Variation of relaxation parameters of aqueous lanthanide nitrates across the series

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Introduction

Lanthanides, i. e., the elements of atomic number Z from 57 (lanthanum) to 71 (lutetium) form an unique series within the Periodic Table. Together with scandium and ytrium these metals display a predominantly trivalent chemistry. All rare earths exist as trivalent ions in solutions. The radii of the RE^{3+} decrease smoothly across the rare earth series to the systematic filling of the 4f shell from lanthanum to lutetium. Since the 4f electrons are well shiellded by the filled $5s^2 5p^6$ shells, the interaction between a rare earth ion and water molecules is predominantly ion-dipole and electrostatic in character. Therefore, the inner shell water coordination is primarily determined by the rare earth ion size ant the strength of the ion-dipole interaction. Lanthanides form an ideal group of ions for study of thermodinamic and kinetic properties of aqueous solutions as a function of ionic size.

In the present work we have investigated the dependence of relaxation parameters of aqueous lanthanide nitrates against cation atomic number. The relaxation process and rates of formation of the complexes $[LnNO_3]_{aq}^{2+}$ have been determined from ultrasound velocity dispersion measurements [1-2].

Results and discusion

Figure 1 presents the dependences of the relaxation frequency f_R, the velocity dispersion c_∞-c_0 and values c_0-c_{H_2O}, where c_0 is the ultrasound velocity at frequency much lower than the relaxation frequency and c_{H_2O} is the ultrasound velocity in solvent for the investigated nitrate solutions at the concentration 0,2 mole/l. As seen, the relaxation frequency reaches a maximum on samarium and then falls down to the heaviest lanthanides. It is interest to consider the parameters which influence f_R and then attempt to interpret this dependence against cation atomic number. The relaxation frequencies are related to a sum of rates constants k_{23} and k_{32}:

$$2\pi f_R = k_{32} + k_{23}\Phi_C. \tag{1}$$

The constant k_{23} is interpreted as the rate of exchange of water molecule in the first coordination sphere of the cation with the anion NO_3^{-1} in the second coordination sphere, k_{32} is the rate for the reverse process, so k_{32} will be dependent on the nature of the anion.The function Φ_C depends on the concentration and cannot in general be precisely determined, but for the lanthanide nitrate salts this variation with concentration is small. Φ_C also depends to some extent on the nature of the cation, for example, on the change type and the ionic radii. Φ_C may be assumed constant for closely related cations

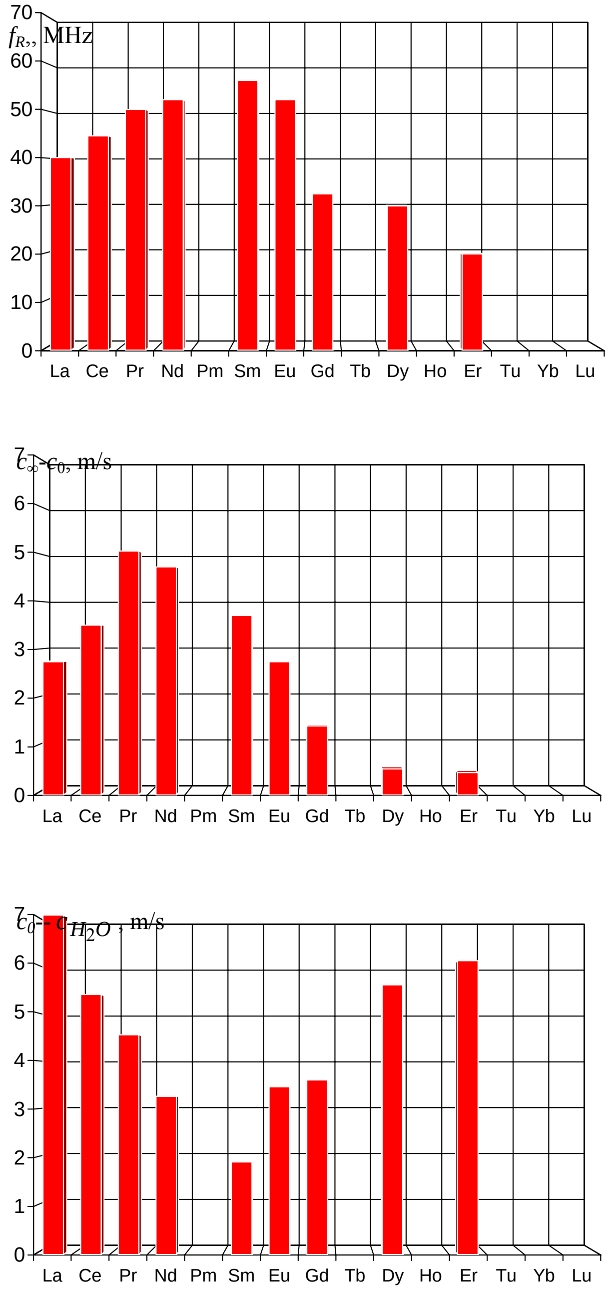

Fig. 1. **Relaxation parameters for lanthanide nitrate solutions at 20°C across the series**

