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Coordination of Ions in Aqueous Solutions of Erbium Chloride from X-ray Diffraction Data

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Abstract—Aqueous solutions of erbium chloride were studied by X-ray diffraction over a broad range of concentrations under standard conditions. The prepeaks observed in the experimental scattering intensity curves were interpreted. The solutions were found to possess two types of structures. Saturated and concentrated solutions down to molar ratio of 1 : 20 have a quasi-crystalline structure defined by inter-ion interactions. Dilute solutions form a water-like structure characterized by a tetrahedral network of hydrogen bonds between water molecules. It was found that prepeaks can also be seen in the intensity curves of dilute solutions, which implies that these solutions retain the so-called long-range order.

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In recent decades, structural organization of aqueous solutions of lanthanides has attracted interest of researchers, which has now increased. However, some aspects of the solution structure have not yet been elucidated. It was found that electrolyte solutions have not only short- but also long-range order. This issue has not received adequate attention, because the presence of persistent interactions between ions at long distances (up to 0.9 nm) in liquid media seemed unlikely. Nevertheless, small-angle maxima present in X-ray scattering intensity curves (**ICs**) of some aqueous solutions of electrolytes unambiguously attest to the existence of ordering at rather long distances. The phenomenon of small-angle maxima for some aqueous solutions of di- and trivalent cations was noted earlier [1–3] but was not studied in detail.

The structure of aqueous solutions of erbium salts has been studied by X-ray diffraction [4–8], EXAFS [9–11], and molecular dynamics [12–14]. Detailed analysis of works dealing with the short-order structure around Er^{3+} ions in aqueous solutions was reported [15]. Note that equilibrium between nine- and eight-coordinate erbium(III) ions occurs in these systems, the latter being formed predominantly. This gives rise to a fractional coordination number of 8.3. The distance to the first-sphere coordinated water molecules $Er^{3+}–OH_2$ is 0.235 nm. Also, this cation forms a second coordination sphere, which comprises, on the average, 14–16 water molecules (the average distance is 0.449 nm). Erbium salts tend to form both contact and non-contact ion pairs in solutions.

Parameters of the local environment of chloride ions were reported in [16–18]. Among the wide set of coordination numbers proposed for Cl^- in the literature, the predominating values are six and seven; modern studies rather attest to a C.N. close to seven. Since it is still difficult to draw an unambiguous conclusion, we assume that the chloride ion can coordinate from six to seven water molecules in dilute aqueous solutions of electrolytes; this number decreases following increase in the concentration. The distance to the coordinated water molecules is 0.310–0.320 nm. The anion does not form a second coordination sphere. Chloride ions tend to form mainly contact ion pairs.

The purpose of this study is to measure X-ray diffraction intensity curves for aqueous solutions of erbium chloride over a broad concentration range, to analyze the curves for the presence of small-angle peaks, and thus to investigate the effect of concentration on the structure formation and on the long-range order in these systems.

EXPERIMENTAL

A solution of erbium chloride ($ErCl_3$: 14.7 H_2O) saturated at 25°C was prepared by dissolving reagent grade hexahydrate in distilled water. To suppress hydrolysis, a specified amount of hydrochloric acid was added. More dilute solutions with salt to water molar ratios of 1 : 20, 1 : 40, 1 : 80, 1 : 160, 1 : 240, and 1 : 320 were prepared by successive dilution.

X-ray diffraction was performed on a Bruker D8 Advance diffractometer in the Bragg–Brentano optical geometry (MoK_α radiation, λ = 0.07107 nm, monochromatized by a zirconium β-filter, scanning range 4° to 130° (2θ), a 0.1° step). The ICs were measured on the free surface of solutions using a specially designed cell and an adjustable vertical lead screen,

