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Local order in aqueous solutions of lanthanum chloride and bromide by x-ray diffraction, EXAFS and Raman spectroscopy

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Abstract

Concentrated aqueous solutions of lanthanum chloride (3.4 molal) and bromide (3.2 molal) were investigated by x-ray diffraction, EXAFS and Raman spectroscopy. The observation of narrow maxima of intensity in the diffraction patterns is well interpreted as arising from positional correlations between the hydrated cations present in these solutions. Raman spectra, exhibiting a single polarized band ($\sim 350 \text{ cm}^{-1}$), suggest that only one kind of aggregate is observed in these solutions. EXAFS results allowed us to establish the distances of (plausibly) nine water molecules around each lanthanum cation. The persistence of lanthanum hydrates has been followed from very concentrated solutions (~ 3 molal) up to diluted ones (~ 0.5 molal) by x-ray diffraction as well as by EXAFS. Previous investigations are discussed, too.

1. Introduction

The structure of the solvation shell of rare earths in aqueous solutions of their salts has been discussed by many experimentalists. Namely, the shape of the hydration shell of the lanthanum cation has been the subject of some controversy [1–6]. In this work the results obtained from three experimental techniques have been assembled in order to investigate whether some convergence is possible to establish a reliable structure: x-ray diffraction, EXAFS and Raman spectroscopy. In x-ray diffraction investigations, a correlation method which consists in the theoretical calculation of the scattering pattern for various models and comparison with the observed pattern was used. This method proved to be appropriate for several concentrated aqueous solutions. We refer, namely, to the investigations of the structure of yttrium and indium chloride and bromide, recently published [7, 8]. Narrow maxima of intensity in the diffraction patterns depending on the concentration have been observed for regions of momentum transfer $Q = 4\pi \sin \theta / \lambda \sim 1 \text{ \AA}^{-1}$. Moreover, the intensity of these maxima change when, for solutions of the same cation, anions are replaced by others with very different scattering power. We should notice that no maximum is observed at this Q domain for the x-ray diffraction patterns of liquid water. The analysis of all these observations have allowed us to elect circumstances

for which the molecular models describing the experimental profiles can be easily built: (i) the value of valence of the ions that constitute the solved salt must be different, favouring mainly the existence of dense electronic clouds around one sole ionic species either cation or anion; (ii) the molecules should be completely dissociated. Furthermore, if the value of the scattering factor of the solvated ion is large when compared with the value of the scattering factor of liquid water, the adequacy of these molecular models is clearly demonstrated. This situation occurs for aqueous solutions of lanthanum salts (see the appendix).

The detection of the existence of positional correlations between the ions of large valence (the centres of the dense electron clouds previously referred to) and between these ions and the counter-ions is possible because variations of the differences of phase of the scattered x-rays can produce large modifications observed in the profile of the total intensity. In contrast, the radial distribution function is almost insensitive to these variations in the differences of phase, which are originated by changes in the electron density when the structure of the *ad hoc* model is modified. Positional correlations of ions that are not in contact can then be detected up to distances of about 10 Å. Investigations of quasi-isomorphic solutions of lanthanum chloride and bromide have the obvious advantage of detecting more easily the correlations with the halide anions. Moreover, this study in a large domain of concentration, allowed us to investigate cation–cation and cation–anion correlations, as well as the persistence of the existence of the lanthanum hydrates.

We should emphasize that the existence of molecular and ionic medium range correlations was investigated, in a large number of electrolyte solutions, some years ago by Prins [9] and Dorosh and Skryshevskü [10] and also that information concerning correlations between ions or molecules that are not in contact has already been discussed in different papers [11–21]. Our research group tried, some years ago, to get a global insight into this theme of the existence of medium range positional correlations in concentrated aqueous solutions [11–13]. The connection between the existence of a ‘first sharp diffraction peak’ (FSDP) in the diffraction patterns of non-crystalline materials (glasses and liquids, mainly melted salts) and the plausibility of an ‘intermediate range order’ has been emphasized in a number of more recent articles [22–33]. Neutron diffraction studies that might suggest the existence of positional correlations of nickel cations in concentrated aqueous solutions have been discussed, too [34–38]. More recently, anomalous x-ray scattering studies on aqueous solutions have been allowed to obtain information, namely, on the hydration shells of the ions. These results are in reasonable agreement with those obtained previously by EXAFS, conventional x-ray studies and Raman spectroscopy [39–44].

2. X-ray diffraction: experiment, data reduction and molecular models

2.1. Experiment and data reduction

Rh K α radiation ($\lambda = 0.6147$ Å) 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 $Q = 4\pi \sin \theta / \lambda \sim 16$ Å $^{-1}$. Several runs were accumulated with a constant number of counts at each point. The aqueous solutions were prepared from their hydrated salts, LaCl $_3$ from Fluka (99.9%) and LaBr $_3$ from Alfa (99.99%), and the composition of the solutions was controlled by chemical analysis. The concentration and the density of the solutions are presented in table 1. The solutions were studied at room temperature by transmission in layers of some tenths of a millimetre thick contained in a plane parallel cell between nitrocellulose windows 30 μ m thick.

Table 1. Concentration and density of the lanthanum halide aqueous solutions investigated.

LaCl ₃		LaBr ₃	
Concentration (molal)	Density 22 °C (g cm ⁻³)	Concentration (molal)	Density 22 °C (g cm ⁻³)
3.40	1.634	3.17	1.893
2.14	1.415	1.93	1.587
1.08	1.224	0.96	1.311
0.51	1.111	0.46	1.147

The measured intensities were first corrected for the scattering coming from the windows of the container, reducing these intensities by the transmittance of the liquid, and afterwards from absorption and polarization. The corrected intensities were scaled to absolute units using the Krogh-Moe method [45]. Finally a correction has been 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 [46] 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 $F(Q) = \sum_{uc} f_j / \sum_{uc} Z_j$ 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 very relevant for distances greater than 2 \AA .

The structural units in the solutions (the units of composition, uc) are always referred to one cation. So for the 3.4 molal LaCl₃ solution they are one La³⁺, three Cl⁻ and 16.3 H₂O molecules and for the 3.2 molal LaBr₃ solution they are one La³⁺, three Br⁻ and 17.5 H₂O molecules.

The coherent scattering factors f_j , corrected for anomalous dispersion, were taken from x-ray tables [47] for Cl, Br and La atoms. Incoherent scattered intensities corrected from the Breit-Dirac recoil factor were calculated from Pálinkás [48] for the Br and the La atoms and from Pálinkás and Radnai [49] for the Cl atom. For H₂O we used the coherent scattering factors and the incoherent scattered intensity from Hajdu [50].

