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Abstract. EXAFS measurements at the In and Br k edges are reported for InBr$_3$ aqueous solutions at various concentrations. The experimental results are in agreement with the structure of indium complexes proposed on the grounds of x-ray diffraction measurements for a concentrated aqueous solution of indium bromide. The analysis of the Fourier-filtered spectra shows that these complexes persist at least until the 1M concentration has been reached.

1. Introduction

The structure of ionic solutions has been, from the first quarter of our century up to the present, a matter of increasing interest in a large variety of investigations. For aqueous solutions that are not very concentrated the Debye–Hückel theory and sophisticated versions [1–6] of this approach have been used; for highly concentrated electrolytical solutions *ad hoc* molecular models are required to interpret the experimental results. De Barros Marques *et al* [7], using x-ray diffraction, investigated concentrated aqueous solutions of indium chloride and of indium bromide. They proposed for those solutions the existence of a liquid-type quasi-close-packing of complexed cations $[In(H_2O)_nX_2]^+$ where X = Cl or Br and $n \simeq 5$–6. The value they indicated for the distance from the indium to the coordinated chloride ion was in agreement with the value given by Ohtaki and Maeda [8] who investigated, also by x-ray diffraction, the structure of mixed aqueous solutions containing indium chloride and lithium chloride. Raman methods [9, 10] had already been used for investigating solutions containing halide salts of indium. The solutions investigated in [9] and [10] are different from those referred to in [7]; other substances have been added to the indium halides, and the coexistence of different types of indium complex has been suggested to interpret the observed behaviour of these ionic liquids. Mathur *et al* [11] studied indium chloride aqueous solutions with values of the concentration not very different from the value given in [7], having suggested for the interpretation of their Raman results the existence of undissociated molecules that were not detected by the authors of [7]. Fratiello *et al* [12] investigated, by the proton magnetic resonance method, a 3.81M solution of InCl$_3$ at $-59\,^{\circ}$C in pure water; they obtained a coordination number of 4.7 water molecules per cation, which is in reasonable agreement with the structure of the cation complexes proposed in [7]. EXAFS spectroscopy was used

in a series of earlier investigations [13–18] on concentrated aqueous solutions of copper, zinc, strontium and cadmium halides, and has proved to be an extremely suitable tool for obtaining precise structural information on such molecular complexes. Application of this technique to solutions of halide salts of indium would thus be a direct way for checking the molecular models suggested by de Barros Marques *et al* [7]. The adequacy of their validity for solutions of lower concentration is discussed.

2. Experimental details

A 4M aqueous solution of indium bromide was prepared from pure anhydrous $InBr_3$ (Fluka, Switzerland) and its composition was controlled by chemical analysis. The 2M, 1M and 0.5M solutions were obtained by successive dilutions. The solutions were contained in a cell of variable thickness, with Mylar windows. As the crystallographic structure of the hydrated crystals was not known we could not use them as reference compounds.

The EXAFS experiments were recorded at the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (Orsay, France) using radiation from the DCI storage ring running at 1.85 GeV with the beam current in the range 200–300 mA. All data were taken at room temperature. The spectra for all samples were obtained on the EXAFS I spectrometer using a Si(331) channel-cut crystal as the monochromator. I_0 and I were measured using two ion chambers.

3. Data analysis

The $\chi(k)$ EXAFS modulations of the absorption coefficient were normalised following a standard procedure [16]; the EXAFS spectra were obtained from the experimental absorption spectra after subtraction of the absorption background obtained by fitting the region below the edge with a Victoreen expression, which was extrapolated beyond the edge. Then μ_0 was simulated using a three-region cubic spline through the EXAFS oscillations beyond the edge. The final result was obtained after removing the remaining long-wavelength oscillations with a smoothing procedure. In converting the scale from photon energy E to the wavevector of the outgoing electron $k = [2m(E - E_0)/h^2]^{1/2}$, E_0 was fixed at the inflection point of the edge: for the indium at 27940 eV and for the Br at 13475 eV.

The normalised $\chi(k)$ oscillations are shown in figures 1 and 2 for the In edge and Br edge respectively. They were found to be almost identical at all the concentrations.