such as the lanthanides. Thus the relaxation frequency f_R will depend mainly on k_{23}. Dependence of f_R against a cation atomic number cannot be explained simply in terms of changes in a cation size. The high electric field strength at the surface of the cation must significantly influence the solvent molecules or the solvent structure in an immediate vicinity of the ion. In the absence of a complete undestanding of the structure and how it is influenced by the presence of ions, it is convenient to regard such structural changes as changes in an average cation coordination number. The variation of f_R is consistent with this assumption that for cations toward the center of the series, where two (or more) coordination numbers become equally probable, the change from one coordination number to another occurs more readily.The rate constants k_{23} and k_{32} refer to the forvard and backward rates for the exchange of anion and water between the first and second coordination spheres of the cation. It is not unreasonable to suppose that the transition state for such a process will involve a coordination number change in both coordination spheres. Consequently, an increase in both $k_{23}$and k_{32} and hence f_R, is anticipated if a change in a coordination number occurs more readily. The smooth variation of f_R across the series suggests that the change in an average coordination number occurs gradually.

The magnitude of the ultrasound velocity dispersion c_∞-c_0 also describes nonlinear dependence across the series. Using the interpretation that the dispersion in the lanthanide nitrate solutions is caused by an association process with formation of inner sphere complexes $[LnNO_3]_{aq}^{2+}$, then a magnitude of an ultrasound dispersion may be a quantity of complexation. As seen, the lowest dispersion is observed for erbium nitrate, so in this solution exists the minimum of inner sphere substitutions, then the amount of inner complexes increases through Dy, Gd, Eu, Sm, Nd and reaches a maximum on Pr, and later decreases to La.

The value c_0-c_{H_2O} shows minimum in the solutions of $Sm(NO_3)_3$. The radii of rare earth ions decrease from La to Lu (lanthanide contraction). As a consequence, the surface change density on the rare earth ion increases from La to Lu, and this shoud give rise to an increase in the extent of the ion-dipole interactions between the rare earth ion and water molecules around the RE^{3+}. The result from this radius decrease is that the total amount of ionic hydration increases from La to Nd and from Tb to Lu. Spedding et al. [3-4] have proposed that the inner sphere hytration number of the ions of the heavy rare earths (Tb-Lu) are smaller by one than for the light rare earths (La-Nd), and that between Pm and Gd exist as intermediate forms in aqueous solutions. Authors [5] had confirmed the fact that in the case of rare earth ions the hydration process has an electrostatic character. According to their theoretical model the local electrostatic field is equivalent to an electrostriction pressure. The local density around an Ln^{3+} ion was obtained from the state equation of pure water at high preasure. The hydration numbers obtained by this model agree with the experimental results and show a progressive diminution of one molecule of water from La^{3+} to Lu^{3+}.

From simple geometrical considerations it also follows that a change in the lanthanide aquo-ion structure can occur [6]. If one accepts the radius of the water molecule as equal to $1{,}38.10^{-8}$m and the octahedral radii of lanthanide(III) ions according to Ahrens and Pauling, it follows that:

$$\frac{r_{Pm^{3+}}}{r_{H_2O}}=0{,}740,\ \frac{r_{Sm^{3+}}}{r_{H_20}}=0{,}732\ \text{(Ahrens)},$$

$$\frac{r_{Gd^{3+}}}{r_{H_2O}}=0{,}739,\ \frac{r_{Tb^{3+}}}{r_{H_2O}}=0{,}725\ \text{(Pauling)}.$$

Now the minimum radii ratio is 0, 732 and this is passed at Sm^{3+} according to Ahrens or at Tb^{3+} according to Pauling.

Hence, our ultrasound velocity measurements in lanthanide nitrate solutions indicate the variation of the amount of complexes $[LnNO_3]^{2+}$ and the interaction between individual ions RE^{3+} and water molecules across the series.

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Lantanoidų nitratų vandeninių tirpalų relaksacinių parametrų kitimas lantanoidų eilėje

Reziumė

Tyrinėta, kaip lantanoidų nitratų vandeninių tirpalų relaksacinis dažnis, dispersijos dydis ir žemo dažnio ultragarso greičių tirpale bei tirpiklyje skirtumai priklauso nuo elemento eilės numerio. Nustatyta, kad relaksacinis dažnis pradžioje didėja, pasiekia maksimumą ties Sm, po to sunkiesiems elementams mažėja. Greičių skirtumas tirpale ir tirpiklyje taip pat yra mažiausias $Sm(NO_3)_3$ tirpalui. Tai aiškinama koordinacinio skaičiaus kitimu lantanoidų eilėje. Didžiausias dispersijos dydis nustatytas $Nd(NO_3)_3$ tirpalui, mažiausias - $Er(NO_3)_3$ tirpalui. Kadangi ultragarso greičio dispersiją sukelia relaksacinis procesas, kurio priežastis yra lantanoidų jonų ir NO_3^{-1} asociacija, daroma išvada, kad daugiausia vidinių kompleksų esti $Nd(NO_3)_3$ tirpaluose.