X-ray diffraction patterns of the more concentrated aqueous solutions (~3 molal) of lanthanum chloride and bromide are presented in figure 1. The first maximum of intensity (near 0.9 \AA^{-1}) observed for LaCl₃ decreases strongly for LaBr₃ solutions, while a reversed situation appears for the second maximum. The pair correlation functions $g(r)$, calculated after Fourier inversion of the experimental intensities for these solutions, are displayed in figure 2.

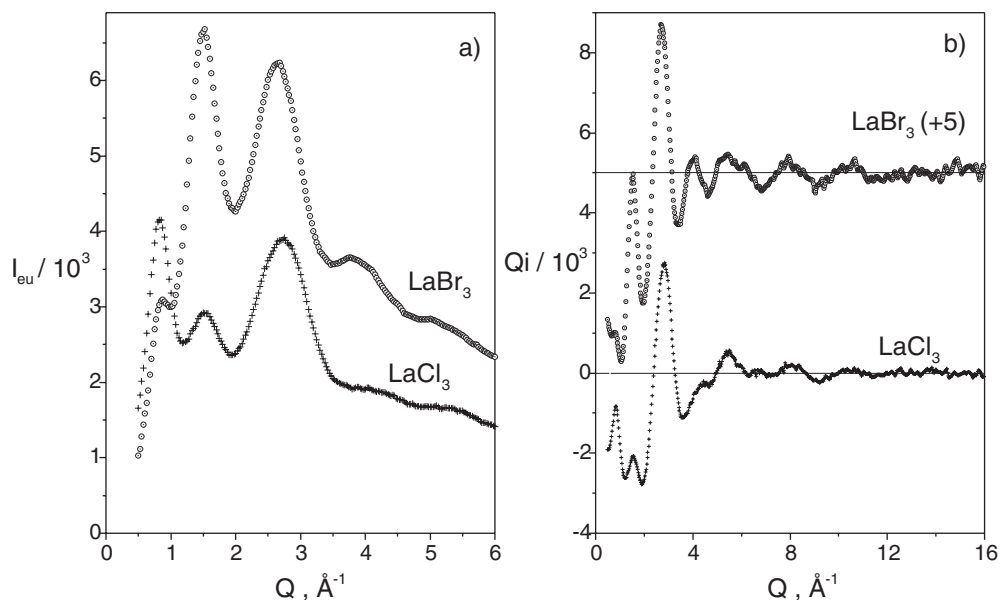


Figure 1. X-ray diffraction patterns of 3.17 molal LaBr_3 and of 3.40 molal LaCl_3 aqueous solutions: (a) $I_{eu}(Q)$; (b) $Qi(Q)$. For clarity, curves are shifted +5 in (b) for LaBr_3 .

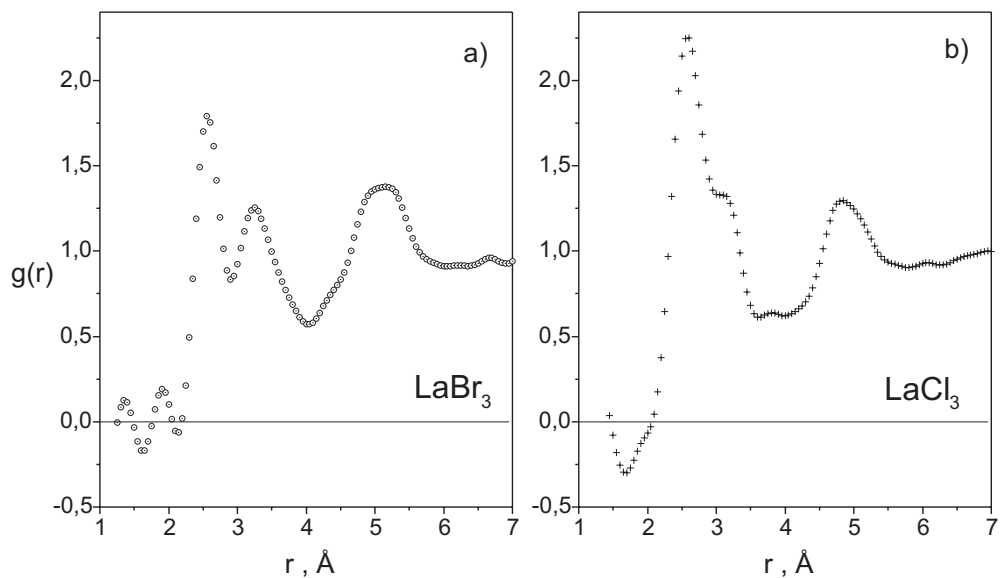


Figure 2. Experimental pair correlation function $g(r)$: (a) for 3.17 molal LaBr_3 aqueous solution; (b) for 3.40 molal LaCl_3 aqueous solution.

X-ray diffraction patterns of the more diluted lanthanum chloride aqueous solutions are presented in figure 3. The position of the first maximum of intensity (below 0.9\AA^{-1}) changes proportionally versus the one-third power of the molar concentration (see the inset).

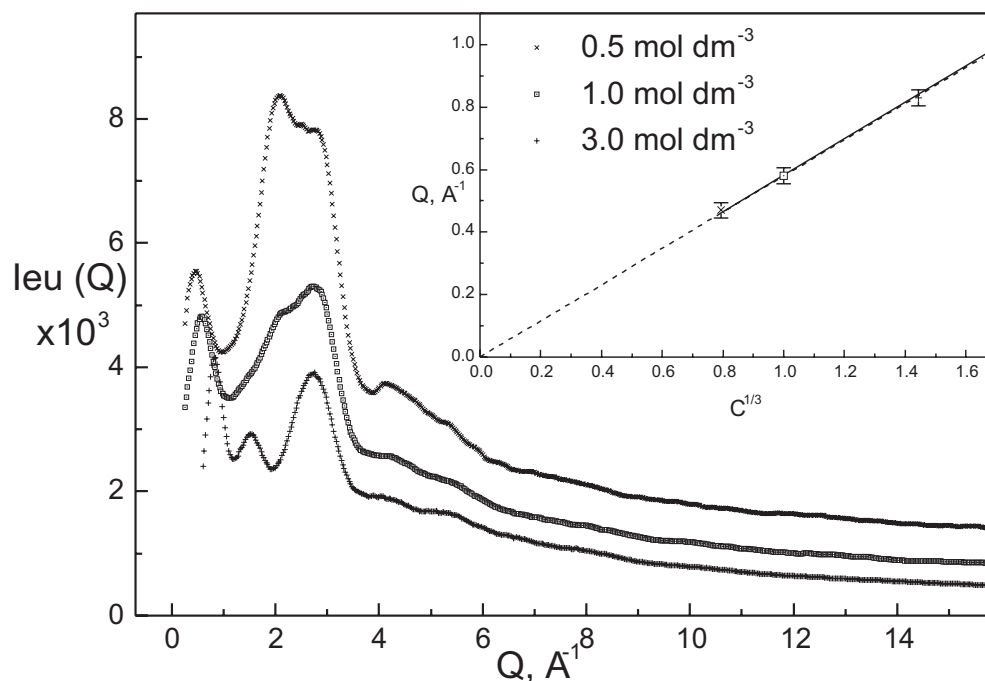


Figure 3. X-ray diffraction patterns of LaCl_3 aqueous solutions: (+) ~ 3 molal; (\square) 1 molal; (\times) ~ 0.5 molal. The variation of the abscissa Q of the first maximum of intensity versus the one-third power of the molar concentration is presented in the inset. The straight line is calculated considering that each shell of scatters (hydrated cations) is ordered as a face-centred cubic lattice (see text).