The Fourier transforms of $k^3\chi(k)$ from k-space to R-space were performed in the 60–644 eV (3.85 to 12.65 Å^{-1}) energy range for the In edge and in the 60–670 eV (3.85 to 13 Å^{-1}) range for the Br one, using a Haning window. Figures 3 and 4 show the moduli of the Fourier transforms plotted versus R. The Fourier transform consists mainly of one peak with unphysical features below 1.5 Å due to all the imperfections of the subtraction of the background. For the In edge the main peak is centred at 2.2 Å while for the Br edge it is at 2.35 Å (values uncorrected for the phase shift).
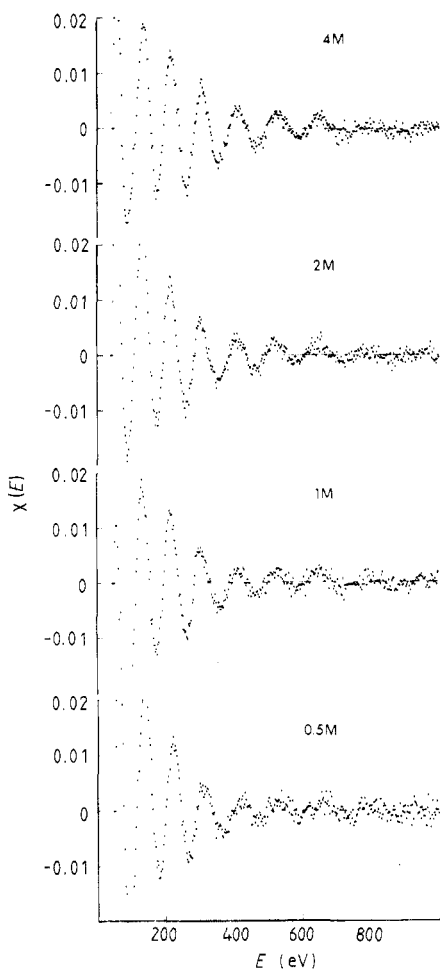
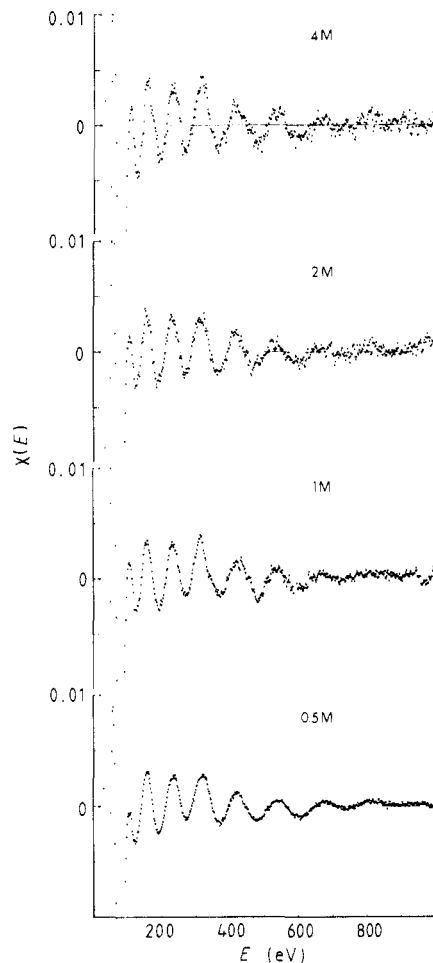**Figure 1.** Experimental EXAFS spectra at the In edge for 4M, 2M, 1M and 0.5M InBr₃ aqueous solutions.

Figure 2. Experimental EXAFS spectra at the Br edge for 4M, 2M, 1M and 0.5M InBr₃ aqueous solutions.

The main peak has been isolated and back-transformed into k-space. A two-shell fit was then applied to the filtered spectra using the formula

$$\chi(k) = -\sum_j \frac{N_j}{kR_j^2} |f_j(\pi)| \exp(-2\sigma_j^2 k^2 - 2R_j/\lambda) \sin(2kR_j + 2\eta_1 + \arg f_j(\pi))$$

which in single-scattering theory and in the plane-wave approximation describes the EXAFS oscillations for a Gaussian distribution of neighbours around a central atom. Here N_j is the number of atoms of type j at a distance R_j from the absorbing atom, $|f_j(\pi)|$ is the back-scattering amplitude, σ_j is the relative mean square displacement between the scattering atom and the absorbing one, $\lambda(k)$ is the electron mean free path which has been taken to be of the form k/Γ [19], and η_1 is the central-atom phase shift.

