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# Coordination of Ions in Aqueous Solutions of Dysprosium Chloride according to the X-ray Diffraction Data

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**Abstract**—Aqueous solutions of dysprosium chloride in a wide concentration range are studied by X-ray diffraction analysis under standard conditions. The scattered X-ray radiation intensity curves are characterized by prepeaks at low values of the wave vector. Their interpretation and an analysis of changes at different concentrations are performed. The structure of concentrated solutions is formed due to interionic interactions of different types. On the contrary, dilute solutions are characterized by the determining role of the quasi-tetrahedral structure of the solvent. The prepeaks are also observed on the intensity curves of dilute solutions, indicating that these solutions retain the "long-range" ordering.

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## INTRODUCTION

The problem about the structural organization of solutions of lanthanide ions is not completely clarified nowadays, in spite of numerous publications issued within forty recent years. On the one hand, a substantial scatter in estimates of the coordination number of lanthanide ions does not allow a reliable structural description to be performed. On the other hand, the advanced models mainly describe the nearest environment of cations but do not concern the interaction at long distances. However, it turned out that, in the case of solutions containing multicharged cations, a simple analysis of primary X-ray diffraction data makes it possible to draw quite certain conclusions that qualitatively characterize their long-range ordering.

The purpose of this work is to monitor the changes in the structural organization in dysprosium chloride solutions that occur with a change in the concentration of these systems on the basis of X-ray diffraction data obtained in a wide concentration range.

The short-range order formed by the $Dy^{3+}$ ion in aqueous solutions of its salts was studied by different methods. The brief results of the neutron diffraction analysis are the following: coordination number 7.4 ± 0.5, $R(Dy^{3+}–O) = 0.237$ nm [1], coordination number 8, $R = 0.239$ nm [2]; EXAFS method: coordination number 8.1, $R = 0.237$ nm [3], coordination number 9, $R = 0.239$ nm [4], coordination number 8, $R = 0.237$ nm [5], coordination number 9, $R = 0.239$ nm [6]; and molecular dynamics method: coordination number 8.36, $R = 0.236$ nm [7, 8]. It was proposed on the basis of the detailed analysis of the published results that the average coordination number was 8.5 and the average $Dy^{3+}–O$ distance was 0.238 nm [9]. The cation forms the second coordination sphere of 14–16 water molecules with the distance from the cation to the coordination sphere ranging from 0.445 to 0.455 nm.

The structure of the nearest environment of the $Cl^-$ ion in aqueous solutions was studied in many works that were devoted specially to this problem and considered this anion only as a counterion for the studied cations. However, no unambiguous quantitative description of the hydrate sphere of the chloride ion has been obtained so far. At present, it is known that the coordination number of the chloride ion is six or seven with the distance to the coordinated water molecule equal to 0.310–0.320 nm. The anion forms no stable second coordination sphere.

## EXPERIMENTAL

A solution of dysprosium trichloride saturated at 25°C was prepared by the dissolution of its crystalline hydrate (reagent grade) in 0.01 M HCl to suppress hydrolysis with respect to the cation. More dilute solutions with the salt to water molar ratios equal to 1 : 20, 1 : 40, 1 : 80, 1 : 160, 1 : 240, and 1 : 320 were prepared by consecutive dilution according to the known dependences of their density on the concentration [10].

**The X-ray diffraction experiment** was carried out on a Bruker D8 Advance diffractometer ($MoK_\alpha$ radiation, $\lambda = 0.071$ nm, zirconium β filter) in a $2\theta$ range of 4°–130° with an increment of 0.1° in the Bragg–Brentano optics. A specially produced deep cell with lead edges and a controlled lead valve were used for recording solutions. The lead valve was mounted above the free liquid surface, which made it possible to cut off a parasitic scattering, which is inevitably present at small detection angles. The scattering intensity from the samples was detected with a VÅNTEC-1 position-sensitive detector (Bruker). The primary experimental data were smoothed in the Origin 7.5 program using the FFT filtration [11], and background and absorption corrections were applied. The mathematical apparatus accomplished in the algorithm of the KURVLR program package [12] was used for the calculation of the radial distribution functions (RDF) of the atomic electron density expressed as RDF = $4\pi r^2(\rho - \rho_0)$.

## RESULTS AND DISCUSSION

The experimental dependences of the X-ray radiation scattering intensity in dysprosium chloride solutions on the wave vector $s = 4\pi\sin\theta/\lambda$ (intensity curves) are shown in Fig. 1. It is noteworthy that the intensity curve shape of highly concentrated solutions differs strongly from that of water-like intensity curve shapes for dilute solutions.

