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Investigation of the hydration phenomenon in 3-1 electrolyte solutions

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Abstract

The apparent molar compressibilities φ_K of aqueous 3-1 electrolyte solutions have been determined from ultrasound velocity and density measurements at 20° C. The values of φ_K have been extrapolated to infinite dilution, and the total hydration numbers *Zo* for investigated solutions were estimated from the data $\varphi_K{}^0$. A correlation between the hydration and the atomic number of elements of the Periodic Table are discussed. Non monotonic variation of the hydration number was obtained for lanthanide nitrate solutions across the series. The lower hydration numbers values for the nitrate solutions, compared with chloride and bromide, are interpreted by the formation of inner sphere complexes $[LnNO_3]^{2+}$.

Keywords: apparent molar compressibility φ_K, hydration number, structural properties.

Introduction

The hydration of metal ions is a fundamental phenomenon in aqueous solutions. Metal ions play an important role in chemical and biological systems and the hydration of ions in these systems is a key issue to understand the chemical and dynamical processes. Lanthanide (III) ions are often used as structural probes in biological system to obtain some information on the binding sites of the Ca^{2+} ion. Terbium (III) and europium (III) are used as luminescent probes, while gadolinium (III) is an effective proton relaxation agent. Also, their use in technology is growing rapidly as their properties are more fully explored.

For the last decade, solvation processes of metal ions have been extensively studied using various techniques [1-6]. Each of methods (absorption and luminescence spectroscopy, NMR, etc.) require special conditions: temperature, pressure, concentration, etc. For example, X-ray experiments require high concentration of salt and there is the question of whether the results would be applicable for diluted solutions.

Despite a large amount of works, there are no strict structural models of electrolyte solutions, nor well-substantiated parameters of ion hydration spheres [7]. Dissolution of an electrolyte in water is accompanied by electrostriction of the solvent under the action of the electrostatic field of newly formed ions. Change in the compressibility of the solution serves as a measure of ions hydration in ultrasound methods. So, the application of acoustic methods have showed extensive possibility in the fields of solution chemistry, particularly, on study of structural properties of salts.

In this work the authors undertook a systematic study of the apparent molar compressibility of the 3-1 electrolyte solutions and a correlation between the hydration and the atomic number of elements of the Periodic Table.

Results and discussion

The apparent molar compressibilities φ_K of the electrolyte solutions have been determined from ultrasound velocity and density measurements at 20°C. The ultrasound velocity measurements were carried out with ultrasonic interferometers [8-9] at the frequencies 3÷15 MHz, the measurement uncertainties were (3÷15) cm/s. The better accuracy is obtained by the ultrasonic-laser interferometer [10]. In the case of chloride and bromide solutions, where there is no relaxation, higher frequencies were selected in order to minimize the influence of diffraction and to achieve a higher accuracy. In nitrate solutions the relaxation was observed and it was necessary to use low frequencies outside the relaxation region. In this case experimentally determined diffraction corrections were introduced. The density was measured by the 25 ml capillary pycnometer with the uncertainty $(0.3\div1)\cdot10^{-4}$ g/cm^3. All other experimental details were described in our earlier works.

The structural properties of the solutions, say the coefficient of adiabatic compressibility β and the apparent molar compressibility φ_K, have been calculated by means of the following relations:

$$\beta = 1/pc^2, \tag{1}$$

$$\varphi_K = 1000/C\rho_0 \times (\rho_0\beta - \rho\beta_0) + \beta_0 \times M_2/\rho_0, \tag{2}$$

where *c* is the ultrasound velocity in solutions, *C* is the molar concentration expressed in mol/l of the solute, ρ_0 and ρ are densities of the solvent and solutions, M_2 is the molecular weight of the salt, β_0 is the adiabatic compressibility of the solvent.

Scandium, Yttrium and Lanthanum nitrate solutions

The dependence of apparent molar compressibility φ_K on the square-root of concentration of $Sc(NO_3)_3$, $Y(NO_3)_3$ and $La(NO_3)_3$ solutions is shown in Fig.1. Scandium, yttrium and lanthanum belong to III B group of elements within the Periodic Table, their outer electron configurations are: Sc-3d^{1}4s^2, Y-4d^{1}5s^2 and La-5d^{1}6s^2. As the valency of cations is the same and the anion is kept constant, the dependence of variation of apparent molar compressibility can be related to the properties of the cation.

According to the Masson theory [11], φ_K is a linear function of $C^{1/2}$ and the expression is

$$\varphi_K = \varphi_K{}^0 + S_K C^{1/2}, \tag{3}$$

where φ_K^0 is the apparent molar compressibility of the infinitely diluted solution and S_K is the slope of the dependency. S_K can be theoretically calculated, and for 3-1 electrolytes $S_K=92.4\times10^{-15} m^5 \cdot l^{1/2}/N \cdot mol^{3/2}$.

