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Structure of concentrated aqueous solutions of indium chloride and bromide. Modelling of the structure of electrolyte solutions

M I Cabaço, A M Gaspar, C M de Moraes and M Alves Marques

Centro de Física da Matéria Condensada da Universidade de Lisboa, Avenida Prof. Gama Pinto, 2, 1649-003 Lisboa, Portugal, and Departamento de Física, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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Abstract. Concentrated aqueous solutions of indium bromide (3.06 mol dm^{-3}) and chloride (3.22 mol dm^{-3}) were investigated by x-ray diffraction. In order to interpret the profile of the diffraction patterns, the existence of positional correlations between cation complexes and between cation complexes and (free) anions extending to distances beyond 7 \AA is discussed. These complexes are constituted by the coordination around the indium cation of two anions, bromide or chloride, and five (six? for the bromide solutions) water molecules. The structure of these complexes was previously investigated by Raman spectroscopy and by EXAFS. Results of these and of other investigations are compared with those recently obtained.

1. Introduction

The investigation of the structure of concentrated aqueous solutions ($\sim 3 \text{ mol dm}^{-3}$) of halides of indium is the aim of the work presented here. Quasi-saturated solutions of the same salts were investigated with some success in 1982 [1] where our method of studying concentrated aqueous solutions was described. It seems pertinent, however, to refer to how relevant are some of the positional correlations beyond the direct contact between particles that occur in the case of the present solutions at distances near 9 \AA , to produce an intense maximum of intensity at about 0.9 \AA^{-1} . These correlations may be described by a structure referred to as a *liquid-type quasi-close-packing* (LTQCP) of the ions with the highest value of electric charge. The essential features of the LTQCP structure have already been detected in concentrated aqueous solutions of salts where one ion has an electric charge with a value that exceeds the value of the counter-ion, e.g. AlCl_3 , MgCl_2 , Li_2SO_4 [2], InBr_3 , InCl_3 [1], $\text{In}(\text{NO}_3)_3$, $\text{In}_2(\text{SO}_4)_3$, $\text{In}(\text{ClO}_4)_3$ [3], YBr_3 , YCl_3 [4]. In these investigated solutions around the ions of largest electric charge— Al^{3+} , Mg^{2+} , SO_4^{2-} , In^{3+} and Y^{3+} —an assembly of molecules (and sometimes of counter-ions) is pulled by the strong electrostatic field of that ion and constitutes a cloud of molecular units (ions and molecules). In these clouds the different molecules are closer to each other than they are, on average, in the molecular distribution that exists in liquid pure water at the same temperature. So the scattering power of the cloud is larger than the scattering power of an assembly of molecules that in liquid pure water occupy the same volume. In some cases, inside the cloud, a true molecular complex is constituted [5–8]. These molecular complexes exhibit a relative scattering power (compared to the water in the solution) that may be estimated by the ratio $[F_{eff}(cc)/F_{eff}(w)]^2$ where $F_{eff}(cc)$ is the effective scattering factor of the cation complex and $F_{eff}(w)$ is the effective scattering power of an assembly of water molecules

which in the liquid pure water would occupy, approximately, the same volume as the cation complex (see the appendix). A rough calculation of this ratio at values of the momentum transfer $Q = 4 \sin \theta / \lambda \sim 0.9 \text{ \AA}^{-1}$ shows that indium complexes scatter more than an order of magnitude compared with an assembly of water molecules occupying an equivalent volume. Therefore these scattering clouds play a relevant role in the interpretation of the intensity of the x-rays scattered by the concentrated aqueous solutions for those Q values.

For concentrated aqueous solutions of indium chloride and bromide Raman spectroscopy experiments [7] indicated apparently the existence of complexes constituted around the indium cations. EXAFS investigations [9, 10] gave us values of distances that correspond to relevant bonds inside these complexes. These two different types of experiment are the basis of the conception of our molecular models.

Raman spectra of concentrated InBr_3 and InCl_3 aqueous solutions exhibit bands for which frequency values are not very different from the values observed for the liquid pure water as well as some new bands, too [7]. Among these new bands, we can distinguish diffuse (and weak) bands from intense and narrow ones. The frequency of the first ones changes when the solvent (hydrogenated water) is replaced by deuterated water, while the second ones keep the same values. One of these intense bands, observed at $\sim 195 \text{ cm}^{-1}$ for the InBr_3 solution and at $\sim 295 \text{ cm}^{-1}$ for the InCl_3 solution, is a single band, very intense, polarized, and with a profile not dependent on the concentration of the solution (1.8 to 4.0 mol dm^{-3}). We have suggested the attribution of the 195 cm^{-1} band to the activity of a stretching vibrational mode $\text{In}^{3+}\text{-Br}^-$ of the indium complexes with *one* coordinated bromide anion or of *two* coordinated bromide anions *in a straight line with the cation*, without considering oscillations of water molecules. This second hypothesis, *two* coordinated anions, agrees with EXAFS results, which suggest *two* anions coordinated to each cation, on average.

