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Variation of Far Order in Aqueous Solutions of Lanthanides Trichlorides as Function of Concentration

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Abstract—X-ray diffraction studies of aqueous solutions of La(III), Pr(III), Nd(III), Sm(III), Gd(III), Dy(III), Er(III), and Lu(III) chlorides have been carried out in a wide range of concentrations. The small-angle maxima at the experimental scattering functions have been assigned; it has been shown that a far order exists in all the studied systems. The changes of scattering functions are discussed; average distances of particles interaction have been estimated. It has been shown that the structure of the concentrated solutions differs significantly from that of the diluted solutions.

Keywords: lanthanide, coordination number, hydration number, X-ray diffraction

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Changes of coordination number in the series of triple-charged lanthanide cations and the related changes of physicochemical properties of their salts solutions has been a subject of a number of studies. Structural organization of the above-mentioned systems has been studied by direct structural methods as well as by computer simulation [1–12]. Still, to the best of our knowledge, a single study has dealt with structural reorganizations in aqueous lanthanides salts at the change of concentration [5]. This work is aimed to fill in the gap by analysis of structural changes in aqueous solutions of lanthanide chlorides at relatively large distances in the course of the system dilution.

Figure 1 shows the intensity of X-ray scattering with saturated aqueous solutions of lanthanides chlorides as a function of the wave vector $s = 4\pi\sin\Theta/\lambda$; such plots are hereafter referred to for brevity as intensity curves. For better representation, the intensity curves are displayed in the *s* range from 6 to 120 nm^{-1} with avertical shift of 1.2×10^4 pulse/s.

Intensity curves of the solutions were similar. In all intensity curves, a sharp and the most intense maximum was found at low *s*, 9.34–9.50 nm^{-1}. The appearance of the small-angle maxima has been earlier observed in solutions of other salts as well, such maxima have been referred to as "pre-peaks" [5, 13]. The origin of pre-peaks has not been clearly explained in the literature. The presence of pre-peaks in the case of lanthanide salts solutions has been assigned to manifestation of the intercation distances [14] or to "positional correlations between hydrated cations" [5].

Before discussing the assignment of experimental intensity curves, it should be noted that crystal hydrates of lanthanide chlorides are known to form two isostructural series: $LnCl_3 \cdot 7H_2O$ (La–Pr) and $LnCl_3 \cdot 6H_2O$ (Nd–Lu) [15]. The nearest coordination surrounding of the cation in those crystal hydrates consists of two chlorine atoms and, respectively, seven or six water molecules. We attempted to compare the intensity curves of saturated solutions of Pr and Nd chlorides with positions of lines in simulated X-ray diffraction profiles, in order to probe the possibility of the so-called quasi crystalline structure of those systems [16]. The comparison showed that the positions of the most intense lines in the simulated profiles overlapped with the range of intensity curves pre-peaks, but did not correlate with the positions of the first maxima in the intensity curves. Furthermore, results of spectroscopic and ultrasonic studies of aqueous solutions of lanthanide salts have disclaimed the presence of chlorine ions in the first coordination shell of the cations even at a high salt concentration