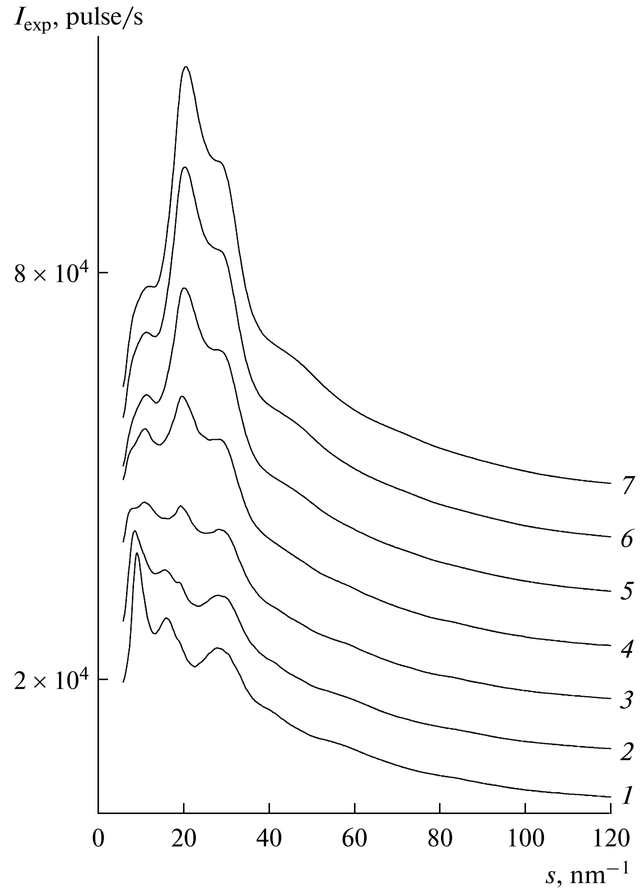

Fig. 1. Experimental dependences of the X-ray scattering intensity in aqueous solutions of erbium chloride with molar ratios of (*1*) 1 : 14.7, (*2*) 1 : 20, (*3*) 1 : 40, (*4*) 1 : 80, (*5*) 1 : 160, (*6*) 1 : 240, and (*7*) 1 : 320 on the wave vector *s*.

which made it possible to restrain the projection of the incident radiation at small angles within the cell boundaries. The scattering intensity from the samples was detected by a VÅNTEC-1 position-sensitive detector (Bruker). The atomic-electron density radial distribution functions (**RDF**) were calculated using the mathematical tools implemented in the algorithm of the KURVLR program package [19].

RESULTS AND DISCUSSION

The X-ray scattering intensity curves for aqueous solutions of erbium chloride versus the wave vector $s = 4\pi\sin\theta/\lambda$ over a broad concentration range are shown in Fig. 1. For better visualization of small details, the ICs are shown in the range of 6–120 nm^{-1}, each curve being vertically shifted by 7×10^3 pulses per second. A characteristic feature of each of the presented ICs is the presence of peaks at small scattering angles (s = 8.80–15.70 nm^{-1}). The distances (***R***) were roughly estimated from the positions of prepeaks by the formula $R = 7.72/s$ [20].

The ICs of a saturated solution shows an intense small-angle peak at 9.34 nm^{-1}. Since Er^{3+} ions are the species that scatter the X-rays most strongly in this system, this peak is likely to show the long-range distances between these ions. Using the above formula, these distances can be estimated as 0.826 nm. In a saturated solution, the ions do not form complete C.N. due to deficiency of the solvent. This gives rise to a structure with alternating cations and anions. Presumably, anions are arranged between partially hydrated cations off the axis through the cation centers, these anions acting as electrostatic fragments of erbium ion attraction. The distances between the anions are possibly reflected by the second, less intense peak at 16.31 nm^{-1}. The corresponding distance was estimated very roughly using the same formula to be 0.473 nm. The scattering ability of chloride ions is much lower, which accounts for the lower intensity of this peak. The ion radius of chloride ions is estimated as ~0.18 nm. Hence, the distance of 0.473 nm implies the presence of water molecules between the anions. In addition, this peak may be due to the distances between cations and anions in ion associates. It was found by X-ray diffraction [1] that the Er^{3+}–Cl^- distances in the $ErCl_3 : 6H_2O$ crystal hydrate are 0.506 nm (in a 3.63 M solution of erbium(III) chloride, this distance is 0.479 nm). The value we found is smaller than the reported values. This only emphasizes that scattering from non-contact ion associates is included in this peak as a constituent. Apart from the listed peaks, the curves for concentrated solutions have a common slightly sloping peak at ~28 nm^{-1}, which is transformed in dilute solutions into a shoulder of the principal peak and which is characteristic of aqueous systems. It is hardly possible that in a saturated solution containing four ions per ~15 water molecules, this peak reflects the intrinsic structure of the solvent. However, in the case of RDF of water and dilute aqueous solutions, it corresponds to distances between the solvent molecules (~0.450 nm). Hence, in a saturated solution, there is a set of scattering groups at the same distance, which make a contribution to this peak but are likely to comprise not only water molecules.