The existence of two types of indium complex, one with *one* coordinated anion and other with *three* coordinated anions, in equal proportions, to obtain the same mean value of 'two' in agreement with EXAFS and x-ray diffraction results, does not seem acceptable. In fact a molecular aggregate with *one* anion and a molecular aggregate with *three* coordinated anions would not coordinate the same *ligand*, the anion, at distances with similar values, neither would it produce stretching vibrational modes with similar values of the frequencies. The Raman band observed at $\sim 195 \text{ cm}^{-1}$ in the InBr_3 solution is clearly a single band (as is the band at $\sim 295 \text{ cm}^{-1}$ in the InCl_3 solution), so the coexistence of two types of complex does not seem to be plausible. EXAFS experiments permitted us to obtain only one value for the distance $\text{In}^{3+}\text{-Br}^-$ (or for $\text{In}^{3+}\text{-Cl}^-$), so the coexistence of two types of aggregate may be, for the two reasons, rejected.

The EXAFS experiments permitted us to obtain for indium bromide solutions (1 to 4 mol dm^{-3}) the values of the distances $\text{In}^{3+}\text{-Br}^-$ ($2.54 \pm 0.02 \text{ \AA}$) and $\text{In}^{3+}\text{-O}$ ($2.71 \pm 0.02 \text{ \AA}$) at room temperature and pressure. We should point out that the value of the distance $\text{In}^{3+}\text{-Br}^-$ is a mean of the values obtained from EXAFS experiments checking on the indium and on the bromine edges [9]. These experiments suggest the existence of two bromide anions and five (or six?) water molecules around each indium cation. EXAFS experiments permitted us also to obtain for indium chloride solutions (0.5 to 4 mol dm^{-3}) the values of the distances $\text{In}^{3+}\text{-Cl}^-$ ($2.35 \pm 0.02 \text{ \AA}$) and $\text{In}^{3+}\text{-O}$ ($2.52 \pm 0.02 \text{ \AA}$) [10]. The existence of two chloride anions and five water molecules was suggested, too. These values of distances, $\text{In}^{3+}\text{-Br}^-$ and $\text{In}^{3+}\text{-Cl}^-$, do not agree with the previous values found in different conditions of coordination observed either in different solutions [11, 12] or in crystals [13].

Both Raman and EXAFS results converge to the plausible existence of cation complexes in solution of which the structure can be described as bipyramidal with two anions (bromide or chloride) in the 'poles' and five (or six? for the InBr_3 solution) water molecules in the 'equatorial plane'.

The observed x-ray diffracted intensity can be interpreted in its main part by an appropriate structural arrangement of the solvated cations. For the investigated solutions this arrangement is a *local close packing* of the solvated cations, even if this structure does not overpass the first shell of neighbours. The existence of a shell of neighbours at a distance that is the characteristic distance between first neighbours in a face-centred cubic lattice seems to be essential to the interpretation of the well distinguished maximum near $Q_0 \sim 0.9 \text{ \AA}^{-1}$ in the investigated solutions. In fact, the Q_0 value for which the maximum of interferences is observed is calculated from the maximum of the Debye function $\sin(Qr)/(Qr)$, r being the mutual distance between the closest neighbours in a close-packing arrangement. At these distances many different positional correlations should be taken into account, certainly, but the predominant role of these scattering clouds is obvious. It is not necessary that the probability of occurrence of the neighbour in the first shell of close-packed particles be *one*; this probability may be perhaps sometimes smaller than one. However we think that a molecular model, where positional correlations between one cation complex and any of its 12 neighbours are not assumed, cannot reproduce satisfactorily the experimental intensity.

The argument for the existence of a close packing is as follows. The existence of the structure (LTQCP) may be suggested by the perception of a tendency of the ions of high electric charge to coordinate the largest possible hydration *cloud*. *Cubic close packing* is the cubic arrangement of ions where the largest interionic distance for a given (macroscopic) density is found. So, such a structure may be expected in solutions where divalent (or trivalent) ions are present because an intense electrostatic field around themselves coordinates to these ions a large number of water molecules. The counter-ions (anions in this case) are assumed as located in the *holes* of the structural arrangement. We think that the competition, between the cations, for the largest possible solvation cloud is determinant for the close-packing arrangement at the level of the first neighbours. But we do not think that a very regular arrangement, over the *direct contact* between two solvated cations may be assumed as relevant.

J A Prins investigated with success, by x-ray diffraction, the existence of molecular and ionic long range correlations in a large number of electrolyte solutions [14]. He obtained a comprehensive series of x-ray diffraction patterns and suggested the existence of a *superarrangement* of ions in those solutions to interpret his results. However this scientist assumed, we think, an excessively long range order in concentrated aqueous solutions. His point of view is transparent in the description of table I in [2]. We should like to emphasize that in J A Prins' articles the value of the distance between the closest neighbours is in agreement with the value calculated from a *close-packing* structure.

We have not yet investigated the lowest value of the concentration of a salt that may retain the *liquid-type close-packing* (suggested as an adequate model for the dynamical structure of concentrated aqueous solutions).