This difference is primarily caused by the manifestation of the so-called prepeaks [13, 14] in a range of small $s$ values. A correct interpretation of small-angle maxima is an important stage for the understanding of the structural organization of a solution as a whole. It was earlier assumed that the prepeaks were due to the appearance of stable intercationic distances in the structure of solutions of lanthanide salts [14, 15]. The linear dependence of the prepeak position on the value of $C^{1/3}$ ($C$ is the molarity of the solution [14]) was also observed but, unfortunately, no comments were given. In fact, based on a comparatively sharp shape of the prepeaks in the curves of 1 : 16.5 and 1 : 20 solutions, these maxima can be explained by intercationic interactions. In addition, a weakly pronounced shoulder at 8.07 nm$^{-1}$ is observed in the intensity curves of a 1 : 40 solution. This shoulder can also be explained by the manifestation of intercationic distances, whose increase can reasonably be expected with dilution.

Undoubtedly, the prepeaks show the existence of some pseudo-periodicity or, in other words, some statistical average ordering in a solution that extends to comparatively “long” distances. In addition, the prepeaks are detected in the intensity curves of aqueous electrolyte solutions containing cations with the high complexation ability. We obtained the intensity curves for solutions of aluminum, scandium, and iron(III) chlorides with comparable concentrations. It is seen from Fig. 2 that the intensity curves of these solutions also have prepeaks but differ, nevertheless, from the intensity curves of a dysprosium chloride solution. The shapes of the curves of solutions of $AlCl_3$, $ScCl_3$, and $FeCl_3$ are mainly similar to the intensity curve of water thus showing the determining role of the water-like structure of these solutions in the total scattering pattern, while the intensity curves of a $DyCl_3$ solution differs from the latter. These solutions have the same stoichiometry of dissolved salts and differ in the physicochemical nature of the cations only. In turn, these cations, in spite of the same charge, differ in both sizes and structures of the external electronic shells and, hence, in the formed nearest environment. The $Al^{3+}$ and $Fe^{3+}$ ions have the coordination number 6, and that of the $Sc^{3+}$ ion is close to seven. However, the short-range order of cations only indirectly affects the formation of the prepeaks. The difference in the intensity curves is probably due to the difference in the arrangement of the cations at long distances and also by a special arrangement of the chloride ions in a solution of dysprosium chloride unlike other solutions.

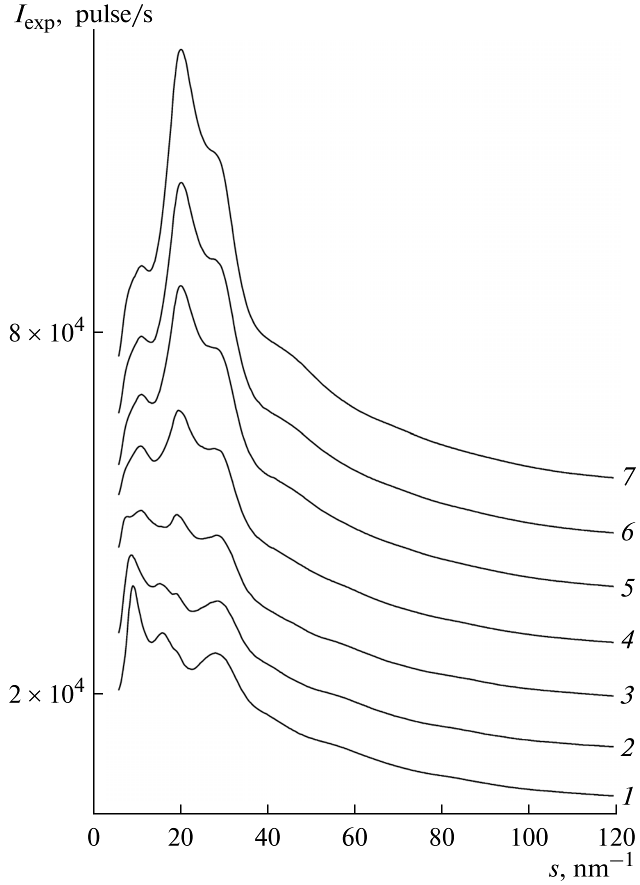

**Fig. 1.** Experimental dependences of the X-ray radiation scattering intensity in aqueous solutions of dysprosium chloride of the molar ratios (*1*) 1 : 16.5, (*2*) 1 : 20, (*3*) 1 : 40, (*4*) 1 : 80, (*5*) 1 : 160, (*6*) 1 : 240, and (*7*) 1 : 320 on the wave vector $s$.