The total-atom phase shifts $2\eta_1 + \arg f_j(\pi)$ and the back-scattering amplitudes used were those calculated by Teo and Lee [20]. These theoretical functions have already
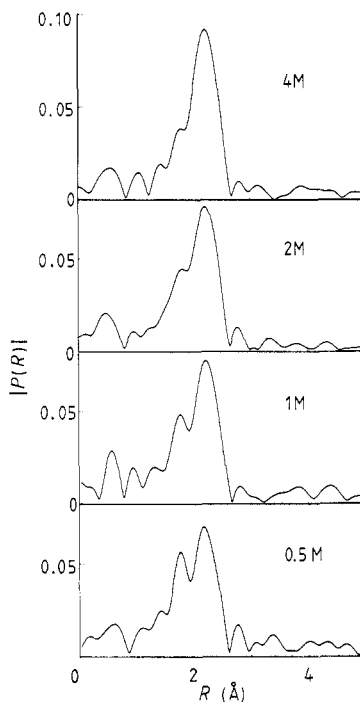
Figure 3. Fourier transforms at the In edge for 4M, 2M, 1M and 0.5M $InBr_3$ aqueous solutions.
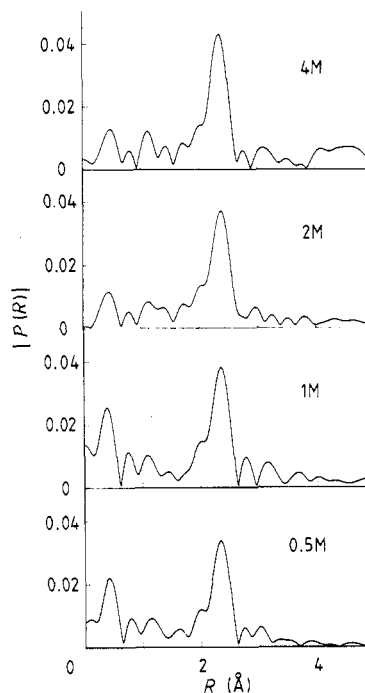
Figure 4. Fourier transforms at the Br edge for 4M, 2M, 1M and 0.5M $InBr_3$ aqueous solutions.

been used to reconstruct, at both edges, the EXAFS spectra of $CuBr_2$ and $ZnBr_2$ crystals [16] and of $CdBr_2$ crystal [18]. N_j, R_j, σ_j and ΔE_0 were determined with a fitting program which takes into account two shells of neighbours. For the In edge we started with $\Gamma = 0.32$ Å^{-2}, the value used for the $CdBr_2$ aqueous solutions (as Cd and In have contiguous atomic numbers), and for the Br edge we started with $\Gamma = 0.22$ Å^{-2}. The fits were obtained over an energy domain spanning from 80 to 660 eV; the choice of so high an energy limit for the beginning of the fitting procedure was dictated by the use of theoretical phase shifts calculated in the plane-wave approximation instead of quantities extracted from a model compound; this last solution was not allowed because the $InBr_3$ solid is very hygroscopic, and it was therefore impossible to prepare such a sample for an EXAFS experiment. Therefore we have chosen to cut out the low-energy part of the spectrum in order to be sure that the mathematical model used is definitely valid.