Correlations between cations were investigated in aqueous solutions of chlorides of different heavy and light cations [15]. Information concerning correlations between ions or molecules that are not in contact has already been discussed in different papers [16–20]. Investigations by neutron diffraction [21] that might suggest the existence of positional correlations of nickel cations in concentrated aqueous solutions have been discussed also by a number of scientists [22, 23].

2. Experiment and data reduction

Rh $K\alpha$ radiation ($\lambda = 0.6147 \text{ \AA}$) monochromatized by reflection from a lithium fluoride crystal was used. The intensities were measured on a Philips θ - 2θ horizontal goniometer, slightly modified, with a scintillator counter. The angular range of the scattering angle

cover $2^\circ \leq 2\theta \leq 103^\circ$, hence allowing measurements up to a momentum transfer $Q = 4 \sin \theta / \lambda \sim 16 \text{ \AA}^{-1}$. Several runs were accumulated with constant counts at each point. The aqueous solutions were prepared from their hydrated salts and the composition of the solutions controlled by chemical analysis of the cation and the anion (3.22 mol dm^{-3} for InCl_3 , 3.06 mol dm^{-3} for InBr_3). The solutions were studied at room temperature by transmission in layers of some tenths of a millimetre thick contained in a plate cell between nitrocellulose windows 30 \mu m thick. The densities at 295 K are 1.556 g cm^{-3} for InCl_3 and 1.896 g cm^{-3} for InBr_3 .

The measured intensities were corrected first from the scattering of the cell and afterwards from absorption and polarization. The corrected intensities were scaled to absolute units using the Krogh-Moe method [24]. Finally a correction was made to take into account either some x-ray background which is not eliminated by the correction of the empty cell or Compton scattering which is only approximately estimated.

Finbak's method reformulated by Warren [25] was applied to the experimental data and used to calculate the following total pair correlation function of the solution $g(r)$:

$$g(r) = 1 + \left(2\pi^2 r \rho_e \sum_{uc} Z_j \right)^{-1} \int_0^{Q_{max}} Q i'(Q) e^{-bQ^2} \sin(rQ) dQ \quad (1)$$

where ρ_e is the average scattering density of the solution, Z_j the atomic numbers and $i'(Q)$ the reduced intensity defined as:

$$i'(Q) = \left(I_{eu}(Q) - \sum_{uc} f_j^2 \right) / F^2(Q) = i(Q) / F^2(Q). \quad (2)$$

$I_{eu}(Q)$ is the total intensity and $i(Q)$ is the so-called dependent intensity.

The sharpening factor $F(Q) = \sum_{uc} f_j^2 / \sum_{uc} Z_j$ and the sum extends over all four atomic species in the solution. The b in the modification function e^{-bQ^2} was set equal to 0.01 \AA^2 . Different values of Q_{max} were tried for the Krogh-Moe method as well as in the Fourier inversion. In the data analysis presented here we used Q values up to 14 \AA^{-1} . This cut-off produces spurious peaks and decreases the spatial resolution, but this is not relevant for distances greater than 2 \AA .

The structural units in the solutions (the units of composition, uc) are always referred to one cation: for the InCl_3 solution one In^{3+} , three Cl^- and $14.2 \text{ H}_2\text{O}$ molecules; for the InBr_3 solution, one In^{3+} , three Br^- and $14.4 \text{ H}_2\text{O}$ molecules. The volume of the structural unit is 538 \AA^3 for InBr_3 and 515 \AA^3 for InCl_3 .

The coherent scattering factors f_j , corrected for anomalous dispersion, were obtained from Cromer and Mann [26] for Cl^- , Br^- and In^{3+} . For H_2O we used those from Hajdu [27]. Incoherent scattered intensities corrected from the Breit-Dirac recoil factor were calculated from Pálinkás and Radnai [28] for Cl^- and from Hajdu [29] for Br^- . For In^{3+} an extrapolation was done from the In atom [30] based on Freeman and Watson [31].

3. Results and discussion

3.1. Experimental results

X-ray diffraction patterns of concentrated aqueous solutions ($\sim 3 \text{ mol dm}^{-3}$) of indium bromide and chloride are presented in figure 1. The first maxima of intensity (near 0.9 \AA^{-1}) are found for Q values clearly smaller than the corresponding ones in quasi-saturated solutions [1]. The pair correlation functions $g(r)$, calculated after Fourier inversion of the experimental intensities for these solutions, are displayed in figure 2.