2.2. Molecular models

To interpret the x-ray diffraction patterns obtained with concentrated aqueous solutions of salts where one ion has a higher valence than the other one, we built molecular models under some general considerations. It is assumed that the ions of higher valence (of high electric charge) compete between themselves for the largest possible solvation cloud of water molecules. So to estimate the distances between the first neighbours a cubic close-packing arrangement was assumed, because this structure is the cubic arrangement of ions where the largest inter-ionic distances are obtained, for a given density. In this context, to reproduce the experimental intensity, a relatively small number of different alternative models may be considered. For these highly concentrated solutions the scattering units are only the ions of larger valence, the La^{3+} cations, with their hydration shells, the counter-ions, Br^- or Cl^- anions, and a small number, about eight, of 'free' water molecules. We should stress once more, in this article, that positional correlations between the relevant scatters may easily be detected, sometimes up to 10 \AA , for aqueous solutions with ten to 15 water molecules per solvated salt. The intensity of the first maximum near 0.9 \AA^{-1} , observed here for concentrated solutions of lanthanum bromide, is drastically reduced by destructive interferences produced by the counter-ions (see figure 1).

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:

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

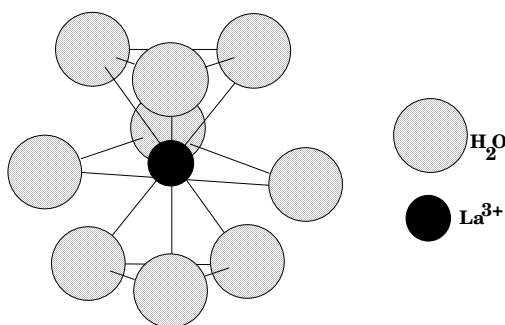


Figure 4. Approximate shape of the cation complex in concentrated aqueous solutions of lanthanum halides (hydrate H9, see text).

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.

Each lanthanum cation is assumed to be surrounded, *in principle*, by 12 closest neighbours at a mean distance estimated from a face centred cubic lattice. The actual values of the cation–cation distances fluctuate adequately about the mean value. The method of calculation of the intensity has already been indicated [7–9, 11–13, 51]. We consider two different internal configurations in distinct regions: the first configuration, near the *central particle*, is a discrete distribution; the other one, which starts at an adequate distance from the central particle and goes up to larger distances, is simulated by a random continuous distribution. This continuous distribution may, plausibly, simulate the spaced averaged structure of the solutions as they are ‘seen’ by an arbitrary central particle at large distances in the bulk of the liquid. In order to simulate an adequate structure in agreement with the experimental pattern we should consider that some of the 12 cations of the first shell of closest cation neighbours are included in this continuous distribution.

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 random distribution. A realistic fixation of the value of the threshold r_{th} of this distribution results from an assumption of the number N_c of the first neighbours (the ions with larger valence), which are, plausibly, positional correlated with the central ion with an *ad hoc* value of a fluctuation around their mean positions. Hence the other $(12 - N_c)$ ions are included in the continuous distribution. The intensity, $i_c(Q)$, originated by the continuous distribution, ought to be smaller than the value obtained for the intensity from the discrete region, $i_d(Q)$, in the range of Q values useful for the discussion of the plausibility of the models. Indeed, it seems to us that it is convenient to minimize the influence of a contribution originated from a region where the arrangement of the molecules and ions is more uncertain (see later, figure 5).

The expression *liquid type quasi-close packing* (LTQCP) means that the face centred cubic order is used only for estimating the distances between neighbour cations around the central one. So, only a fraction of this first shell of neighbour cations ($N_c < 12$) is considered in the discrete distribution. If 12 first neighbours were assumed in the discrete distribution when our models were built, the maxima calculated around 0.9 \AA^{-1} and at 1.7 \AA^{-1} would turn out to be inadequately enhanced.

The inadequacy of the assumption of 12 first neighbour cations in the discrete distribution has already been verified. Hence we suggested in [7] and [13] that a mean of the intensities,