4. Results

Figure 5 shows the inverse Fourier transform at the indium edge for the concentrations studied. For all the concentrations, the Fourier filtering was done between 1.84 and 2.66 Å (values uncorrected for the phase shift, as indicated above). As can be seen, the results are very similar for 4M up to 1M. Only the 0.5M result is different from those for the more concentrated solutions. This indicates that the local environment of the indium cation remains almost unaltered until the 1M concentration is reached, and that a
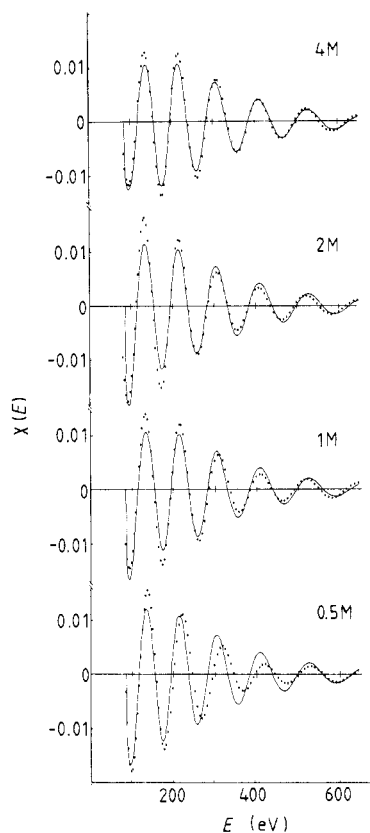
Figure 5. Fourier-filtered first shells (dots) and their fits (full curves) for 4M, 2M and 1M InBr₃ aqueous solutions at the In edge: 2 Br ions at 2.53 Å and 5.4 O ions at 2.71Å. For the 0.5M solution, the same theoretical model is compared with the experimental result, showing the inadequacy of this model.

modification of the structure seems to occur only at a lower concentration, such as 0.5M. The results of the fit are shown in figure 5 and table 1. We started with the 4M aqueous solution of indium bromide, for which the x-ray results [7] provided a model for the indium complex. For the indium edge our best fit to the EXAFS experimental result is obtained with 2.0 ± 0.1 bromine ions linked to one indium cation at 2.53 ± 0.02 Å (σ = 0.080 ± 0.005 Å) and 5.4 ± 0.8 oxygen atoms at 2.71 ± 0.02 Å (σ = 0.14 ± 0.01 Å). For this edge we found ΔE_0 = 6 eV and Γ = 0.06 Å^{-2}. The merit index quoted in table 1 stands for the quantity

$$F = \sum_{N_{pts}} (\chi_{exp} - \chi_{the})^2/\chi^2_{exp}.$$

To obtain this from the classical expression for the merit index [21], we have dropped the normalisation factor extracted from the number of independent data points, since this figure will remain constant throughout the analysis for a given edge (all the data reduction has been done in exactly the same way). We have also normalised with χ^2_{exp} in order to give us an idea of the quality of the fit in moving from one edge to another.

We see from table 1 that this merit index increases slightly as concentration is reduced, but that basically the same structural model applies to all the three samples. Any change of the coordination parameters rapidly destroys the quality of the fit—
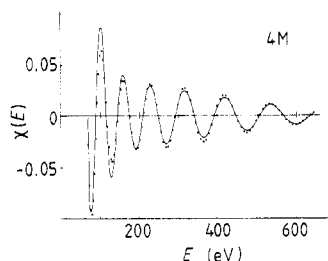
Figure 6. Fourier-filtered first shells (dots) and their fits (full curve) for a 4M InBr$_3$ aqueous solution at the Br edge: 0.7 In ions at 2.55 Å and a second subshell of five O ions at 3.60 Å.

Table 1. Structural results for the indium edge.

Concentration	Bromine			Oxygen			MF (%)
	R (Å)	N	σ (Å)	R (Å)	N	σ (Å)	
4M	2.53	2.1	0.08	2.71	5.4	0.14	1.6
2M	2.53	2.0	0.08	2.71	5.6	0.13	4.9
1M	2.53	2.1	0.08	2.71	5.6	0.14	4.5

Table 2. Structural results for the bromine edge.

Concentration	Indium			Oxygen			MF (%)
	R (Å)	N	σ (Å)	R (Å)	N	σ (Å)	
4M	2.55	0.7	0.07	3.60	5.0	0.17	8.6
2M	2.55	0.6	0.07	3.60	5.0	0.17	13.0
1M	2.55	0.6	0.07	3.60	4.7	0.18	10.0

obviously at high energy for the bromine parameters and mostly at low energy for the oxygen ones.