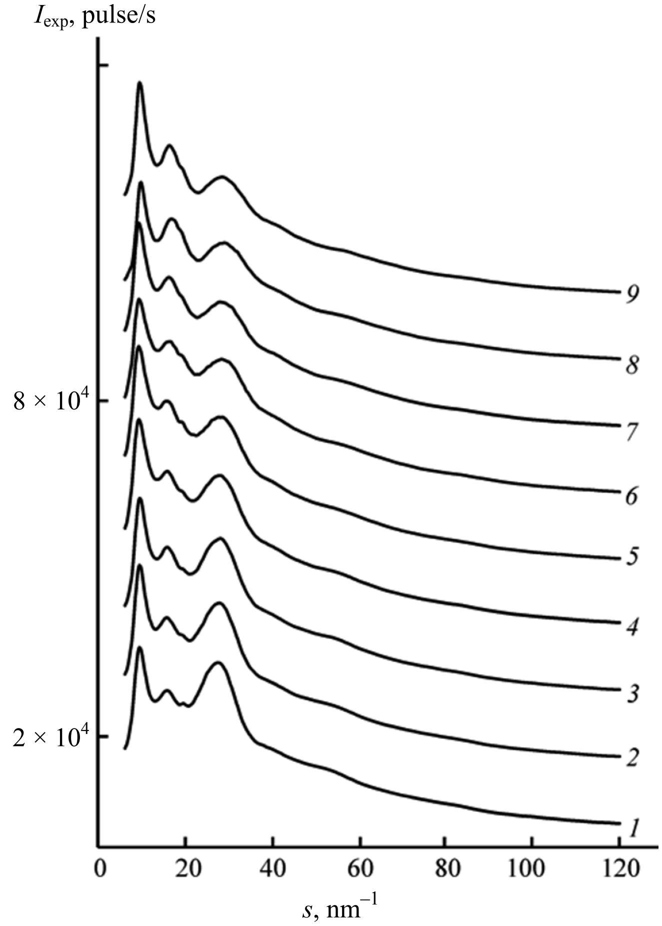

Fig. 1. Experimental X-ray scattering intensity as a function of wave vector of aqueous solutions saturated at 25°C: $LaCl_3$ (*1*), $PrCl_3$ (*2*), $NdCl_3$ (*3*), $SmCl_3$ (*4*), $GdCl_3$ (*5*), $DyCl_3$ (*6*), $ErCl_3$ (*7*), $YbCl_3$ (*8*), and $LuCl_3$ (*9*).

[17–19]. Hence, the close similarity of structures of the studied concentrated solutions with those of corresponding crystal hydrates could not be anticipated.

Nevertheless, the presence of pre-peaks definitely reflected certain pseudo-periodicity in the solution, or, more accurately, the statistical ordering at relatively large length scale. In the highly concentrated systems, solvent was deficient and could not form complete hydrate shells of isolated ions. That was evident from simple calculation of the sum of the most probable hydration numbers: ≈ 8–9 (Ln^{3+}) and ≈ 6(Cl^-). Hence, the basic unit of the solution defining its pseudo-periodicity could be a cation complex containing the first, purely hydrate, shell as well as chloride ions, forced to coordinate into the complex within boundaries of the second and the third coordination shells. Partially non-uniform distribution of the anions with respect to the cation resulted in formation of the pre-peaks by the cation–cation distances as well as by a set of close but unequal anion-anion distances. The following equation (previously suggested to determine the intercation distances [14] was used to estimate the pseudo-period value: $R = 7.725/s$; the pseudo-period was of 0.813–0.827 nm (saturated solutions) and of 0.827–0.878 nm (1 : 20 solutions).

The second, weaker peak at 15.84 nm^{-1} reflected likely the interanion distances. The scattering ability of chlorine is much lower than that of the cations, thus accounting for lower intensity of that peak. Furthermore, that peak could result from periodicity of distances between the cations and the anions in the ion associates. Note that the secondary peak intensity increased in the series of salts from lanthanum chloride to lutetium chloride.

Figure 2 demonstrates the intensity curves of the studied solutions of the 1 : 20 composition (salt : water). Upon addi-tion of water, the cation complexes somewhat swelled, and, therefore, the intercomplex distances increased. That caused the pre-peaks to shift towards lower s (8.87–9.19 nm^{-1}) with simultaneous decrease in their intensity. Noteworthily, similar effect was observed earlier [5, 13, 14, 20], and the following scaling law was found: $s_{\max,i} \sim c_i^{1/3}$ [11]. Our results did not follow that law.

The most significant changes in the intensity curves were observed upon dilution of the systems to reach the 1:40 composition (Fig. 3). The first maximum in the curves was complex and reflected the transition from the solvent-lacking structures to those of dilute solutions. It was clearly seen that in the cases of $LaCl_3$ and $PrCl_3$ solutions that maximum appeared as a smooth plateau, whereas for other salts, starting from $NdCl_3$, the first maximum separated in two components. We suppose that the small-angle component still reflected the periodicity of the distance between cation complexes, whereas the second component was due to a set of interion and intermolecular interactions in the developing solvent network. The increase of contribution of the solvent-solvent interactions into the total structure was further evidenced by increasing intensity of the peaks at 19.5–20.7 nm^{-1}. In this range the water peak usually appears. The latter observation could also correspond to the decrease in the lanthanides coordination number with the increasing ion weight. Indeed, the decrease in the number of water molecules in the cation coordination sphere led to the