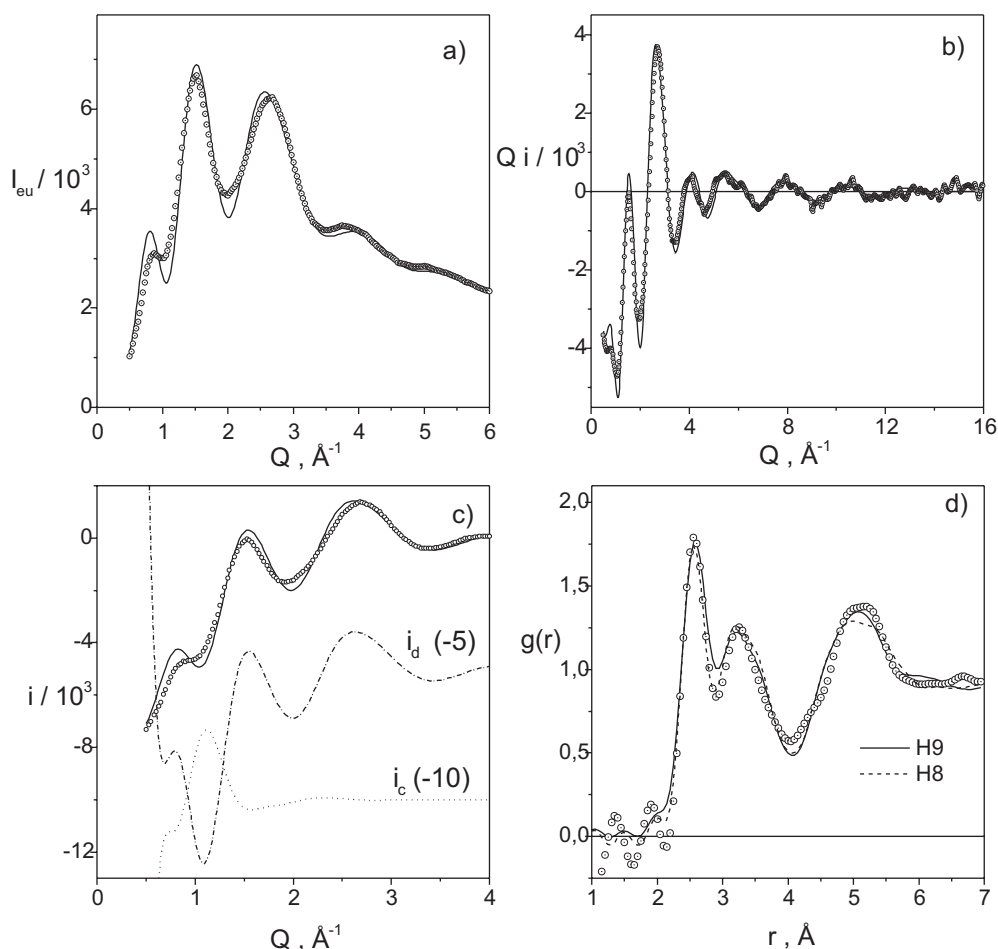


Figure 5. Molecular model CP(H9) of the 3.17 molal LaBr_3 aqueous solution. Calculated (—) and experimental ($\circ \circ \circ$) intensities: (a) $I_{eu}(Q)$; (b) $Qi(Q)$; (c) Contributions to the dependent intensity $i(Q)$ of the scattering obtained from the discrete molecular distribution of ions 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) Experimental ($\circ \circ \circ$) and calculated pair correlation function $g(r)$: (—) for the model CP (H9) and (— · —) for the model CP (H8).

calculated one from a model where twelve neighbours are positionally correlated and the other from another model with a smoother order in this first neighbourhood should be considered. Now, here and in [8], we have adopted an attitude that seems to us (physically) more realistic by considering adequately the number N_c below the value 'twelve'. In the models described here for these concentrated solutions of lanthanum only one half of the first shell of the *close-packed* lanthanum hydrates was considered in the discrete distribution ($N_c = 6$).

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 the reasons referred to, only from 0.7 \AA^{-1} .

Two types of lanthanum hydrate are considered in this article (H9 and H8). In hydrate H9 we assume that nine water molecules are located around the cation, six in the vertices of a

Table 2. LaBr₃ and LaCl₃ aqueous solutions structural data: cation hydrates of the molecular models. Values of the mutual distances r , r.m.s. fluctuations Δr , weight of each correlation w . The distances concerning water molecules were obtained from the positions of their oxygen atom. Distances are in Å^a.

Correlations	La ³⁺					
	Hydrate H9			Hydrate H8		
	r	Δr	w	r	Δr	w
cation–water (h)	2.54	0.05	12	2.55	0.04	16
	2.73	0.06	6			
water (h)–water (h)	3.00	0.06	24	2.90	0.06	24
	3.10	0.06	12	4.20	0.26	24
	3.70	0.16	6	5.10	0.39	8
	4.70	0.26	6			
	4.80	0.26	12			
	4.90	0.26	12			

^a (h) means ‘hydration’.

triangular prism at a distance of 2.54 Å from the central cation and the other three in the three vertices of an equatorial triangle assumed in a triangular prism at a distance of 2.73 Å from the central cation (figure 4 and table 2). This hydrate is similar to the hydration shell indicated by Broach *et al* [52] for the crystals of yttrium ethyl sulphate (the shape of this solvation shell has been discussed by Mackay *et al* [53]). The hydrate H8 is a regular cube with eight coordinated water molecules in the vertices, at a distance of 2.55 Å from the cation (symmetry O_h). When the contrary is not specified the shapes of the hydrates considered in our molecular models are of the type H9.

The hydrates are *close packed*. Anions and water molecules are approximately distributed over the middle points of two next neighbour hydrated cations in agreement with the available volume allowed by the *close packing* and taking into account also electrostatic interactions. The water molecules that cannot 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 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 hydrate (see tables 2 and 3). The values of Δr indicated in table 2 for the internal distances of cation hydrates may seem to be excessive. We must consider, however, that in the hydrates the orientation of the water molecules is not very regular (if the values of their relevant multipoles are taken into account in indicative calculations) and a range of values of distances will be expected for (slightly) different aggregates. A *close-packed* (CP) simulation gives a reasonable agreement with the experimental x-ray structural results obtained for the concentrated (~3 molal) aqueous solutions of lanthanum bromide (see figure 5).

In this model nine water molecules are assumed as coordinated by the lanthanum cation (H9), one water molecule (per cation) is in the middle points of the cation–cation distances (referred to as water I in table 3), and one water molecule is located in the tetrahedral holes of the close packing (water II in table 3); the other five water molecules are *ad hoc* distributed in the octahedral holes of the close packing (water III).

The calculated intensities and experimental are compared in figure 5(a) and 5(b). 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 distribution of ions and molecules i_c , and the total intensity i_t ($i_t = i_d + i_c$) are presented in figure 5(c). The pair correlation functions $g(r)$ obtained from the calculated intensities after Fourier inversion are presented in figure 5(d).

We have also calculated the intensity scattered when the hydrate is constituted by eight water molecules (H8) instead of nine, which, together with the pair correlation function obtained (also displayed in figure 5(d) for comparison), is in good agreement with the experimental curves. The comparison in the region of $r \approx 2.6 \text{ \AA}$ of the profiles of pair correlation functions $g(r)$ corresponding to these two models (with eight or with nine hydration water molecules) does not allow us to conclude unambiguously which solvation hydrate is more plausible.

In contrast with the close-packed models we considered a model without close packing (WCP), where the cation complexes are assumed to be not so strictly correlated: the values of the distances between the closest neighbour cation hydrates were assumed to be simulated by a continuum starting at 5.3 \AA . This structure, which is a modification of model CP, has only well defined correlations between particles almost in direct contact. Either this structure or the CP model 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 1 \AA^{-1} .

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 hydrated cations with the 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. As the second variant, the first shell of cation hydrates was assumed to be ordered as a simple cubic lattice of the cation hydrates with the anions and free water molecules distributed over the vacant sites. None of the variants permitted us to obtain an agreement as good as the one obtained with the close-packed (CP) model presented here.

The molecular model of the LaCl_3 solution was obtained by substituting, in the model CP proposed for the LaBr_3 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 6, table 4).

In figure 7 are presented the intensities produced by groups of correlated pairs for both lanthanum chloride and lanthanum bromide solutions. 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 cation complex–anion correlations (in the middle points of the cation–cation distances). As for the interactions between all the water molecules (the hydration water molecules included) no marked influence in the x-ray pattern is apparent.