According to the tentative calculation by the sum of the most probable hydrate numbers (the hydrate number of $Dy^{3+}$ is approximately 8–9 and that of $Cl^-$ is ~6), in highly concentrated solutions of dysprosium (1 : 16.5, 1 : 20) there is a deficient of the solvent for the formation of intrinsic (not generalized with adjacent ions) hydrate shells by all ions. Therefore, a cat-

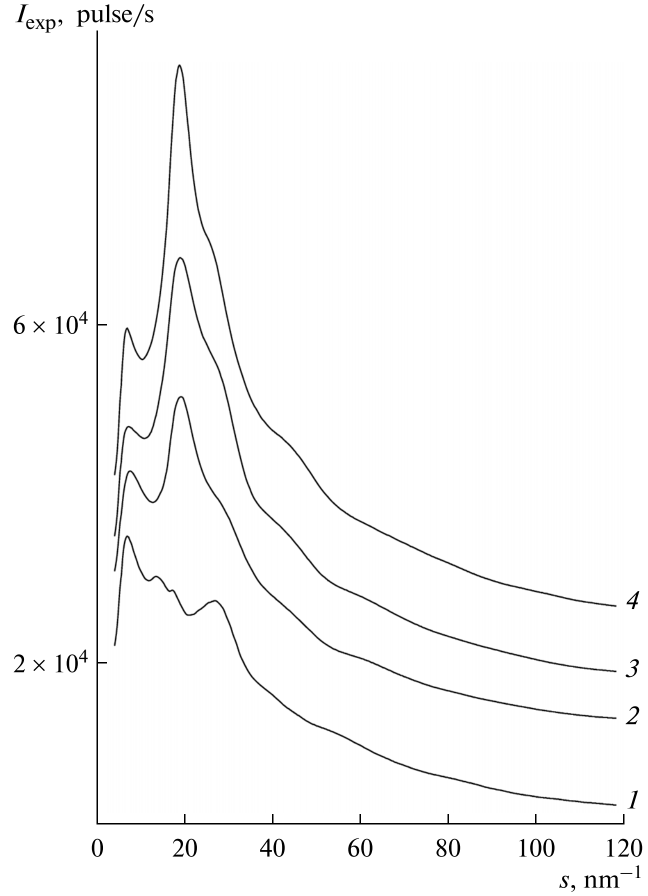

**Fig. 2.** Experimental dependences of the X-ray radiation scattering intensity in aqueous solutions of (*1*) dysprosium, (*2*) iron(III), (*3*) scandium, and (*4*) aluminum chlorides on the wave vector *s*.

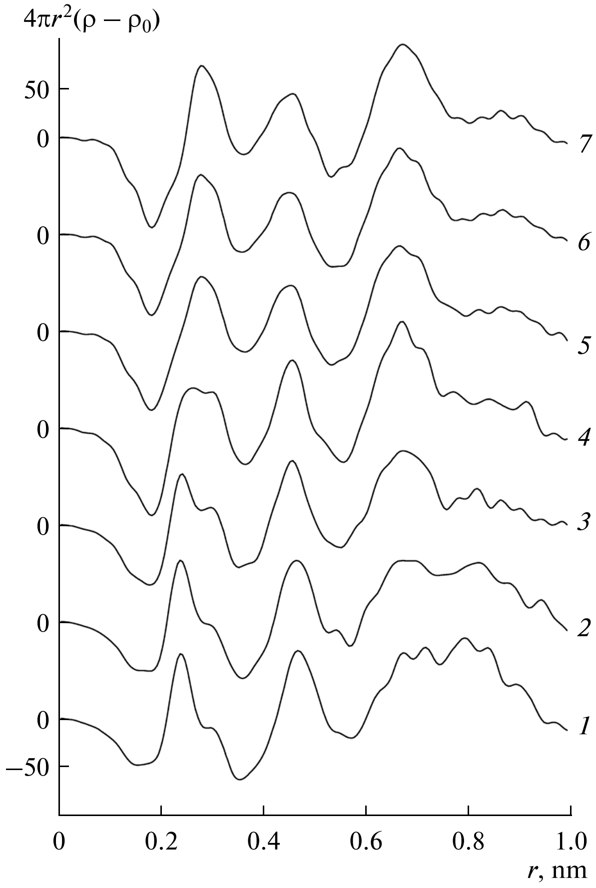

**Fig. 3.** Radial distribution functions of aqueous solutions of dysprosium chloride of the molar ratios: (*1*) 1 : 16.5, (*2*) 1 : 20, (*3*) 1 : 40, (*4*) 1 : 80, (*5*) 1 : 160, (*6*) 1 : 240, and (*7*) 1 : 320.

ionic complex also containing (in addition to the first exclusively hydrate shell) chloride ions forcedly associated in conventional limits of the second and third coordination shells can be proposed as a basis structural unit of the solution. This assumption is confirmed by the conclusions of spectroscopic and ultrasonic studies for aqueous solutions of lanthanides. The results of these studies indicate the absence of contact cation-anionic pairs in chloride solutions of lanthanide [16, 17].