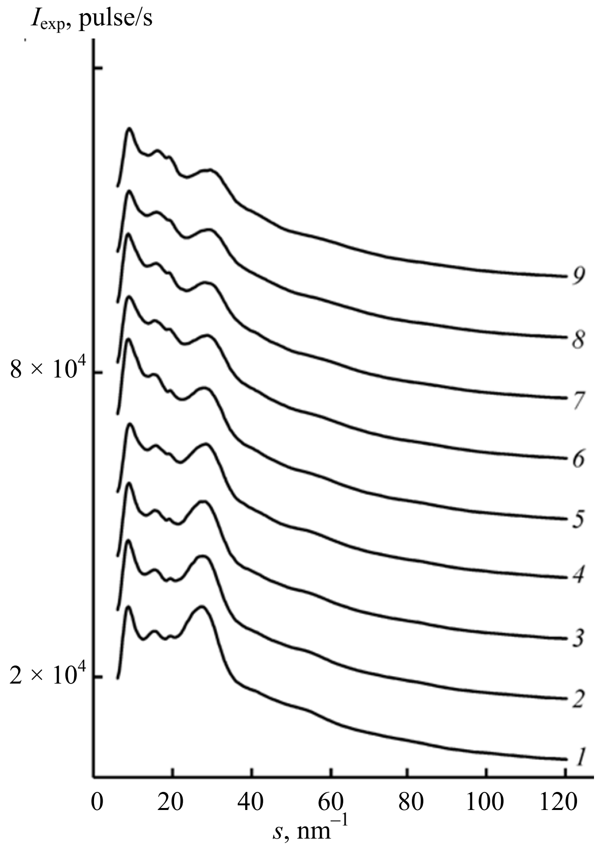

Fig. 2. Experimental X-ray scattering intensity as a function of wave vector of aqueous solutions of $LaCl_3$ (*1*), $PrCl_3$ (*2*), $NdCl_3$ (*3*), $SmCl_3$ (*4*), $GdCl_3$ (*5*), $DyCl_3$ (*6*), $ErCl_3$ (*7*), $YbCl_3$ (*8*), $LuCl_3$ (*9*); solution composition of 1 : 20.

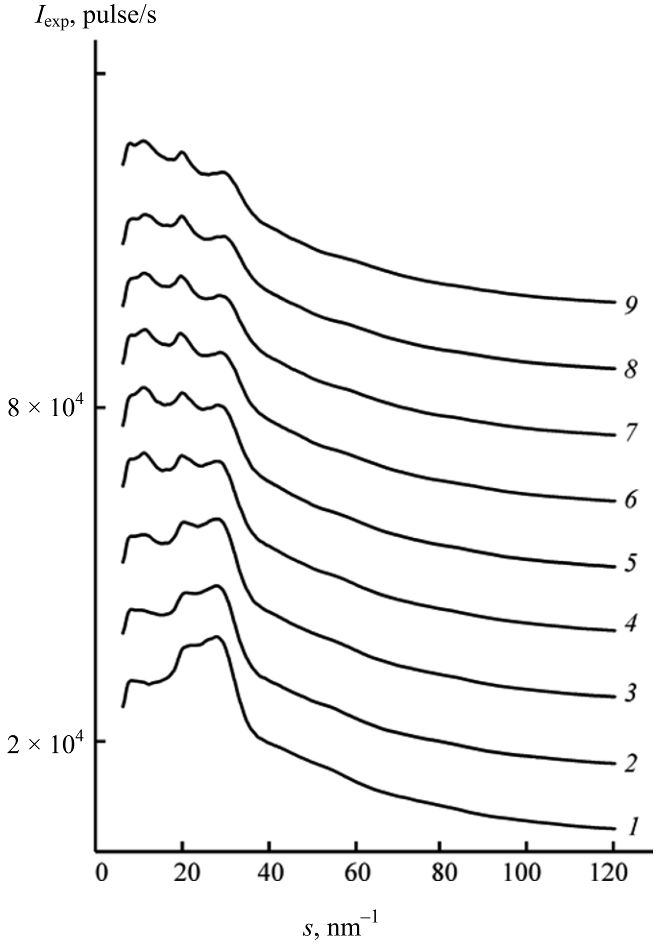

Fig. 3. Experimental X-ray scattering intensity as a function of wave vector of aqueous solutions of $LaCl_3$ (*1*), $PrCl_3$ (*2*), $NdCl_3$ (*3*), $SmCl_3$ (*4*), $GdCl_3$ (*5*), $DyCl_3$ (*6*), $ErCl_3$ (*7*), $YbCl_3$ (*8*), $LuCl_3$ (*9*); solution composition of 1 : 40.

increased water amount in the free solvent and, therefore, enhanced their impact into the free water structure.

