (dots) and calculated structure functions (solid strong lines) are shown for the solutions investigated. Contributions of the continuum are also shown by weak solid lines.

RESULTS

Inspection of the radial curves

The functions $i(s)$, after multiplication by s^2 , are shown in Fig. 1. In Fig. 2 the radial distribution functions $D(r)$ are given, while in Fig. 3 radial curves are reported as difference functions $D(r) - 4\pi r^2 \rho_0$, as they better display the medium range structure. In Fig. 2, the $D(r)$ of the 4 M solution exhibits three peaks at about 2.05, 2.60, and 3.35 Å. On the basis of the ionic radii of the species and of previous diffractometric works,^{1,7,20-24} these distances can be ascribed without ambiguity to the pairs Ni²⁺-H₂O, Ni²⁺-Br⁻, and Br⁻-H₂O, respectively. In the case of the 2 M solution, while the peaks at 2.05 and 3.35 Å are still present, the intermediate one is replaced by a shoulder at about 2.80 Å. In this case the greater abundance of water makes direct H₂O-H₂O interactions (usually falling at about 2.80 Å) more important than the Ni²⁺-Br⁻ ones; the Ni²⁺-Br⁻ distances are probably masked in the large envelope of the peak, as, on the other hand, are H₂O-H₂O distances under the peak Ni²⁺-Br⁻ in

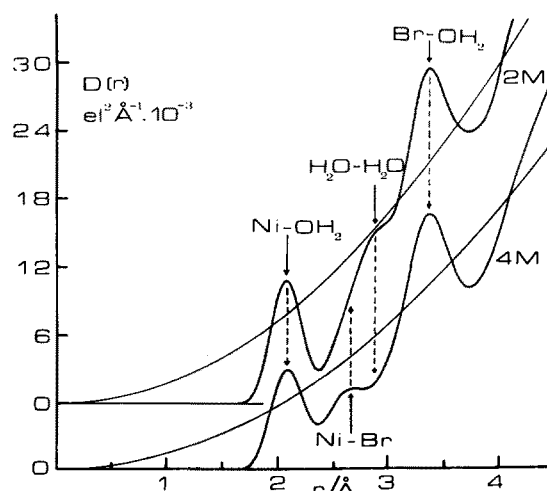


FIG. 2. Radial distribution functions $D(r)$ are shown; the parabolic curves represent the $4\pi r^2 \rho_0$ functions.