Molecular models for the more diluted lanthanum solutions (see table 1) were not built. But a proportionality between the values of the abscissa, Q_0 , of the maxima of interferences observed slightly below 1 \AA^{-1} (in the diffraction patterns of the three investigated aqueous solutions of lanthanum chloride) and the one-third power of the molar concentration of the solution is well verified (see inset of figure 3). Moreover the slope of the straight line that contains the representative points of the forementioned proportionality agrees rather well with the value corresponding to a face-centred cubic lattice (close-packing). So our hypothesis of the existence of a quasi-close-packing of lanthanum hydrates in concentrated aqueous solutions of lanthanum chloride, and, in consonance, of lanthanum bromide, may be considered as very plausible.

Table 3. ~ 3.2 molal LaBr_3 and ~ 3.4 molal LaCl_3 aqueous solution structural data: the more relevant discrete 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 \AA^a .

Correlations	LaBr ₃ Model CP								LaCl ₃ Model CP Hydrate H9				
	Hydrate H8				Hydrate H9								
	r	Δr	w	r_{th}	r	Δr	w	r_{th}	r	Δr	w	r_{th}	
cation–cation	9.5	1.2	6	10.1	9.5	1.2	6	10.1	9.2	1.1	6	9.7	
cation–water (h)	7.6	0.9	48		7.1	0.8	8		6.8	1.0	8		
					7.8	0.8	16		7.5	1.0	16		
					7.9	0.8	16		7.6	1.0	16		
					8.0	1.0	16		7.7	1.0	16		
					8.1	1.0	8		7.8	1.0	8		
water (h)–water (h)						
	9.8	1.2	64	10.5	10.2	1.2	16	10.6	9.7	1.1	8	9.8	
	5.4	0.7	24		4.7	0.4	4		4.4	0.3	4		
	6.1	0.8	24		6.1	0.6	24		5.8	0.9	32		
					6.2	0.6	8		6.0	0.9	24		
					6.3	0.6	24		6.2	0.9	8		
					6.6	0.7	16		6.3	0.9	8		
					6.8	0.7	8		6.5	0.9	8		
					6.9	0.7	24		6.6	0.9	24		
						
		7.6	0.9	96		8.9	1.0	40		8.0	1.1	32	
		8.3	1.2	96		9.0	1.0	40		8.6	1.1	48	
						9.1	1.0	40		8.7	1.1	56	
						9.2	1.0	40		8.8	1.1	16	
						9.3	1.0	16		8.9	1.1	48	
						
	9.5	1.2	96		9.9	1.2	16		9.2	1.1	76		
	10.0	1.2	72	10.2	10.2	1.2	8	10.3	9.5	1.1	32	9.9	
cation–anion (f)	5.1	0.4	12		4.8	0.4	4		4.7	0.3	12		
					4.9	0.4	8						
cation–water I (f)	8.01	1.3	12	8.4	8.2	1.3	12	8.3	7.9	1.3	12	8.1	
	4.8	0.4	12	6.6	4.8	0.4	4	6.6	4.6	0.3	4	6.4	
cation–water II (f)	5.8	0.4	16	8.3	5.8	0.5	8	8.3	5.6	0.5	8	8.1	
cation–water III (f)	4.7	0.4	8	5.1	5.7	0.5	32	7.3	5.5	0.5	24	6.8	

^a (h) ‘hydration’ and (f) ‘free’; water I indicates the water molecules located in the middle points of the distances cation–cation, water II refers to the water molecules located in the tetrahedral holes of the close packing and water III refers to the water molecules distributed in the octahedral holes of the close packing.

3. EXAFS: experiments, data analysis and results

3.1. Experimental details

EXAFS experiments on lanthanum bromide and lanthanum chloride aqueous solutions for different concentrations (~ 3 molal, 2 molal, 1 molal and 0.5 molal—see table 1) were done at ESRF on beamline BM29.

The EXAFS experiments were performed in the transmission mode at the La K edge (38 924.6 eV) using a Si 311 flat monochromator and ionization cameras filled with krypton

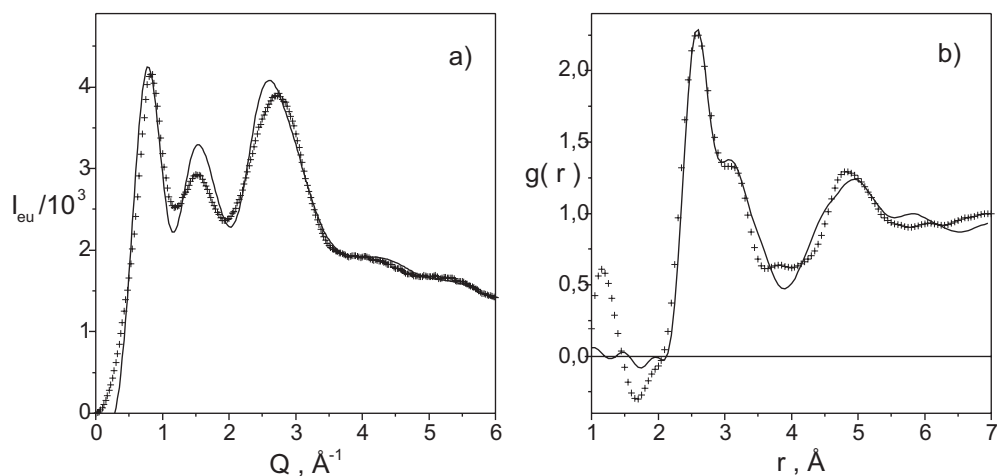


Figure 6. Molecular model CP of the LaCl_3 solution. Calculated (—) and experimental (+++): (a) intensities $I_{eu}(Q)$; (b) pair correlation function $g(r)$.

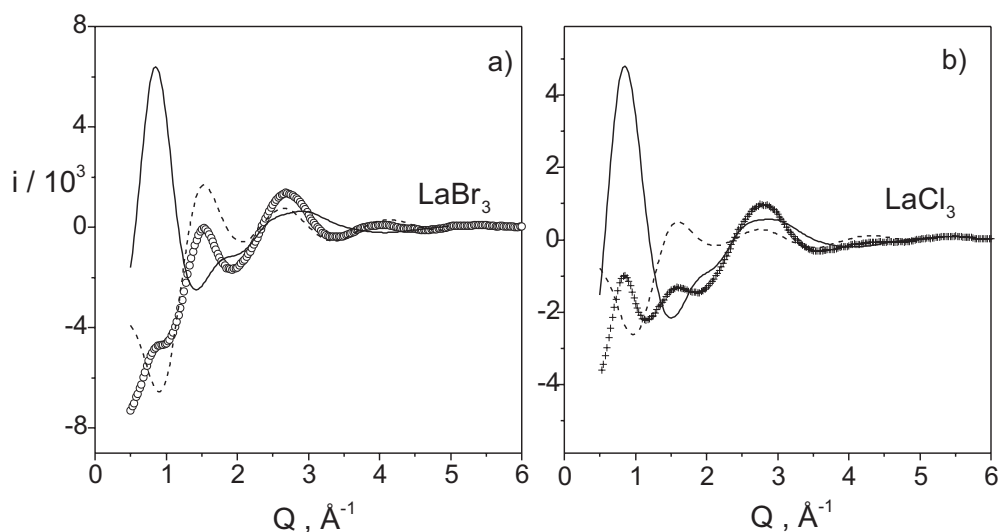


Figure 7. Relevancy of the contributions to the calculated dependent intensity $i(Q)$ from different pairs of ions or water molecules of the models CP (H9) compared with experimental dependent intensity for the ~ 3 molal aqueous solutions of LaBr_3 (o o o) (a) and LaCl_3 (+++ (b): all the pairs involved in the close-packing assemblies (first-neighbour pairs 1st N) (—), all the pairs in which one particle is the free anion (---).

as detectors for I and I_0 . La_2O_3 was used as reference. The samples were contained in planoparallel cells with collodium or kapton windows. All data were taken at room temperature.