In the cases of more dilute solutions (compositions of 1 : 80, Fig. 4 and 1 : 120, Fig. 5), pre-peaks were again observed in the intensity curves (shoulder in the case of lanthanum). As compared with the corresponding concentrated solutions, the pre-peaks were weaker, broadened, and shifted towards higher *s* values (10.9–11.9 nm^{-1}). The origin of pre-peaks appearance is somewhat different. As all ions at such dilutions were fully hydrated, the observed maxima reflected the periodicity of distance between centers of the isolated hydrate complexes (both anions and cations), or, in other words, the average interion distances. The comparison of the small-angle regions of the intensity curves of the salts solutions with that of water showed that in the case of dilute solutions the pre-peaks were partially associated with the own structural component of solvent. Evidently, the increased contribution of water molecules interaction was the cause of the pre-peaks position shift towards higher *s*. From the pre-peaks positions, the set of interparticle distances showed the periodicity at the 0.651–0.707 nm scale. From the Figures it is seen that the intensity curves in the case of lighter cations salt were closer in shape to that of water than to those of heavier cations salts. We suppose that it was due to higher scattering ability of the heavy ions and, therefore, more significant contribution of the related distances into the total scattering intensity.

The overall trend of the change in the intensity curves upon the solutions dilution was also remarkable. Let us consider the main peak and its right-

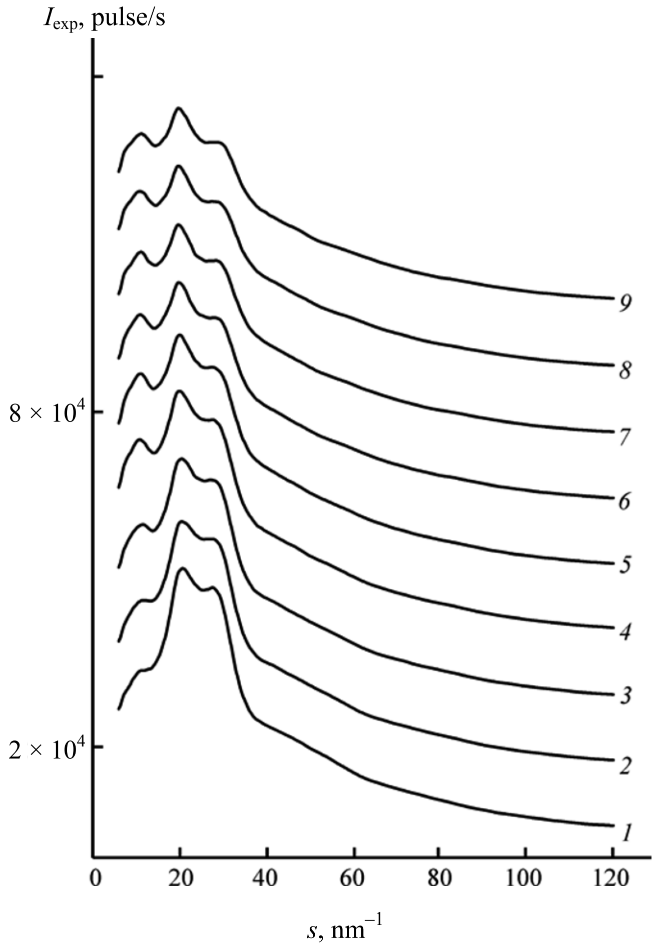

Fig. 4. Experimental X-ray scattering intensity as a function of wave vector of aqueous solutions of $LaCl_3$ (*1*), $PrCl_3$ (*2*), $NdCl_3$ (*3*), $SmCl_3$ (*4*), $GdCl_3$ (*5*), $DyCl_3$ (*6*), $ErCl_3$ (*7*), $YbCl_3$ (*8*), $LuCl_3$ (*9*); solution composition of 1 : 80.