Dilution of the solution to a 1 : 20 molar ratio results in a shift of the first prepeak to shorter distances (down to 8.87 nm^{-1}). This implies an increase in the distance between the cations in a real solution. The second peak also shifts to smaller distances (down to 15.84 nm^{-1}), which means an increase in the distance in the scattering groups with chloride ions. This was to be expected because the addition of water naturally leads to greater distances between the ions. In addition, a small peak appears in the IC at 19.15 nm^{-1}, indicating the onset of formation of fragments of the intrinsic solvent structure.

On going to the system with 1 : 40 molar ratio, the pattern of the intensity curve changes. The prepeak is separated into a low-intensity peak and a shoulder on its left side. The peak position shifts to longer distances (to 11.09 nm^{-1}). The second prepeak disappears, and the intensity of the peak at 19.15 nm^{-1} increases. The behavior of the first prepeak reflects the decrease in the distance between ions in the solution. It could seem that dilution should, conversely, increase this distance; however, this is not the case. In our opinion, this phenomenon can be explained as follows. Saturated and concentrated solutions (down to 1 : 20 molar ratio) do not have enough water molecules to complete even the first coordination sphere of ions, and this results in direct ion contacts with one another. Presumably, a network of alternating cations and anions defined by inter-ion interactions with inclusion of water molecules is formed throughout the whole solution bulk. So-called pseudocrystalline structure is thus formed. The decrease in the concentration to 1 : 20 molar ratio draws this network apart only slightly, which is traced as an increase in the distances between the cations. Going to a more dilute system (1 : 40) brings about considerable changes in the whole solution structure. Now there are enough solvent molecules to form not only the first coordination sphere of the ions present but also the second coordination sphere of cations. The ion network is destroyed and a network of water molecules is formed. The solution structure changes from pseudocrystalline to water-like, and the small-angle peak starts to reflect scattering from non-contact ion associates. Note, however, that fragments with stable long-range interactions between the ions are still retained in this system as indicated by the mentioned shoulder on the left of the prepeak.

The intensity curve of a more dilute solution (1 : 80) supports our assumption. The rather intensive prepeak still persists, indicating that the system contains a considerable number of ion associates. The major peak now is the characteristic peak of water at 19.95 nm^{-1} with a right-hand shoulder typical of intensity curves of the solvent. This means that the structure of water becomes predominant. Further dilution of the solution leads regularly only to an increase in the intensity of the characteristic peak of the solvent and a decrease in the prepeak intensity. Note, however, that the prepeak is still retained in a relatively dilute solution (1 : 320). Thus, the rather long-range inter-ion interactions operate also in dilute systems.