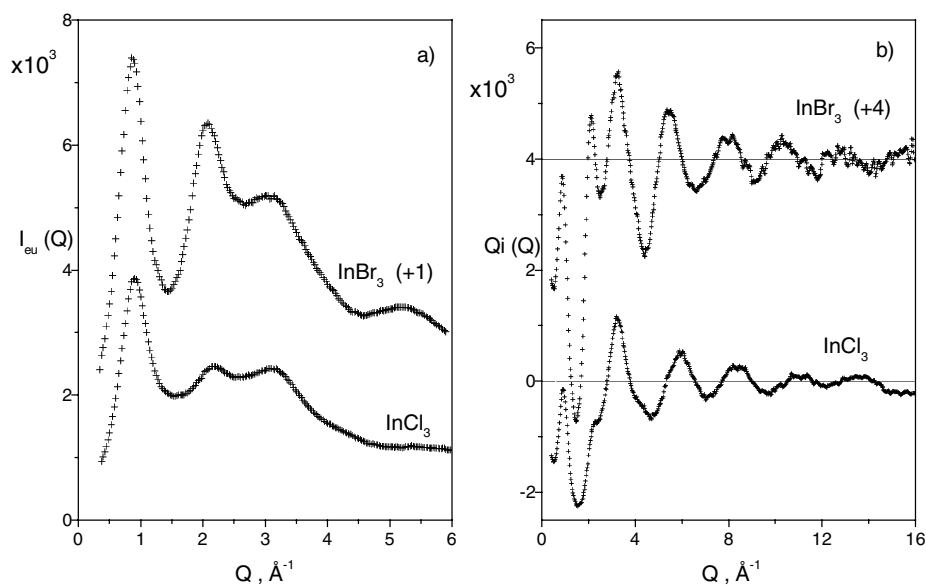


Figure 1. X-ray diffraction patterns of a 3.06 mol dm^{-3} InBr_3 aqueous solution and of a 3.22 mol dm^{-3} InCl_3 aqueous solution: (a) $I_{eu}(Q)$; (b) $Q_i(Q)$. For clarity, curves are shifted, +1 in (a) and +4 in (b) for InBr_3 .

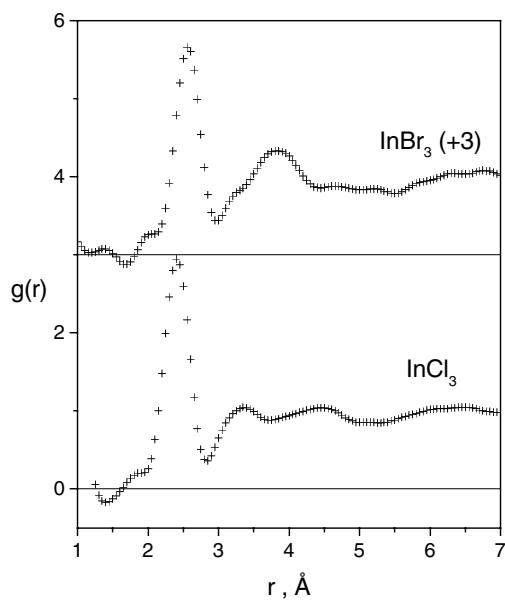


Figure 2. Experimental pair correlation function $g(r)$ for a 3.06 mol dm^{-3} InBr_3 aqueous solution and for a 3.22 mol dm^{-3} InCl_3 aqueous solution. For clarity, for InBr_3 the curve is shifted +3.

3.2. Molecular models

The analysis of the x-ray diffraction patterns of concentrated aqueous solutions of indium halides may be, apparently, interpreted by the existence of a *liquid-type close packing* of the

indium complexes. We admit that the competition of the ions that create around them the more intense electrostatic field determines an (approximately) cubic structure where they are as distant as possible; a strong cation–anion electrostatic attraction requires a dense arrangement in the solution. This is the assumed close packing (see below models CP of the indium bromide solution and of the indium chloride solution).

The cooperation of the x-rays scattered by the different ions and molecules produces a total dependent intensity that may be computed by the Debye formula:

$$i(Q) = \sum_{i \neq k} f_i f_k \frac{\sin(Qr_{ik})}{Qr_{ik}} \quad (3)$$

f_i being the atomic or molecular scattering factors, r_{ik} the distances between the atoms or molecules i and k . The validity of this approximation is founded in the spherical symmetry around each atom or molecule approximately fulfilled on average within the volume of the coherence of the Rayleigh scattering. The method of calculation has already been indicated [1–4, 14, 32, 33]. So, we consider two different internal configurations in distinct regions: the first configuration, near the *central particle* is crystalline type (discrete distribution); the other one which starts at an adequate distance from the central particle and goes up to large distances is simulated by a random (uniform) distribution. This uniform distribution may, plausibly, simulate the space averaged structure of the solutions as they are ‘seen’ by an arbitrary central particle at large distances in the bulk of the liquid. The value r_{th} of the threshold of this continuum is fixed as realistically as possible although attention should be paid to the value of the scattered intensity produced by this uniform distribution. This intensity, $i_c(Q)$, ought to be smaller than the value obtained for the intensity from the crystalline region, $i_d(Q)$, in the range of Q values useful for the discussion of the plausibility of the models (it is convenient to minimize the influence of a contribution originating from a region where the arrangement of the molecules and ions is uncertain). So, in these models only one half of the first shell of the close-packed indium complexes was considered in the crystalline distribution. The calculated (total) intensity, $I_{eu}(Q)$, in electron units, that corresponds to the molecular models, idealized to interpret the profile of the observed x-ray intensity, is presented in each figure from 0.5 \AA^{-1} up to high values of Q but it is trustworthy, for those reasons, only from 0.7 \AA^{-1} . The experimental intensity is given alongside for reference. The intensities corresponding to some variants of the more plausible models were calculated in order to determine the influence of modifications of the structures that are compatible with the available volume inside the concentrated aqueous solutions. Two variants were tested. The first one was a close packing of solvated cations with the free anions distributed over the tetrahedral holes of the face-centred cubic lattice instead of being located in the middle points of the cation–cation distance. The second variant was a simple cubic lattice of the cation complexes with the free units distributed over the vacant sites. None of the variants permitted us to obtain an agreement as good as the one obtained with the CP model presented here.