The ratio $R = 7.725/s$ can be used to obtain an estimate of the revealed pseudo-period. Note that intercationic distances have previously been proposed to be determined by this formula [15]. Nevertheless, the assumed pseudo-period is estimated by values of 0.813 and 0.856 nm for 1 : 16.5 and 1 : 20 solutions, respectively.

However, in this range of distances, the calculated radial distribution functions do not convincingly correspond to the estimates, because these ranges are presented by complicatedly formed maxima (Fig. 3). This can be explained by the fact that the prepeaks represent the overall effect of interactions between comparatively intense scattering agents of X-ray radiation. This means that, along with the intercationic interactions, the prepeaks can be formed by a contribution from interanionic interactions that appear both at distances close to the intercationic distances and shorter distances. The second peaks in the intensity curves of highly concentrated solutions at 16.15 and 15.52 nm$^{-1}$ serve as the most probable confirmation. In our opinion, these peaks are formed by shorter interanionic distances.

Compared to concentrated solutions, the prepeaks for dilute solutions are less intense and determined by the wide base, and their maxima are shifted to higher values of the wave vector (11.09–11.41 nm$^{-1}$). This means that they are determined by interparticle interactions at shorter distances. In turn, this behavior of the prepeaks doubts about versatility of the earlier proposal that the reason for the appearance of the prepeaks is determined by the intercationic interactions only.

The intensity curve of a 1 : 40 solution has a transition shape that resembles the intensity curve shapes of both highly concentrated and dilute solutions and is considered as that reflecting the transition state of the solution, being an intermediate between the structural level with a solvent deficient and the level with the independent hydration of ions. Naturally, the assumption that the prepeaks in the intensity curves are determined by the interparticle distances of different types can be extended to dilute solutions as well. All ions gain intrinsic hydrate environments with dilution. Therefore, it can be asserted that the observed small-angle maxima are totally formed by the distances between the centers of isolated hydrate complexes of the ions, that is, cation-cationic, cation-anionic, and anion-anionic distances. In addition, the intrinsic structural ordering of the solvent is partially imposed on the prepeaks. According to the formula mentioned above, the estimation of this totality of distances lies in a region of 0.677–0.697 nm.

The radial distribution functions for the studied solutions are shown in Fig. 3. Only the first two groups of maxima can be interpreted most reliably. For highly concentrated solutions, the first maximum at 0.240–0.242 nm is determined by the distances from the cation to its first hydrate shell. The shoulder observed at ~0.300 nm reflects the distances between the anion and its nearest hydrate environment. The interactions between the contacting water molecules also contribute to this shoulder.

As the solution is consequently diluted and the ions form intrinsic hydrate shells, the shoulder at ~0.300 nm is gradually transformed into a peak determined by the increasing contribution from pair interactions $O(H_2O)–O(H_2O)$. Finally, at a high degree of dilution, the interactions of the ions with their nearest hydrate environment become indiscernible against the background of intermolecular interactions, which is indicated by the single maximum at 0.285 nm.

The second maxima at 0.468–0.469 nm correspond to the distances of interactions of the ions with their second conventional coordination shells. First, for concentrated solutions these are cation–anion distances. The position of the second maximum gradually shifts from 0.460 to 0.450 nm with the dilution of the solutions, which is reasonably explained by the enhanced formation of the intrinsic fragmentary tetrahedral structure of water, namely, the distances at the tetrahedron edge. In addition, the anions in the second coordination spheres of the cations are gradually replaced by the solvent molecules (the distance to them is 0.451 nm).

The third group of peaks, as already mentioned, includes a significant number of contributions from interactions of different types. These are the manifestation of the distances between independently hydrated ions and, of course, the contribution from the intrinsic structure of the solvent.

Based on the above presented data, we may conclude that solutions of dysprosium chloride are characterized by the intrinsic structure differed from that of solutions of aluminum, scandium, and iron(III) chlorides.

The structure of concentrated solutions of dysprosium chloride up to a molar ratio of 1 : 40 is formed due to interionic interactions of different types. Structural fragments of the pure solvent are not almost observed. On the contrary, more dilute solutions are characterized by the determining role of the quasi-tetrahedral structure of the solvent, whose network contains the hydrate complexes of the ions.

The small-angle maxima are retained in the studied solutions in all concentration range, which unambiguously indicates that the interionic interactions at long distances are retained in comparatively dilute systems as well.

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