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Ion Coordination in Aqueous Solutions of Cerium Nitrate from X-ray Diffraction Data

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Abstract—Aqueous solutions of cerium nitrate were studied by X-ray diffraction over a wide concentration range under standard conditions. The presence of prepeaks on experimental X-ray diffraction intensity curves can be explained by the long-range order of ions. With a decrease in the concentration of cerium nitrate, the pseudoperiodic distribution of composite cation–anion complexes changes to an even interionic distribution in the water network of a solvent, which is reflected by the intensity curves. The experimental radial distribution functions were calculated and interpreted.

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INTRODUCTION

Modern applied and theoretical interest in the study of solutions of cerium salts is due to a great variety of practical applications of cerium. On the one hand, the use of solutions of Ce^{3+} ions for analytical purposes and their high complexing ability are universally known; on the other hand, recent data show that cerium salts can be promising in the medicobiologic aspect as drugs exhibiting antiviral and anticancer properties.

A review of crystallographic investigations of the short-range order of the cerium ion [1] suggests a three-face centered trigonal prism as the most probable geometry of its coordination sphere in dilute solutions. The distance from the central metal ion to six coordinated water molecules of the first sphere is 0.250 nm; other three water molecules are 0.263 nm distant. The second coordination sphere in solvent-abundant solutions consists of about 18 water molecules at a distance of 0.465 nm.

The structure of the nitrate anion seems to be a triangle probably changing its geometry from equilateral to isosceles in the field of multiply charged cations [2]. Based on numerous data from direct or indirect measurements of the short-range order around the nitrate ion, some believe that its most probable environment in dilute aqueous solutions can be thought of as nonahydrate [3]. At the same time, cation–anion association takes place in concentrated solutions [4–6].

The present work was intended to continue our series of X-ray diffraction studies of solutions of lanthanide salts, mainly being focused on the so-called “long-range order” [7–9]. The goal of this work was to qualitatively follow structural changes due to ionic association that occur as the concentration decreases, starting from the saturation point.

EXPERIMENTAL

Aqueous solutions of cerium(III) nitrate with molar salt-to-water ratios of 1 : 11, 1 : 20, 1 : 40, 1 : 80, 1 : 160, 1 : 240, and 1 : 320 were prepared by serial dilution. The concentrations of the prepared solutions were checked by using the following formula for their density: $\rho_{298} = 0.99998 + 0.25595m - 0.01715m^2$ (m is molality). This formula had been derived by processing closely convergent sets of data taken from different sources [10–12].

X-ray diffraction experiments were carried out on a Bruker D8 Advance diffractometer (MoK_α radiation, $\lambda = 0.07107$ nm, a zirconium β-filter, $2\theta = 4°–130°$, scan step 0.103°) according to the Bragg–Brentano focusing scheme. A deep cell with lead walls and a lead screen located over the free surface of a liquid sample were used to prevent parasitic scattering from air inevitably accompanying small-angle X-ray diffraction experiments for liquid systems. The reflection intensities were measured by a position-sensitive VÅNTEC-1 detector (Bruker). Primary data were smoothened with the Origin 7.5 program using FFT filtration [13] and corrected for the background and for the absorption by the samples. The radial distribution functions (RDF) of the atomic electron density, $RDF = 4\pi r^2(\rho - \rho_o)$, were calculated using the body of mathematics implemented in the algorithm of the KURVLR program package [14].