The results obtained by EXAFS [9, 10] were, as already stated in the introduction, used to define, with a reasonable approximation, the shape and the size of the indium complex, which is a bipyramid with the coordinated water molecules in an *equatorial* plane and the two coordinated anions in the *poles*, with the indium cation in the centre (see table 1, figure 3). These complexes are *close packed*. Free anions and water molecules are distributed over the middle points of two next neighbour cations in agreement with the available volume allowed by the close packing and taking into account also electrostatic interactions. The water molecules that can not be located in the middle point between the cations are distributed in the available holes of this *face-centred cubic lattice* (tetrahedral and octahedral holes). Gaussian fluctuations of the values of the distances between the ions or molecules are adequately adjusted in each

Table 1. $3.06 \text{ mol dm}^{-3} \text{ InBr}_3$ and $3.22 \text{ mol dm}^{-3} \text{ InCl}_3$ aqueous solution structural data: cation complexes of molecular models. Values of the mutual distances r obtained from EXAFS experiments [5, 6], r.m.s. fluctuations Δr and weight of each correlation w , concerning each kind of correlation (see text). The distances concerning water molecules were obtained from the positions of their oxygen atom. Distances are in (\AA).

Correlations	InBr_3 Model CP			InCl_3 Model CP		
	r	Δr	w	r	Δr	w
cation–anion(c)	2.55	0.06	4	2.35	0.06	4
cation–water(h)	2.70	0.06	10	2.52	0.06	10
anion(c)–anion(c)	5.10	0.19	2	4.70	0.19	2
anion(c)–water(h)	3.70	0.19	20	3.40	0.19	20
water(h)–water(h)	3.10	0.19	10	3.00	0.13	10
	5.10	0.26	10	4.80	0.13	10

(c) means ‘coordinated’ and (h) means ‘hydration’.

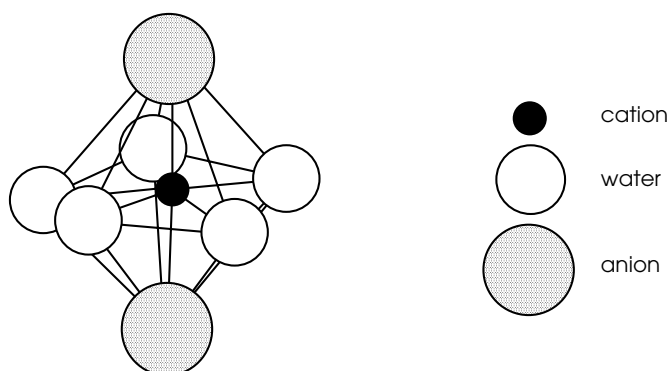


Figure 3. Approximate shape of the cation complex in concentrated aqueous solutions of indium halides.

concentrated aqueous solution. The values of these fluctuations Δr are larger for longer distances and of the order of 15% if the correlated atoms or molecules do not belong to the same complex (see tables 1 and 2). The values of Δr indicated in table 1 for the internal distances of cation complexes may seem to be excessive. We must consider, however, that in hydration complexes the orientation of the water molecules is not very regular (if the values of their relevant multipoles are taken into account) and a range of values of distances will be expected for the (slightly) different aggregates. A *close-packed model* (CP) simulation gives a reasonable agreement with the experimental x-ray structural results obtained for the concentrated ($\sim 3 \text{ mol dm}^{-3}$) aqueous solutions of indium bromide (see figure 4).

In this model five water molecules are assumed as coordinated by the indium cation, three water molecules (per cation) are distributed in the middle points of the cation–cation distances and two water molecules are located in the tetrahedral holes of the close-packing.

The calculated intensities are compared with experimental ones in figure 4(a); in figure 4(b) are the intensities $Qi(Q)$. The contribution to the dependent intensity $i(Q)$ of the scattering of the discrete molecular distribution of the ions and molecules of the idealized models i_d , the contribution of the continuum (uniform) distribution of ions and molecules i_c , and the total intensity i_t ($i_t = i_d + i_c$) are represented in figure 4(c). The pair correlation functions $g(r)$ obtained from the calculated intensities are presented in figure 4(d).