On figure 6 we show a fit for the bromine edge. For the 4M solution we found 0.7 ± 0.05 indium ions linked to one bromine at 2.55 ± 0.02 Å ($\sigma = 0.071 \pm 0.005$ Å) and 5 oxygen atoms at 3.60 Å ($\sigma = 0.17$ Å), which on average may correspond to two bromine ions linked to one indium and one free bromine ion. Table 2 gives the entire set of results for the bromine edge. We should make several comments.

(i) The structural values obtained around the bromine are in excellent agreement with those extracted from the analysis for the indium edge when the same pair of atoms is concerned; this is a good check of the validity of the result.

(ii) The numerical value of the merit index is at least twice that obtained for the indium edge; it can be verified, by starting the fitting procedure at higher energies, that this discrepancy arises from the low-energy part of the spectrum, where additionally oxygen and indium have to be taken into account simultaneously (notice that, in Teo and Lee's calculations, the back-scattering amplitudes of these two elements are comparable in this range of energy).
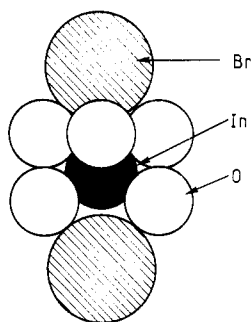
Figure 7. A model for the cation complexes of InBr₃ aqueous solutions.

As already found in published studies of aqueous electrolytic solutions, the exact modelling of the water coordination of the anions is very difficult. The main reason for this is that free bromine ions are left in the solution; these ions are surrounded by a poorly defined oxygen shell, which contributes to the overall signal for the bromine edge. We see therefore that the degree of disorder of this environment, together with the rapid decrease of the back-scattering amplitude of the oxygen, leads to a contribution where the coordination number N and the disorder parameter σ couple strongly; in fact, the quality of the fit does not change significantly when the oxygen coordination is varied by ± one atom.

5. Discussion and conclusion

The x-ray studies of de Barros Marques $et\ al$ [7] on the structure of a 4.23M aqueous solution of indium bromide indicated the presence of $[InBr_2(H_2O)_n]^+$ complexes in that solution (with $n = 5$ or 6). Although those authors focused their attention on how the indium complexes contribute to the overall structuring of the solution, the model proposed by them for the In^{3+} complexes is in good agreement with the EXAFS results. The indium complexes were assumed in their models to have the shape of a bipyramid with the indium cation lying at the centre, the two halogenide ions on the axis at two opposite vertices, 2.60 Å from the centre, and five or six water molecules at the vertices of the bases, also 2.60 Å away from the indium cation.

Because of the better accuracy of the distance measurements made using EXAFS, this model can be improved: using the inter-atomic distances and assuming a value of six for the water coordination of indium, we obtain the shape shown in figure 7, where the two planes of oxygen atoms are separated by 0.32 Å and this deformed octahedron is capped by the two bromine atoms and has at its centre the indium one. Therefore, three oxygen atoms are located at 3.6 Å from the bromine ion while three other ones are at 3.84 Å. The large Debye–Waller factors associated with this bond are in agreement with the suggestion of two close values for the distances from the bromine to the oxygen atoms, and this ties in with the difficulty of modelling the oxygen coordination correctly. As already pointed out, the EXAFS data are not in themselves sufficient grounds for asserting that complexes where In is fourfold coordinated cannot exist, since our results range between 4.6 and 6.2 water molecules around one indium atom. However, the x-ray diffraction results are essentially in line with an oxygen coordination ranging between 5 and 6, and therefore indicate that this model is the best one and that it remains the best

until the 1M solution is reached, with some evolution due to the amount of free bromine into the medium.

At lower concentration (0.5M) this type of organisation seems to disappear partly, since the same structural model cannot be used to represent the experimental result correctly (figure 5). All the attempts to fit the data lead to a slight decrease of the indium–bromine distance (by 0.03 Å) and a decrease of the coordination numbers. Nevertheless, these results are physically not very satisfactory; they can be explained by assuming that some of the indium atoms are now isolated in the solution, a proportion of them still being involved in $InBr_2$ complexes. However, the exact overall model is more difficult to describe with accuracy.

Acknowledgments

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