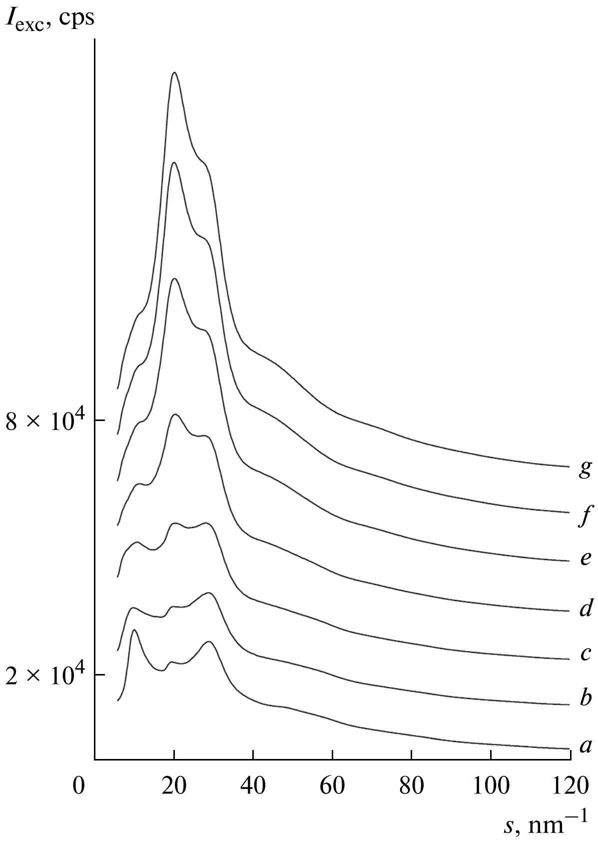

Fig. 1. Experimental plots of the X-ray diffraction intensities vs. the wave vector s for aqueous solutions of cerium nitrate. The molar ratios are (*a*) 1 : 11, (*b*) 1 : 20, (*c*) 1 : 40, (*d*) 1 : 80, (*e*) 1 : 160, (*f*) 1 : 240, and (*g*) 1 : 320.

RESULTS AND DISCUSSION

Experimental plots of the X-ray diffraction intensities vs. the wave vector $s = 4\pi \sin\theta/\lambda$ (intensity curves (ICs)) for solutions of cerium nitrate of different concentrations are shown in Fig. 1. For dilute solutions (Fig. 1, *e*–*g*), the ICs generally resemble the IC of pure water; this suggests that the structures of these solutions largely depend on the matrix of a free solvent. In contrast, the fundamentally different IC patterns for highly concentrated solutions (Fig. 1, *a*, *b*) provide evidence for structures formed by coordination of ions since the solvent is deficient under these conditions. Accordingly, the range of medium concentrations shows transition-type ICs (Fig. 1, *c*, *d*) combining the features characteristic of highly concentrated and highly diluted solutions.

The most intriguing point to be discussed is the presence of so-called prepeaks on the ICs of highly concentrated solutions. Prepeaks are intensity maxima in the small-angle scattering range. For a saturated solution, this maximum at $s = 10.454$ nm^{-1} is most intense. With a decrease in the concentration, the prepeak becomes less intense and initially shifts to lower s values (for the 1 : 20 solution, $s = 10.137$ nm^{-1}) but then to its greater values ($s = 11.088$ nm^{-1} for the 1 : 40 solution and 11.564 nm^{-1} for the 1 : 80 solution). At higher dilution, the prepeak degenerates into a slight inflection on the left slopes of the ICs. We find it expedient to compare preliminary data for solutions of cerium nitrate and the data for solutions of lanthanum nitrate studied in [7]. The neighborhood of lanthanum and cerium in the Periodic System implies, at first sight, a close structural similarity of the same salts of these cations and, consequently, their similar IC patterns. Comparison of the ICs of these systems shows that they are not very similar (Fig. 2). Specifically, the prepeaks on the ICs of the cerium solutions are shifted to slightly higher s values against those for the lanthanum solutions. In addition, the prepeak intensity for the cerium solution drops relatively faster with dilution than does the prepeak intensity for the lanthanum solution. These two observations deserve a special explanation.

Spectroscopic [15–21] and ultrasonic studies [22] have revealed direct cation–anion contacts in aqueous solutions of lanthanide nitrates. The nitrate ion is assumed to be coordinated to a lanthanide ion in either mono- or bidentate fashions. For a 1 : 20 solution of lanthanum nitrate, the number of nitrate anions per lanthanum cation is 1.4 [23]. Also note that the reported solubility of cerium nitrate [24–26] is higher than the solubilities of lanthanum and praseodymium nitrates (these elements follow cerium in the Periodic System) [25, 27]. This can be due to either coordination of two anions to the cation in highly concentrated solutions of cerium or bidentate coordination of the nitrate anion, in contrast to its presumably monodentate coordination in solutions of lanthanum and praseodymium. The different structures of the short-range order undoubtedly affect the long-range order, which in turn produces nonmonotonic changes in the IC patterns for solutions of cerium and lanthanum of equal concentrations.