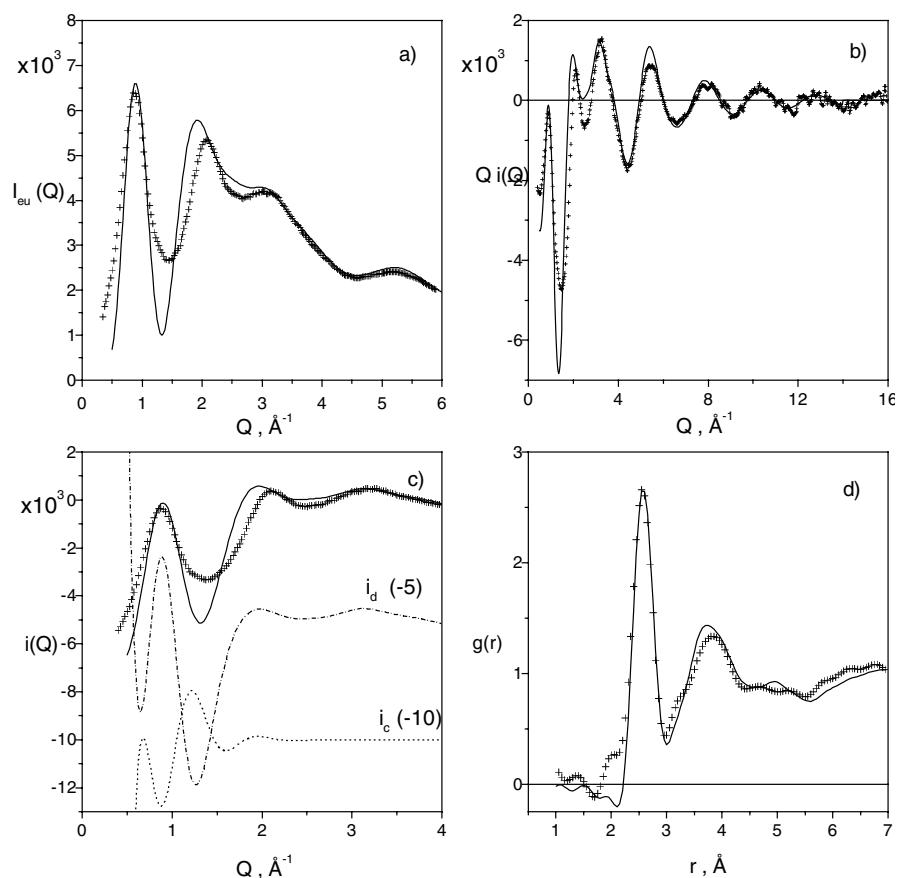


Figure 4. Molecular model CP of the 3.06 mol dm^{-3} InBr_3 aqueous solution. Calculated (—) and experimental (+ + +) intensities: (a) $I_{eu}(Q)$; (b) $Qi(Q)$; (c) contributions to the dependent intensity $i(Q)$ of the scattering obtained from the discrete molecular distribution of ions and water molecules i_d (— · —) and from the continuum (uniform) molecular distribution i_c (· · · · ·). For clarity, curves are shifted -5 for i_d , -10 for i_c . (d) Calculated (—) and experimental (+ + +) pair correlation function $g(r)$.

We have also calculated the intensity scattered when the number of hydration water molecules is six instead of five. Both the intensities and the pair correlation function obtained show a good agreement with the experimental curves. The comparison in the region of $r \approx 2.6 \text{ \AA}$ of the profiles of the pair correlation function $g(r)$ corresponding to these two close-packed models (CP and the other with six hydration water molecules) does not allow us to conclude which solvation complex is more plausible.

In contrast with these *close-packed* models we considered a model without close packing (WCP) where the cation complexes are assumed as not correlated: the values of the distances between the closest neighbour cation complexes were assumed as irregularly distributed, adequately simulated by a continuum. This structure, which is a modification of model CP, has only correlations between particles almost in direct contact. Either this structure or the close-packed one display similar pair correlation functions for short distances (up to 4 \AA), but the model without close packing is not adequate to describe the first intense and narrow maximum of intensity observed at Q values close to 0.9 \AA^{-1} . The existence, that seems

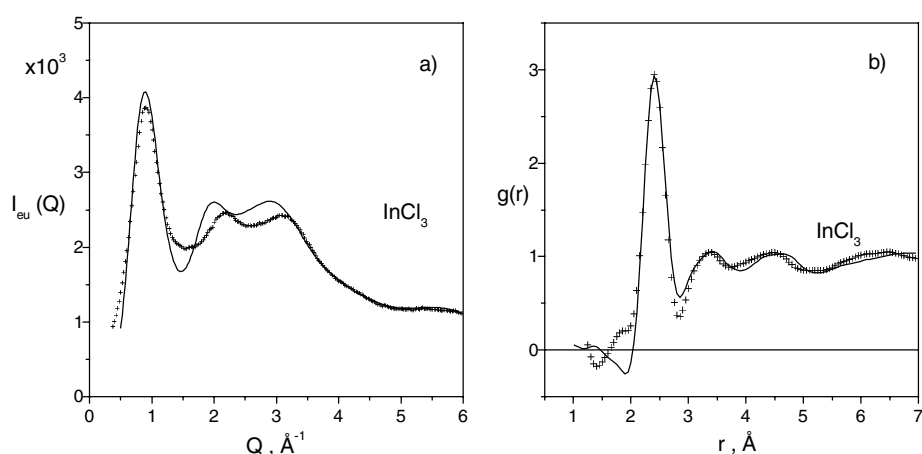


Figure 5. Molecular model CP of the indium chloride solution. Calculated (—) and experimental (+ + +): (a) intensities $I_{eu}(Q)$; (b) pair correlation function $g(r)$.

to be plausible even in concentrated solutions, of regions where the *crystallinity* is not so marked may, perhaps, produce an intensity with a value which is found between the calculated intensity from the *crystalline* models (CP) and the calculated intensity from a *without order* configuration (WCP).