3.2. Data analysis and results

The normalized EXAFS function is given by

$$\chi(E) = [\mu(E) - \mu_0(E)]/\mu_0(E) \quad (4)$$

where μ is the measured absorption and μ_0 is the smooth post-edge background term. In order to relate $\chi(E)$ to structural parameters, it is necessary to convert the energy into the photoelectron wavevector k defined by $k = [2m(E - E_0)/h^2]^{1/2}$, where E is the energy of the incident beam and E_0 the energy of the beam at the absorption edge.

In the single-scattering theories and in the plane-wave approximation the formula which describes the EXAFS oscillations for a Gaussian distribution of neighbours around a central atom may be written as follows:

$$\chi(k) = - \sum_j \frac{N_j}{kR_j^2} |f_j(\pi)| \exp(-2\sigma_j^2 k^2) \exp(-2R_j/\lambda_e) \sin[2kR_j + 2\delta'_j \Psi_j]. \quad (5)$$

Here N_j is the number of scattering atoms at a distance R_j , each with a backscattering factor $|f_j(\pi)|$ which is energy dependent. λ_e is the elastic mean free path of the photoelectron. σ_j is the relative mean square displacement between the scattering atom and the central one, δ'_j is the phase shift due to the passage of the photoelectron through the potential of the emitting atom and Ψ_j is the phase of the backscattering factor.

The $\chi(k)$ EXAFS modulations of the absorption coefficient were normalized following a standard procedure: 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. EXAFS simulations and Fourier transforms were carried out using the program EXCURVE90 [54], a program for multishell fitting based on curved wave theory. The EXAFS spectra were weighed by k to compensate for the diminishing amplitude at high k values. Phase shifts were calculated internally by the program EXCURVE90.

For each halide all the spectra have been analysed over the same energy range of about 44–1290 eV (corresponding to a wavevector range of about 3.3–18 Å⁻¹). The spectra were Fourier filtered to remove features at distances below 1.5 Å, but not to leave long-distance features of the quasi-radial distribution function (i.e. no noise removal was attempted). The experimental spectra of $k\chi(k)$, the EXAFS simulation on the lanthanum edge and its Fourier transforms are shown in figure 8 for the ~3 molal lanthanum chloride and in figure 9 for the ~3 molal lanthanum bromide aqueous solutions. The spectra were found to be almost identical at all concentrations of each halide solution.

The first coordination shell of lanthanum contains only oxygen atoms; no halide ions were found. For the lanthanum hydrate a model was tried with the lanthanum cation surrounded by nine water molecules in a tricapped trigonal prismatic structure as suggested by Broach *et al* [52] and discussed by Mackay *et al* [53] (figure 4).

The values obtained for that model based on six water molecules at a short distance and the three other water molecules at a larger one are indicated in table 4, the so-called H9 hydrate.

The fitting index FI, for a number of points n_p , is defined as

$$FI = \sum_i^{n_p} \frac{[\chi(k_i)^{the} - \chi(k_i)^{exp}]^2}{n_p}. \quad (6)$$

The values of the fitting index obtained using EXCURVE90 for the EXAFS data of the chloride and bromide aqueous solutions are slightly better for this model than those obtained for a model with all the oxygens of the water molecules at the same distance. For this last one the coordination number N , left free, does not exceed 8 (see table 5).

From these results it seems to us that an EXAFS model with nine oxygen atoms, six at at ~2.56 Å with a Debye–Waller factor smaller than the three others, which are at ~2.73 Å from

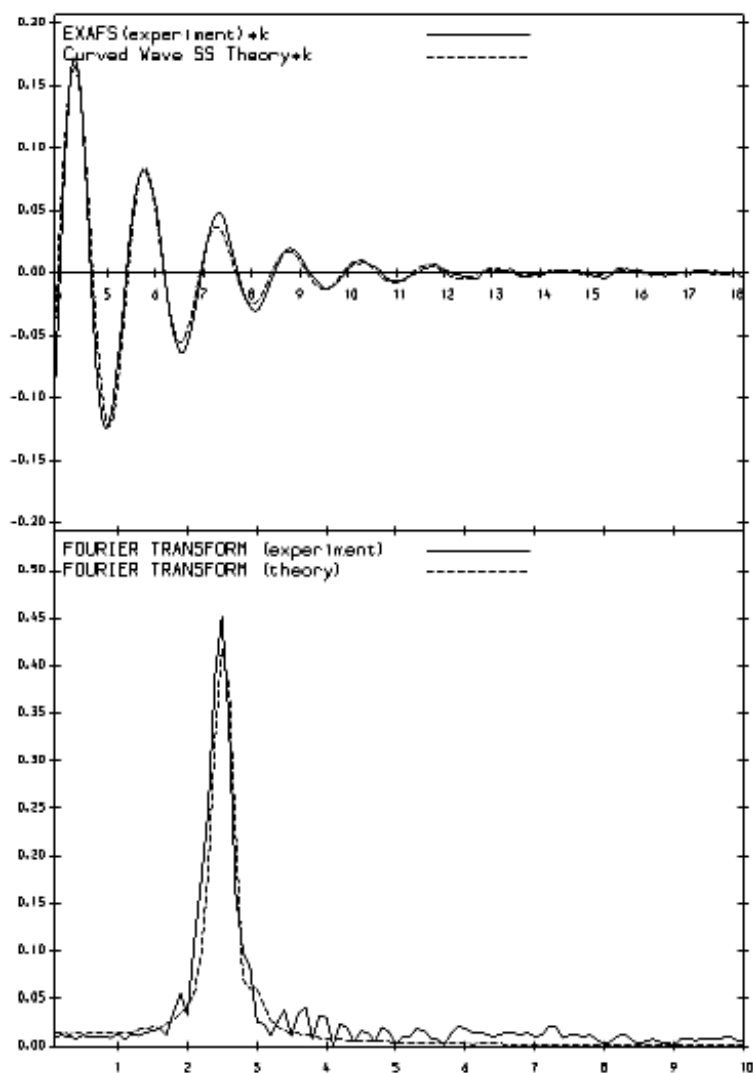


Figure 8. EXAFS spectra for the La K edge of 3.40 molal LaCl_3 aqueous solution: (—) experiment; (· · · · ·) simulation.

the lanthanum, is more adequate than a model with ~ 8 oxygen atoms, all at the same distance from the cation.