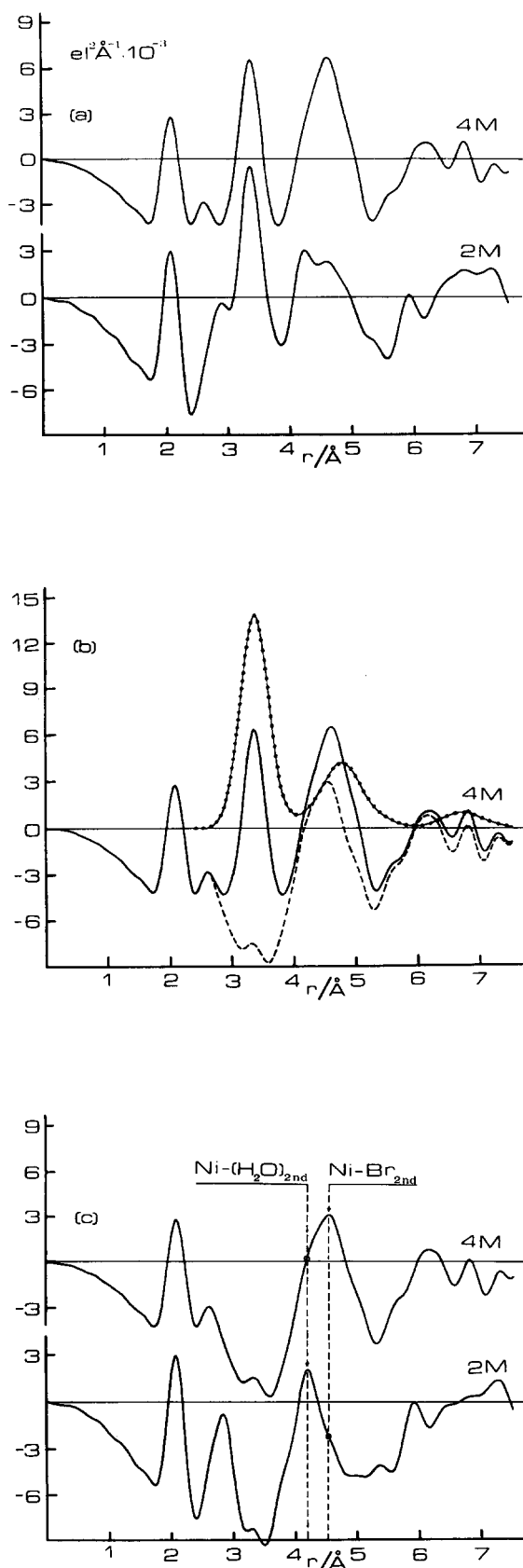


FIG. 3. (a) Difference radial distribution curves, $D(r) - 4\pi r^2 \rho_0$, (b) Difference radial curve of the 4 M solution (solid line), radial contributions coming from $\text{Br}(\text{H}_2\text{O})_6^-$ complexes (dotted solid line) and radial difference curve after subtraction of the dotted curve (dashed line), (c) Difference radial distribution curves of the two solutions, after subtraction of the contributions coming from $\text{Br}(\text{H}_2\text{O})_6^-$ complexes. The 4 M curve is the same (dashed) curve in (b).

the 4 M solution. On the whole, these observations confirm that $\text{Ni}^{2+}-\text{Br}^-$ interactions are more evident than the $\text{Ni}^{2+}-\text{Cl}^-$ ones, thus encouraging the quantitative analysis.

In Fig. 3(a), besides the peaks just discussed, a meaningful multicomponent peak appears in the 4–5 \AA range. Important contributions to peaks in this distance region are usually provided by interactions among cations and water molecules set in second hydration spheres, $\text{H}_2\text{O}_{\text{II}}$ molecules (the subscript *I* denoting ions or molecules in the first hydration shell, when specification is necessary for clarity). The comparison of the difference curves of the two solutions shows that the peaks at issue are different both in shape and in height; oddly, the peak is higher in the more concentrated solution, where less water is available for second ordered hydration shells. This seems to suggest that, in the 4 M solution, some Br^- ions, Br_{II}^- , set themselves in the second cationic coordination shells. To check this hypothesis, we tried to subtract from the difference radial curves the contributions coming from $\text{Br}^- - \text{H}_2\text{O}$ and $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions in the anionic complexes $\text{Br}(\text{H}_2\text{O})_6^-$, whose existence will be discussed shortly: these contributions are sketched as a dotted line in Fig. 3(b). The results of the subtraction are shown in Fig. 3(c). The residual peaks at 4–5 \AA , while retaining their complex nature, shift their maximum going from 4.1 \AA in the 2 M sample (possible $\text{Ni}^{2+}-\text{H}_2\text{O}_{\text{II}}$ distance) to 4.6 \AA in the 4 M sample (possible $\text{Ni}^{2+}-\text{Br}_{\text{II}}^-$ distance), in agreement with the explanation proposed above.

Analysis of the structure functions

In order to evaluate quantitatively the average number of bonded bromide ions per Ni atom, n_{Br^-} , as well as to obtain a set of structural parameters for the species in solution, model structure functions may be compared, through a least squares procedure,^{1,2,16,17} with the experimental $i(s)$ functions. This implies the choice of a plausible model for the solution, in which each atomic species is surrounded by a region with discrete structure, followed by a uniform distribution of distances (continuum). Direct interactions inside the ordered regions dominate the high s values of the structure functions. Therefore, in order to have indications about the average ionic coordinations and the type of complexes that must be considered for a complete simulation of the $i(s)$'s, an analysis of the high s range of the 4 M solution structure function was carried out. The terms introduced in the calculations were those describing $\text{Ni}^{2+}-\text{H}_2\text{O}$, $\text{Ni}^{2+}-\text{Br}^-$, $\text{H}_2\text{O}-\text{H}_2\text{O}$ and $\text{Br}^- - \text{H}_2\text{O}$ direct interactions. By this procedure it was found that the average number of $\text{Ni}^{2+}-\text{Br}^-$ contacts does not exceed 0.5; the average coordination number of Br^- ions came out a little less than 6 (the value proposed in previous diffractometric investigations^{20,21}), as expected if part of the bromide ions is bound to the Ni^{2+} ions. Thus, the following complexes were introduced in the calculation of the entire structure functions: $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, $\text{Ni}(\text{H}_2\text{O})_5\text{Br}^+$, $\text{Br}(\text{H}_2\text{O})_6^-$ for the free bromide, $\text{Br}(\text{H}_2\text{O})_n^-$ for the bound bromide ($n < 6$). Pair distances, root mean square deviations of the distances, percentage of the complexes $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ni}(\text{H}_2\text{O})_5\text{Br}^+$ (which too sets the amounts of the free and bound bromide complexes) were indepen-

TABLE II. Parameter values (r = distances, Å; σ = root mean square deviations, Å; n = frequency factors) obtained from least squares refinements are given together with their standard errors (in parentheses). Ni²⁺-H₂O parameters are for both Ni(H₂O)₆²⁺ and Ni(H₂O)₅Br⁺ complexes; Br⁻-H₂O parameters are for both Br(H₂O)₆⁻ and Br(H₂O)₄⁻ complexes of free and Ni-bonded bromide ions.