The molecular model of the indium chloride solution was obtained by substituting in the model CP proposed for the indium bromide solution the bromide by chloride anions; final small adjustments of the values used for the distances between molecules and ions around the mean value were assumed for each correlation (figure 5, table 2).

We think that concentrated aqueous solutions of divalent or trivalent cations with monovalent ions may be investigated in order to easily obtain structural information considering the contributions to the dependent intensity $i(Q)$, of three main types of correlation: (i) correlations between the solvated ions that define the *close packing*; (ii) correlations between these solvated ions and the ions (and water molecules) that are approximately located in the middle points of the distances between the cation; (iii) all the other correlations.

It appears that not only the intensities corresponding to *cation-cation* and *cation-anion* (*coordinated*) are relevant to the maximum observed near 0.9 \AA^{-1} , but also other correlations give large contributions. This example makes it easier to understand that the maximum which indicates the presence of the close-packing arrangement in the solution may be visible even with light cations like aluminium or beryllium because the coordination shells of water molecules give noticeable interferences. In figure 6 are represented the intensities produced by groups of correlated pairs. The first group includes all the pairs involved in the *close-packing* assemblies (first neighbours), giving a remarkable constructive contribution close to 0.9 \AA^{-1} . The second group shows, close to 0.9 \AA^{-1} (the minimum being located at 1.2 \AA^{-1}) a pronounced destructive contribution for the intensity, the more significant being the one corresponding to the correlations *cation complex-free anion* (in the middle points of the cation-cation distances). This explains why the intensity of the maximum indicative of the presence of the close packing is not always visible if heavy free counter-ions are present. If we compare the patterns of equimolecular solutions of magnesium chloride and bromide [2] and of yttrium chloride and bromide [4], the intensity of the maximum indicative of the presence of the

Table 2. 3.06 mol dm⁻³ InBr₃ and 3.22 mol dm⁻³ InCl₃ aqueous solution structural data: the more relevant crystalline type components of molecular models (see text). Values of the mutual distances r , r.m.s. fluctuations Δr , weight of the correlation w and threshold of the continuum r_{th} concerning each kind of correlation (see text). Distances are in Å.

Correlations	InBr ₃				InCl ₃			
	r	Δr	w	r_{th}	r	Δr	w	r_{th}
cation–cation	9.1	0.90	6	9.6	9.0	1.22	6	9.6
cation- anion (c)	7.5	0.97	16		7.5	1.22	16	
	9.4	1.03	8	9.6	9.3	1.29	8	9.6
cation–water(h)	6.4	0.97	1.3		6.5	0.97	1.3	
	6.8	0.97	6.7		6.8	0.97	6.7	
	7.4	0.97	17.3		7.4	1.22	9.3	
	—	—	—		—	—	—	
	9.4	1.03	8	9.6	9.3	1.29	8	9.6
cation–anion(f)	4.5	0.45	4	6.3	4.5	0.26	4	6.3
cation–water I(f)	4.5	0.45	12	6.3	4.5	0.39	10	5.9
cation–water II(f)	5.5	0.84	8	5.7	5.5	0.64	4	5.6
anion(c)–anion(c)	5.4	0.97	2.7		5.6	0.97	2.7	
	—	—	—		—	—	—	
	9.1	1.03	8	9.6	9.0	1.29	4	9.1
anion(c)–water(h)	5.1	0.97	1.3		5.1	0.97	5.3	
	5.3	0.97	8		5.5	0.97	2.7	
	5.9	0.97	1.3		6.0	0.97	5.3	
	—	—	—		—	—	—	
	9.1	1.03	17.3	9.6	9.3	1.29	5.3	9.5
water(h)–water(h)	4.1	0.77	1.3		4.3	0.77	1.3	
	5.0	0.97	1.3		5.2	0.77	1.3	
	5.4	0.97	5.3		5.6	0.77	5.3	
	—	—	—		—	—	—	
	7.3	0.97	16		7.2	1.22	12	
	—	—	—		—	—	—	
	9.4	1.03	5.3	9.6	9.4	1.29	6	9.6

(c) means ‘coordinated’, (h) ‘hydration’ and (f) ‘free’; *water I* indicates the water molecules located in the middle points of the cation–cation distances and *water II* refers to the water molecules located in the tetrahedral holes of the close packing.

close packing appears smaller for the solution where the anion has more electrons. As for the interactions between all the water molecules (the hydration water molecules included) no marked influence in the x-ray pattern is apparent (figure 6).