4. Raman: experiment, results and interpretation

Raman experiments were performed on an 3.40 molal LaCl_3 aqueous solution (see table 1). For the preparation of the sample, the water (H_2O) was slowly distilled in Pyrex apparatus in the presence of KMnO_4 to oxidize the organic impurities. The solution was, then, filtered through nitrocellulose membranes prepared in our laboratory.

The Raman spectra were recorded on a Jobin–Yvon T64000 triple monochromator Raman system (focal length 0.640 m, aperture $f/7.5$). The premonochromator stage was used in the

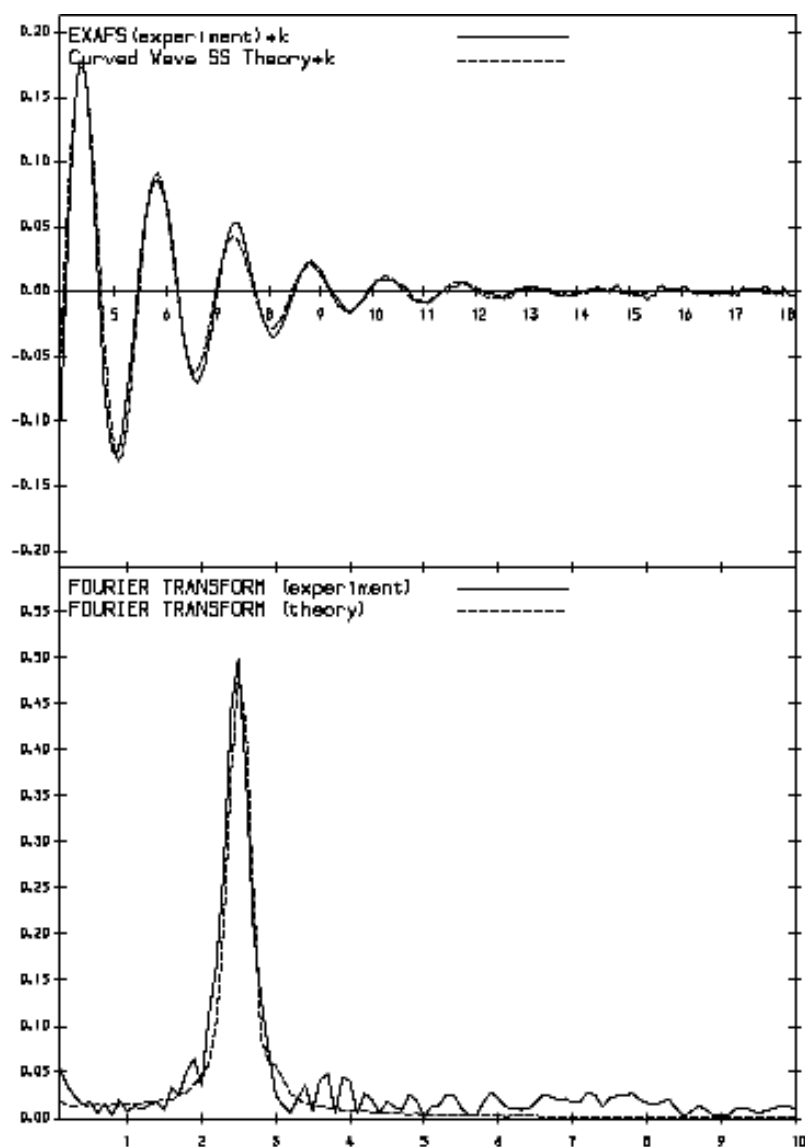


Figure 9. EXAFS spectra for the La K edge of 3.17 molal LaBr_3 aqueous solution: (—) experiment; (· · · · ·) simulation.

subtractive mode. The detection system was a non-intensified charge coupled device (CCD) detector. Radiation of 514.5 nm from an argon ion laser (Coherent, Innova 300-05) was used for excitation and provided ~ 90 mW at the sample position. Relevant slit widths were set to $300 \mu\text{m}$ and the slit between premonochromator and the spectrograph was opened to 14 nm, giving a resolution of approximately 3 cm^{-1} and an estimated error in wavenumber smaller than 1 cm^{-1} . An integration time of 45 s and four scans were used for all the spectra.

Raman spectra showed a weak band, strongly polarized, with a value of the frequency near 350 cm^{-1} in good agreement with the value given by Kanno and Hiraishi [6] (see figure 10). This band corresponds, certainly, to the totally symmetric vibration of the lanthanum hydrate.

Table 4. Numerical values of the parameters used to simulate the La K-edge EXAFS spectra of LaBr₃ and LaCl₃ aqueous solutions for the H9 hydrate. R denotes the distance of the lanthanum from the oxygen of the water molecule. $A = 2\sigma^2$ is a Debye–Waller factor. N is the number of backscattering atoms.

	Concentration (molal)	N_1	R_1	A_1	N_2	R_2	A_2	FI
			(Å)	(Å ²)		(Å)	(Å ²)	
LaBr ₃	3.17	6	2.564	0.011	3	2.723	0.017	0.002 15
	1.93	6	2.561	0.011	3	2.723	0.016	0.001 93
	0.96	6	2.566	0.011	3	2.736	0.017	0.002 04
	0.46	6	2.562	0.011	3	2.737	0.015	0.002 39
LaCl ₃	3.40	6	2.573	0.012	3	2.744	0.015	0.001 89
	2.14	6	2.555	0.011	3	2.714	0.014	0.002 21
	1.08	6	2.566	0.011	3	2.730	0.017	0.001 74
	0.51	6	2.560	0.009	3	2.727	0.013	0.001 99

Uncertainties are 0.005 for R_1 , 0.010 for R_2 , 0.001 for A_1 and 0.003 or 0.004 for A_2 .

Table 5. Numerical values of the parameters used to simulate the La K-edge EXAFS spectra of LaBr₃ and LaCl₃ aqueous solutions for the H8 hydrate. R denotes the distance of the lanthanum from the oxygen of the water molecule. $A = 2\sigma^2$ is a Debye–Waller factor. N is the number of backscattering atoms.