Parameters	NiBr ₂ 2 M			NiBr ₂ 4 M	
	Present Work	Ref. 14	Ref. 15	Present Work	Ref. 15
$r_{\text{Ni}^{2+}-\text{H}_2\text{O}}$	2.066(2)	2.065	2.04	2.079(3)	2.05
$\sigma_{\text{Ni}^{2+}-\text{H}_2\text{O}}$	0.083(2)	0.112	0.089	0.096(4)	0.089
$r_{\text{Ni}^{2+}-\text{Br}^-}$	2.610(9)	2.62	2.58	2.615(9)	2.53
$\sigma_{\text{Ni}^{2+}-\text{Br}^-}$	0.13(1)	0.09	0.13	0.13(1)	0.13
$n_{\text{Ni}^{2+}-\text{Br}^-}$	0.29(3)	0.85	0.18	0.44(6)	0.47
$r_{\text{Br}^-}-\text{H}_2\text{O}$	3.351(3)	3.12	~3.4	3.329(3)	~3.4
$\sigma_{\text{Br}^-}-\text{H}_2\text{O}$	0.210(3)	0.196	...	0.195(3)	...
$r_{\text{H}_2\text{O}_I-\text{H}_2\text{O}_{II}}$	2.804(5)	2.79	...	2.75(1)	...
$\sigma_{\text{H}_2\text{O}_I-\text{H}_2\text{O}_{II}}$	0.05(1)	0.086	...	0.110(9)	...
$n_{\text{H}_2\text{O}_I-\text{H}_2\text{O}_{II}}$	10.2(1)	10.9	...	4.0(1)	...

(per Ni atom)

dently refined. Moreover, interactions due to molecules in cationic second shells were introduced; obviously this involves a H₂O_I-H₂O_{II} term describing the bond between nearest-neighbor and second-neighbor water molecules (following the indication of the previous discussion, for the 4 M solution Ni²⁺-Br_{II}⁻ interactions had to be accounted for). The transition to a continuous distribution of distances was performed as usual.^{1,2,16,17}

The agreement between experimental and calculated structure functions is shown in Fig. 1. The relevant structure parameters obtained from least square refinements are given in Table II, together with the values proposed for the same parameters in the mentioned studies^{14,15} of NiBr₂ solutions.

DISCUSSION AND CONCLUSIONS

Preliminary to a discussion of the results, the confidence limits of the parameters given in Table II must be assessed, especially those of n_{Br^-} value which is a crucial quantity in the study. It has to be emphasized that, in spite of the complexity of the model, the parameters describing direct inter-

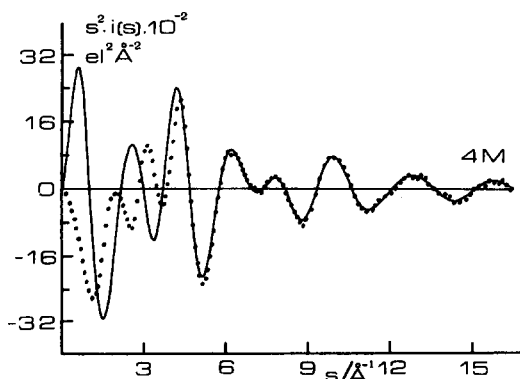


FIG. 4. Experimental structure function of the 4 M solution (dots) and sum of the contributions from the shorter interactions (continuous line).

actions are highly reliable. In fact, these parameters are not much affected by how second shells or continuum are described, as the shorter interactions give dominant contributions at high s . As a proof of this, the simulation of the high s structure function, obtained using direct interactions only, is reported in Fig. 4 for the case of the 4 M solution. However, as we have already discussed,¹ the parameter errors given in parentheses in Table II are the standard deviations based on the goodness of fit in a nonlinear regression and do not give the true uncertainty, which, instead, can be better evaluated through a comparison of the results obtained using different refinement strategies. In this connection, the major problem in the present case was the interference of the Ni²⁺-Br⁻ (distance of about 2.60 Å) and H₂O-H₂O (distance of about 2.80 Å) terms. Thus, if the percentages of Ni bromo complex in the 4 M sample was kept in the range 30%-55%, fits almost as good could be obtained by adjusting the H₂O-H₂O term without any constraint. So, the choice of the most likely n_{Br^-} value has been made using additional criteria, that is, odd parameter values must be rejected (e.g., $r_{\text{H}_2\text{O}-\text{H}_2\text{O}} < 2.70$ Å) and a good description of direct interactions must leave a residual curve $[D(r)_{\text{exp}} - D(r)_{\text{calc}}]$ smooth.¹⁵ As an example, in Fig. 5, experimental $D(r)$, pair distributions at low r , $D_{ij}(r)$, and residual curves $D(r) - \sum D_{ij}(r)$ are given.