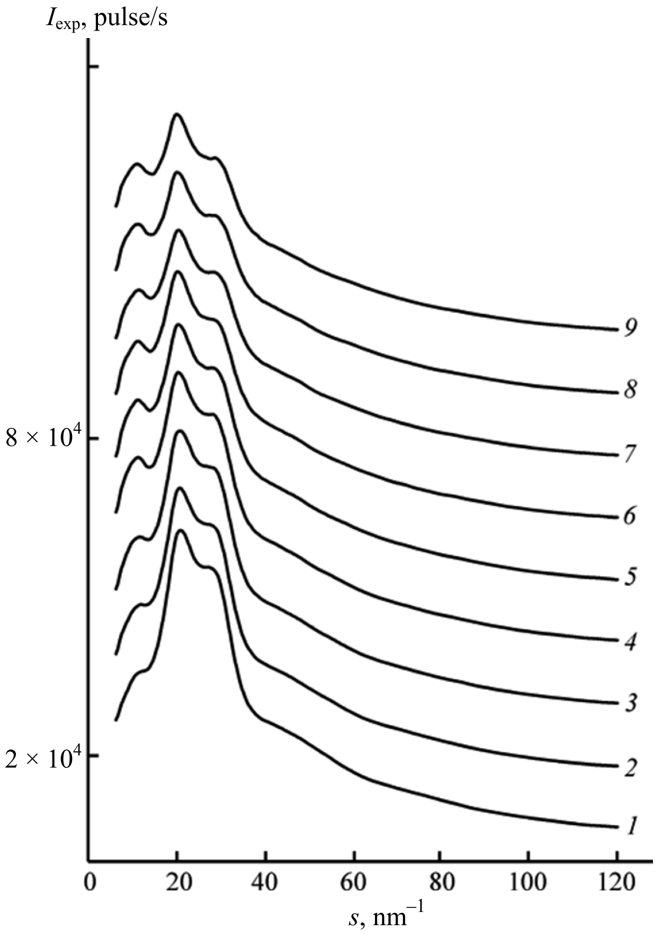

Fig. 5. Experimental X-ray scattering intensity as a function of wave vector of aqueous solutions of $LaCl_3$ (*1*), $PrCl_3$ (*2*), $NdCl_3$ (*3*), $SmCl_3$ (*4*), $GdCl_3$ (*5*), $DyCl_3$ (*6*), $ErCl_3$ (*7*), $YbCl_3$ (*8*), $LuCl_3$ (*9*); solution composition of 1 : 120.

hand shoulder, found in the cases of all dilute solutions at 20–29 nm^{-1}. The onset of the (presumably) aqueous peak appearance was observed in the intensity curves of concentrated solutions in the form of weak inflexion (pre-shoulder) to the right of the main maximum. Upon the solution dilution, the intensity of that peak and the adjacent shoulder increased. That, in turn, reflected the increasing contribution of the developing solvent network at the length scale of about 0.45 nm.

To conclude, the qualitative analysis of the basic X-ray diffraction data of aqueous solutions of lanthanide salts showed some remarkable feature of the solutions structure. In particular, the solution structure continuously changed upon dilution, being significantly different in the cases of dilute and concentrated solutions of the same salt. In the case of concentrated solutions, the intensity curves reflected likely the pseudo-periodical distribution of the cation complexes. In the case of dilute solutions, both salt ions should be considered in order to interpret the curves; their distribution was uniform, and the ions were fully hydrated.

The presence of pre-peaks in the intensity curves of the studied systems showed the far order in the solvents. In the case of concentrated solution, the inter-complex periodicity was observed at the length scale of 0.813–0.878 nm, whereas the interion distances in the dilute solutions showed periodicity at 0.651–0.707 nm.

The smooth change of the intensity curves in the series of the studied salts, its concentration being the same, could point at the absence of sharp change of the cation coordination number: the lanthanides coordination number was likely to decrease smoothly from 9 to 8 with the decreasing ionic radius [1–3]. We suppose that the equilibrium is established in the solution between the 9- and 8-coordinated cations. When moving along the lanthanides series, that equilibrium was continuously shifting from the prevailing 9-coordinated shells to the domination of 8-coordinated spheres. Therefore, the usually published fractional coordination numbers are results of averaging.

EXPERIMENTAL

The saturated (at 25°C) solutions of lanthanides (La, Pr, Nd, Sm, Gd, Dy, Er, and Lu) trichlorides were prepared by dissolving the corresponding crystal hydrates (chemical pure grade) in 0.01 mol/L aqueous hydrogen chloride solution (HCl was added to suppress the salt hydrolysis). Dilute solutions with the salt:water ratios of 1 : 20, 1 : 40, 1 : 80, and 1 : 120 were prepared by sequential dilution. Composition of all solutions was confirmed by measuring their density (the reference data from [21]).

X-ray diffraction analysis was carried out using the Bruker D8 Advance diffractometer (MoK_α radiation, λ 0.071 nm, zirconium β-filter as monochromator, at 4°–130° (2θ) with 0.1° step, the Bragg–Brentano scheme).

The intensity curves of liquid specimens were measured using the specially developed cell with lead flanges along with the adjusted lead screen mounted above the free liquid surface. The design allowed keeping the incident light projection within the cell at small angles. The scattering intensity was measured with the position-sensitive VANTEC-1 detection unit (Bruker). The crude experimental data were smoothed by the FFT filter; the background and the absorption were accounted for as well.

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