4. Conclusion

The interpretation of the x-ray diffraction patterns of concentrated aqueous solutions of indium halides in the range of Q values from ~ 0.9 up to $\sim 3 \text{ \AA}^{-1}$ is realized with success with the intervention of the existence of positional correlations between ions, between ions and water molecules and between water molecules in the range $\sim 4 \text{ \AA}$ up to $\sim 9 \text{ \AA}$. These positional correlations were obtained from a molecular model that may be referred as a *liquid-type quasi-close-packing*.

The essential components of this structure are: (i) the solvated ion of largest valence in the solution is surrounded by 12 closest (alike) neighbours at a distance which value is

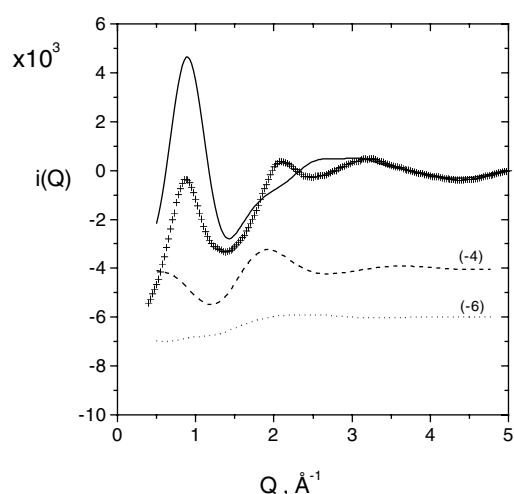


Figure 6. Relevancy of the contributions to the calculated dependent intensity $i(Q)$ from different pairs of ions or water molecules of the model CP compared with experimental dependent intensity (+ + +): all the pairs involved in the close-packing assemblies (first neighbours 1st N) (—), all the pairs in which one particle is included in the close-packed assemblies and the other is the free anion (---); all the correlations between water molecules (· · · · ·).

calculated from a true cubic close packing (face-centred cubic lattice). The value of the probability of presence of each closest neighbour in this shell may be, in some cases, smaller than one; (ii) around each solvated ion the free counter-ions and the free water molecules are distributed in agreement with the respective ionic radii known from appropriate crystalline structures, keeping a plausible electrostatic accommodation; (iii) *ad hoc* values are attributed to the fluctuations of the values of the distances between the positions of the correlated particles.

We think that our method of constructing molecular models taking as the primary structure (skeleton) a close packing of the ions of the largest electric charge may be used with success for concentrated aqueous solutions ($\geq 1 \text{ mol dm}^{-3}$) of salts where one ions has an electric charge that exceeds the value of the counter-ion, in agreement with previous investigations indicated in the introduction [1–4].

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The interpretation of the intensity patterns of concentrated aqueous solutions of salts with ions of different valences has been discussed by us in many international conferences what has been very stimulating to continue our investigations. We thank Fundação Calouste Gulbenkian and Fundação Luso-Americana para o Desenvolvimento for attributed grants. Fundação Calouste Gulbenkian also financed the acquisition of some equipment for these experiments.

Appendix

The *effective scattering factor*, for the solvated indium cations shaped as a bipyramid, may be, roughly, calculated using the same elementary method that is used to estimate atomic scattering factors, the Debye equation:

$$F_{eff} = f_{In^{3+}} + 2 \frac{\sin(R_1 Q)}{R_1 Q} + 5 \frac{\sin(R_2 Q)}{R_2 Q}$$

$$R_1 = 2.5 \text{ \AA}, R_2 = 2.7 \text{ \AA}.$$

At $Q \sim 0.9 \text{ \AA}^{-1}$, $F_{eff}(\text{cc})$ is close to 80 eu. The volume occupied by the cation complex may be roughly estimated subtracting from the volume of the structural unit the volumes occupied by the particles not coordinated to the cation, i.e., one anion and the water molecules not included in the hydration shell. Within the accuracy of this approach a volume of six or seven times the volume of one water molecule in liquid pure water is obtained. $F_{eff}(w)$ may be estimated supposing a tetrahedral arrangement of water molecules 2.8 Å apart. Using once more the Debye equation, a value close to 15 eu is obtained for the $F_{eff}(w)$. Therefore the relative effective scattering power ratio $[F_{eff}(\text{cc})/F_{eff}(w)]^2$ can be estimated as close to 30, which seems sufficient to demonstrate that the indium complex plays a predominant role in the x-ray scattering, namely at Q values close to 0.9 \AA^{-1} .

A lower limit of the value of the mean life Δt of these aggregates may be estimated from the width of the Raman bands observed in the corresponding spectra ($w \sim 20$ to 30 cm^{-1}). The value $\Delta t \sim 10^{-12}$ s is obtained. The consideration of this value allows us to assume that in the volume of coherence of the x-ray scattering, a large number of different orientations of the complexes is contained. So the use of the Debye equation to calculate the effective scattering factors $F_{eff}(\text{cc})$ and $F_{eff}(w)$ seems valid. It should be stressed that the existence of these long-life complexes does not seem to be a necessary condition for interpreting a large scattering power. The consideration of a purely statistical cloud of water molecules induced by a strong electrical field of the cation would be sufficient.

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