Following these criteria, the uncertainty of n_{Br^-} turned out within $\pm 10\%$ in the 4 M solution and a little higher in the 2 M solution, in which the term Ni²⁺-Br⁻, though important for a good fit, has a smaller weight. All these facts considering, we can affirm that undoubtedly our results are consistent with those reported by Wakita *et al.*¹⁵ for both

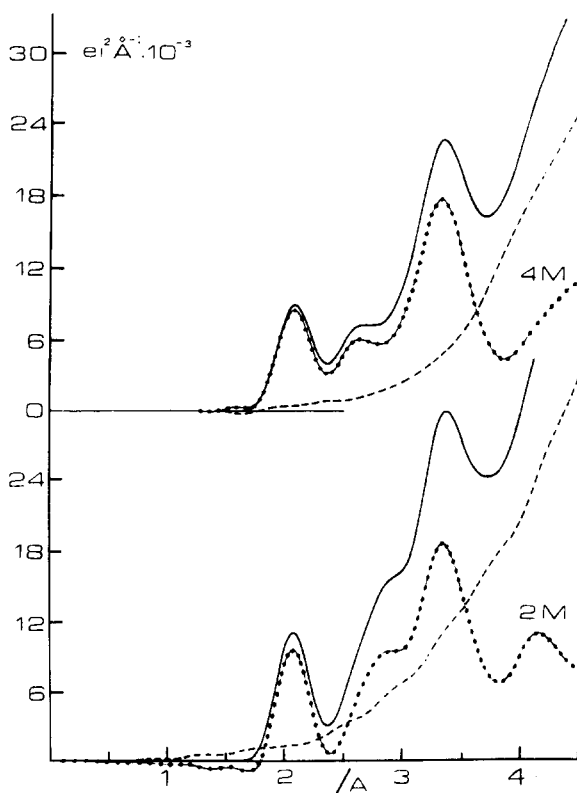


FIG. 5. Radial distribution functions $D(r)$ (solid line), sum of synthetic pair distribution functions from the model, $\sum D_{ij}(r)$ (dotted line) and residual curves $D(r) - \sum D_{ij}(r)$ (dashed line).

solutions, while they are absolutely inconsistent with those proposed by Caminiti *et al.*¹⁴ for the 2 M solution. Referring to the latter, we must observe that the disagreement extends also to the important parameter $r_{\text{Br}^- - \text{H}_2\text{O}}$. In fact, while the value we obtained is similar to the ones given in many other bromide solutions,^{15,20-24} the distance proposed by Caminiti *et al.* (3.12 Å) is unlikely short, even shorter than the distances of the Cl⁻-H₂O pairs,^{1,7} in spite of the greater ionic radius of the Br⁻ ions.

As observed by Wakita *et al.*, the stability constants given in literature for the formation of the species Ni(H₂O)₅Br⁺ cover too a wide range of values to allow a judgement of the diffractometric results on these grounds to be made. However, stability constants proposed by various authors,²⁵ although different according to the different determination method used, concordantly indicate that the Ni²⁺ ions tend to bind Cl⁻ and Br⁻ ions almost to the same extent. It is also for this reason that the results of Caminiti *et al.* do not look much convincing, in that they entail a complexation degree much larger for Ni²⁺-Br⁻ than for Ni²⁺-Cl⁻ pair.

The present study shows that in stoichiometric concentrated solutions of NiBr₂ bromo complexation of the cation takes place. Even in the 2 M solution, the complete omission of Ni²⁺-Br⁻ interactions makes the simulation of the experimental structure function much worse. Because of the discussed similarity of Br⁻ and Cl⁻ ions in the formation of halo complexes with Ni²⁺ ions, the clearer evidence of Ni²⁺-Br⁻ interaction at a given concentration must be ascribed to the greater scattering factor of the bromide that makes the pair distribution function $D_{\text{Ni}^{2+} - \text{Br}^-}$ heavier than the $D_{\text{Ni}^{2+} - \text{Cl}^-}$ one. From this point of view the present result is an indirect confirmation of the existence of halo complexes also in concentrated solutions of NiCl₂.

It will be certainly interesting to compare the present results with those coming from other structural techniques. Actually, few studies similar to those described in the Introduction have been published. The studies of proton, deuteron, and halide relaxation rates^{9,10} estimate an amount of Br⁻ in the first coordination sphere of the Ni²⁺ almost coincident with that proposed for Cl⁻ ions and in good agreement with the present evaluation. Besides, only one EXAFS investigation²⁶ exists, where a small percentage of Ni²⁺-Br⁻ contacts is neither confirmed nor excluded.

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