The aforementioned shift of the prepeaks as well as the additionally noted widening of the base area under the prepeaks for nitrate systems compared to chloride ones [7, 8] allows a more versatile interpretation of the origin of prepeaks. We attribute them to the cooperative stable order of ions, although some researchers believe that the distances between cations are the only contributors [28, 29]. For highly concentrated solutions, the idea of a certain pseudoperiod can make sense. Calculations for $Ln(NO_3)_3$ from the sum of C.N.(Ln^{3+}) ≈ 9 and C.N.(NO_3^-) ≈ 9 show that the amount of the solvent in such solutions is not enough to provide every ion with its own completed hydration shell (not shared by adjacent ions). That is why the cationic complex containing, apart from water molecules, one to two nitrate anions in the first coordination shell can be regarded as a structuring unit of the solution that is responsible for its pseudoperiodic character. The presence of numerous outer-sphere

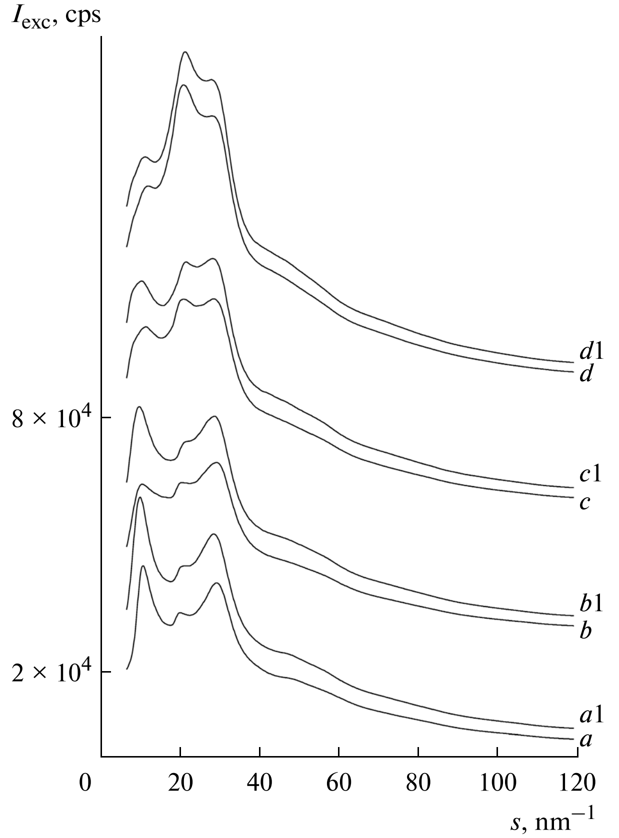

Fig. 2. Experimental plots of the X-ray diffraction intensities vs. the wave vector *s* for aqueous solutions of lanthanum nitrate (letter-and-figure designation) and cerium nitrate (letter designation). The molar ratios are (*a*) 1 : 12.98, (*a*1) 1 : 11, (*b*, *b*1) 1 : 20, (*c*, *c*1) 1 : 40, and (*d*, *d*1) 1 : 80.