	Concentration (molal)	N	R	A_1	FI
			(Å)	(Å ²)	
LaBr ₃	3.17	7.7	2.567	0.016	0.003 66
	1.93	7.7	2.547	0.017	0.005 17
	0.96	7.6	2.557	0.017	0.003 14
	0.46	7.6	2.555	0.016	0.005 26
LaCl ₃	3.40	7.5	2.564	0.017	0.003 32
	2.14	7.6	2.546	0.016	0.004 09
	1.08	7.4	2.549	0.016	0.004 81
	0.51	8.2	2.549	0.017	0.005 10

Uncertainties are 0.4 for N , 0.005 for R and 0.001 for A .

Other Raman bands (with a different value of the vibrational frequency), corresponding plausibly to oscillational motions of the hydration shell of the lanthanum cation, apart from the symmetric ‘breathing’ of the hydrate, were not observed in the spectra. Their activity is certainly small, given the large value of the mutual distances between the coordinated water molecules and the consequent small modification of the polarizability of the hydrate.

5. Conclusion

The results here reported, obtained by x-ray diffraction, EXAFS and Raman spectroscopy, are consistent with the existence of nine water molecules in the first solvation shell of the lanthanum cation.

The interpretation of the x-ray diffraction patterns of concentrated aqueous solutions of lanthanum halides in the range of Q values from $\sim 0.9 \text{ \AA}^{-1}$ 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*.

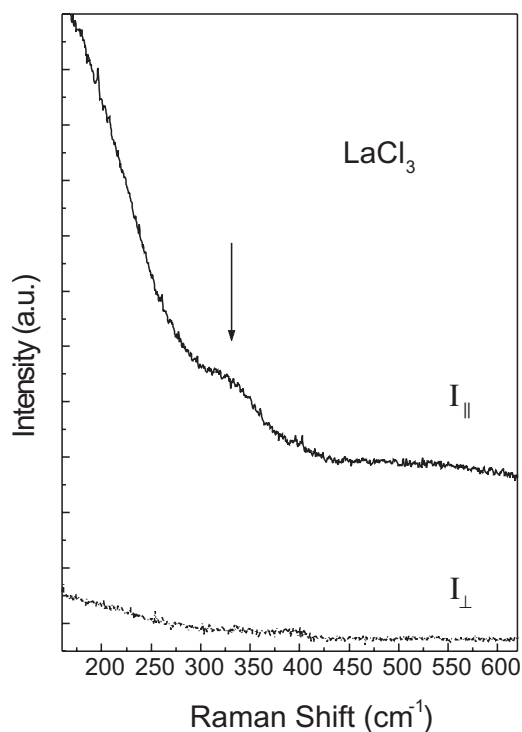


Figure 10. $I_{||}$ and I_{\perp} Raman spectra of 3.40 molal LaCl_3 aqueous solution. The arrow indicates the weak (strongly polarized) band assigned to the symmetric 'pulsation' of the lanthanum hydrate.

The main guidelines of the conception of this structure are the following. (i) The solvated ion of largest valence in the solution is surrounded by 12 closest (alike) neighbours at a distance whose value is calculated from a cubic close packing (face centred cubic lattice). The value of the *probability of presence* of each closest neighbour in this shell was, in this case, assumed as close to *one-half*. (ii) Around each solvated ion the 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 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 at the middle points of the distances between the first neighbour cations; (iii) all the other correlations.

It appears that, not only the intensity resulting from correlations of type (i) is relevant to the maximum observed nearby 0.9 \AA^{-1} , but also correlations (ii) give significant contributions that are mostly negative. This analysis of each type of correlation allows us to understand why 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* (as the coordination shells of water molecules give noticeable constructive interferences in that Q region). This also 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 (because the correlations between the hydrated cations and the free counter-ions produce destructive interference in that Q region).

The existence of these tentative molecular models for the investigated liquids does not mean that the arrangements of the water molecules and ions must be, strictly, the ones proposed, but supports strongly the hypothesis of a *liquid-type close packing* of the ions of larger valence, the lanthanum ions, in these ionic solutions.

A lack of accuracy of this method of correlations to investigate the structure of aqueous solutions is the *a priori* undefined distribution of the fluctuations of the mean distances for each pair of correlated ions or molecules. However, the comparison with the experiment of the calculated scattered intensity, in the Q range from 0.7 \AA^{-1} up to 2.5 \AA^{-1} , is a harsh test for any suggested distribution of the fluctuations.

We have not yet investigated the lowest value of the concentration of a salt that may keep the liquid-type close packing (LTQCP), suggested as an adequate model for the dynamical structure of concentrated aqueous solutions. But a large range of values of the concentration was tested, indeed, for solutions of lanthanum chloride (from ~ 3 molal to ~ 0.5 molal) that show the persistency of the quasi-close-packing distribution of hydrated cations.

We think that our method of building 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 (≥ 1 molal) of salts where one ion has an electric charge that exceeds the value of the counter-ion, in agreement with previous investigations indicated in the introduction.

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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. A M Gaspar acknowledges the financial support given by 'Fundação para a Ciência e Tecnologia'.

Appendix

An estimation of the relative influence of the scattering factors of the hydrated cation compared with the scattering factor of the water molecule may be done as follows. The *effective scattering factor*, for the hydrated lanthanum cations shaped as a tricapped trigonal prism may be, roughly, calculated using the same elementary method that is used to estimate atomic scattering factors, the Debye equation:

$$F_{eff}(H9) = f_{La^{3+}} + f_{H_2O} \left[6 \frac{\sin(R_1 Q)}{R_1 Q} + 3 \frac{\sin(R_2 Q)}{R_2 Q} \right] \quad R_1 = 2.5 \text{ \AA} \quad R_2 = 2.7 \text{ \AA}.$$

At $Q \sim 0.9 \text{ \AA}^{-1}$, $F_{eff}(H9)$ is close to 78 eu. The volume occupied by the cation hydrate may be roughly estimated by subtracting from the volume of the structural unit the volumes

occupied by the particles not coordinated to the cation, i.e. three anions and the water molecules not included in the hydration shell. Within the accuracy of this approach a volume of 8.5 times the volume of one water molecule in liquid pure water is obtained. The effective scattering factor for water $F_{eff}(W)$ is calculated considering a number of water molecules occupying the same volume as the hydrated lanthanum cation. $F_{eff}(W)$ 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 $F_{eff}(W)$. Therefore the relative effective scattering power ratio $[F_{eff}(H9)/F_{eff}(W)]^2$ can be estimated as close to 70, which seems sufficient to demonstrate that the lanthanum hydrate plays a predominant role in the x-ray scattering 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 ($\omega \sim 20$ to 30 cm^{-1}). The value $\Delta t \sim 10^{-12} \text{ s}$ 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 hydrates is contained. So the use of the Debye equation to calculate the effective scattering factors $F_{eff}(H9)$ and $F_{eff}(W)$ seems valid. It should be stressed that the existence of these long-life hydrates 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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