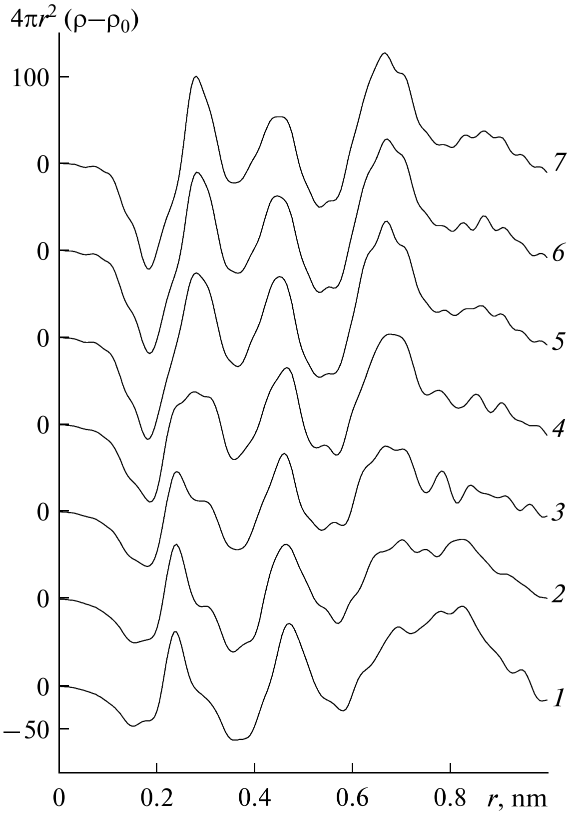

Fig. 2. Radial distribution functions for aqueous solution of erbium chloride with molar ratios of (*1*) 1 : 14.7, (*2*) 1 : 20, (*3*) 1 : 40, (*4*) 1 : 80, (*5*) 1 : 160, (*6*) 1 : 240, (*7*) 1 : 320.

Figure 2 presents the correlation functions for the studied solutions expressed as RDF $4\pi r^2(\rho-\rho_o)$. The peaks in all of the given RDFs are complex, i.e., they include contributions from different types of interparticle interactions. Due to the integral nature of the functions, for distances longer than 0.4 nm, they look like one another and are hardly suitable for analysis of long-range changes. The peak at 0.235 nm in the correlation function of a saturated solution reflects the distances from the Er^{3+} to its first coordunation sphere, $Er^{3+}-(H_2O)_I$. The right-hand shoulder of this peak at ~0.310 nm is largely determined by contributions from the distances between the anion and the water molecules, $Cl^-{-}H_2O$ (~0.315 nm). High intensity of the first peak and small size of the shoulder are due to the fact that the highly charged cations draw off a large portion of solvent molecules for the formation of their coordination spheres. The peak at 0.470 nm is likely to show the distances in cation–anion non-contact ion pairs, as also follows from interpretation of the intensity curves. The extensive correlation present in the RDF in the 0.70–0.90 nm range of distances comprises contributions from various interparticle interactions of a longer distance. Since the set of unstable scattering groups in this range of distances is large and the temperature factor accounts for their considerable variability, this peak is so broad. Nevertheless, the maximum at 0.82 nm predicted based on the prepeak position in the IC (Fig. 1) is clearly seen.

The correlation function of the solution with 1 : 20 molar ratio differs only slightly from that for a saturated solution, indicating that no substantial short-range order changes occur in the system. The position of the first maximum remains the same, which implies that distances from the cation to the first-sphere water molecules do not change. The right-hand shoulder of this peak becomes more resolved. Apart from being due to the $Cl^-{-}OH_2$ distance, it starts to include the increasing number of direct contacts between the water molecules, which usually occurs in dilute aqueous solutions at 0.290 nm distances.

The pattern of the correlation function for solution with 1 : 40 molar ratio somewhat changes. The intensity of the first peak decreases and the intensity of the right-hand shoulder increases. This attests to greater contribution of the nearest distances between the water oxygen atoms to the whole scattering. Note also the shift of the second peak to shorter distances (to 0.460 nm) and narrowing and shift (in the same direction) of the broad third peak. The ~0.450 nm peak present in the RDF of water and dilute aqueous solutions reflects the tetrahedral geometry of the mutual arrangement of solvent molecules; the peak at 0.65 nm is also inherent in neat water. All this emphasizes once again the development of the intrinsic structure of the solvent and the formation of a water-like structure.

Further dilution (1 : 80) results in coalescence of the peak that reflects the hydration of cations with the shoulder characterizing development of the solvent structure. Evidently, the contribution of the intrinsic quasitetrahedral structure becomes predominant. The functions of more dilute solutions only demonstrate strengthening of the water-like structure in the systems.

On the basis of the foregoing it can be concluded that aqueous solutions of erbium chloride may have two types of structures. A saturated or concentrated solution with 1 : 20 molar ratio has a pseudocrystalline structure defined by inter-ion interactions. Dilute solutions have a water-like structure characterized by a tetrahedral network of hydrogen bonds between water molecules. The hydration complexes of ions are incorporated in the solvent matrix.

The presence of prepeaks in the ICs over the whole concentration range attests to the existence of a long-range order in solutions of erbium chloride down to relatively dilute solutions. This order is determined by stable inter-ion interactions.

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