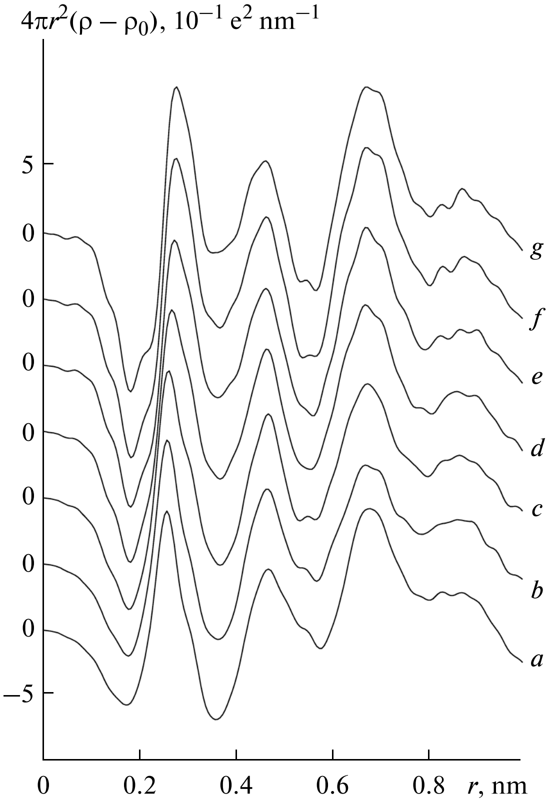

Fig. 3. Radial distribution functions for aqueous solutions of cerium nitrate. The molar ratios are (*a*) 1 : 11, (*b*) 1 : 20, (*c*) 1 : 40, (*d*) 1 : 80, (*e*) 1 : 160, (*f*) 1 : 240, and (*g*) 1 : 320.

nitrate anions with a less ordered mutual arrangement provides a range of distances that are shorter than those between complexes. All this favors the widening of the area under the prepeaks. High dilution of the solutions allows the full hydration of ions; under these conditions, the inner-sphere complexes of the cations with the anions decompose. As a result, the ICs show weak prepeaks (degenerated into shoulders with dilution) due to shorter distances between separately hydrated ions (both cations and anions).

In the second step of this study, we interpreted RDF peaks. Examination of the radial distribution functions of the systems under discussion (Fig. 3) suggests a complicated multicomponent character of their peaks.

The most considerable groups of RDF peaks for concentrated solutions appear at 0.260 nm and, with dilution, monotonically shift toward 0.280 nm. As noted above, they can be interpreted as multicomponent peaks because of their asymmetric shapes. Undoubtedly, they correspond to the Ce^{3+}–$O(H_2O)$, Ce^{3+}–$O(NO_3^-)$ distances in the first coordination shell of the cation (~0.25–0.26 nm), the $O(NO_3^-)$–$O(H_2O)$ distances in the nearest environment of the anion (~0.28 nm), and direct $O(H_2O)$–$O(H_2O)$ contacts (~0.28–0.29 nm). For this reason, it is difficult to rigorously determine the coordination numbers of the metal ions and the distances in their first coordination shells.

The RDF peaks at 0.470 nm, which only slightly shift toward 0.465 nm at high dilution, correspond to the distances between the ions (both the cations and anions) and their second coordination shells. With dilution enabling the intrinsic water structure to appear, these peaks are also contributed by the distances of the edges of tetrahedral fragments formed in the solvent network.

A broadened group of peaks with maxima at 0.67–0.68 nm can be assigned to interspecies interactions occurring in what can conventionally be called third coordination shells. For highly concentrated solutions, these peaks can be contributed by the distances between cations associated through the nitrate anion and the distances between anions associated with the cation. The trigonal planar structure of the nitrate anion allows a variety of spatial orientations relative to its neighbors. This precludes identification of the predominant geometrical shapes of associates. In dilute solutions, interspecies interactions are absent; instead, the peaks are contributed by the distances of individual interionic interactions as well as by the distances between water molecules associated via hydrogen bonding without direct contact with each other.

In conclusion, we should note that analysis of the literature data, as well as nonparallel changes in the ICs for solutions of lanthanum and praseodymium nitrates, suggests a more considerable inner-sphere association of the nitrate anions with the cations. Interpretation of prepeaks on ICs depends on the concentration range involved. For instance, the presence of prepeaks on ICs of highly concentrated solutions indicates a long-range (pseudoperiodic) order of the structures of the solutions. The remnants of the prepeaks on the waterlike ICs of dilute solutions reflect a collection of individual interionic distances.

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