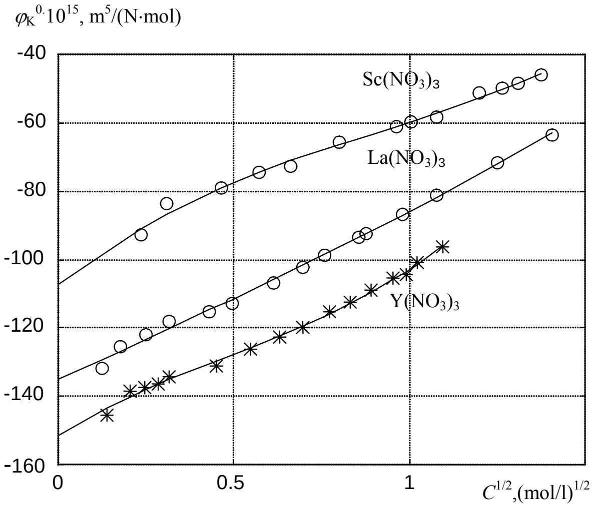

Fig.1. **Variation of apparent molar compressibility**

The experimental slopes for all studied solutions are much less than the theoretical slope. Deviation from the theoretical slope is due to the ion-solvent interactions. In the case of aqueous solutions of electrolytes the major effect of ion-solvent interaction is the phenomenon of hydration and it involves the attachment of the certain number of water molecules to the positive and negative ions. In this investigation the influence of anion is the same, therefore compressibility reflects only cation-solvent interaction. The values of φ_K have been extrapolated to infinite dilution and from the data $\varphi_K{}^0$ the total hydration numbers Z_0 for investigated solutions were determined from the equation:

$$\varphi_{K^0} = Z_0 V_1^0 \beta_0 , \tag{4}$$

where $V_1{}^0$ is the molar volume and β_0 is the adiabatic water compressibility. The values of φ_K^0 and Z_0 for investigated nitrates of the III B group of elements are listed in Table 1.

Table 1. **The data of φ_K^0 and Z_0 for nitrates in aqueous solutions of the III B group of elements**

Electrolyte	$\varphi_K^0 \cdot 10^{15}$, m^5/N·mol	Z_0
Sc(NO$_3$)$_3$	-98.6	11.9
Y(NO$_3$)$_3$	-151.6	18.4
La(NO$_3$)$_3$	-140.0	17.0

The trivalent cations not only influence the water molecules in the first hydration sphere but also diminish the compressibility of the farther water layers. So, the hydration numbers determined from ultrasound measurements data reflect not only the influence of ions on the first hydration layer but also the total change in compressibility due to solute- solvent interactions. Therefore, the hydration numbers determined from compressibility are higher than those obtained by other methods, for example spectroscopic or X-ray methods.

In common case two factors have influence on the compressibility: the hydration and charge density. Ionic radii in aqueous solutions are following: $r_{Sc}{}^{3+}$=53 pm, $r_Y{}^{3+}$=101 pm and $r_{La}{}^{3+}$=122 pm [12]. Consequently the ionic potential and charge density at the surface on these ions decreases substantially on going from Sc(III) to La(III). As seen from Table I, the dependence of the hydration number Z_0 is non-linear, so the ion-solvent interaction cannot be explained simply by the electric field strength. This may be due to individual chemical nature of the investigated cations. One of them is the different coordination number of the cations, e.g. the primary hydration sphere increases across the III B group of elements: Sc^{3+}-6, Y^{3+}-8, La^{3+}-9 [13].

Aluminum, Gallium and Indium nitrate solutions

The values of φ_K^0 and Z_0 for investigated nitrates of the III A group of elements are listed in Table 2.

Table 2. The data of φ_K^0 and Z_0 for nitrates in aqueous solutions of the III A group of elements

Electrolyte	$\varphi_K^0 \cdot 10^{15}$, m^5/N·mol	Z_0
Al(NO$_3$)$_3$	-131.3	15.8
Ga(NO$_3$)$_3$	-124.6	15.2
In(NO$_3$)$_3$	-81.9	10

The variation of the hydration number Z_0 against the parameter z^2/r (z is the valency of metal, r is the radius of the cation) characterising electrostatic interaction between cation and dipoles of water molecules is shown in Fig. 2. As seen, the hydration number Z_0 increases linearly against parameter z^2/r for the III A group of elements: Al^{3+}, Ga^{3+} and In^{3+} differently than for the III B group of elements: Sc^{3+}, Y^{3+} and La^{3+}. So, the acceptor donor interaction between cation and dipoles of the water molecules must be accounted. The nature of the cation-water bond depends on the electron affinity energy of the cation. The comparison of this energy for investigated cations shows that all the III group metal cations attach the electron more actively than ion H_2O^+, and hydration of the cation involves the transference of the electron density from water molecules to the cation, therefore the cation-water bonds have the covalentic character. The intensity of the cation-water interactions depends on the electron configuration of the cation. All the III group of elements of of the Periodic Table can be devided in the two groups: the cations of the „18 electron“ configuration (Ga^{3+}, In^{3+}) and the cations of the inertion gas electron configuration (Al^{3+}, Sc^{3+}, Y^{3+} and La^{3+}). The differences in outer filled orbitals cause a polarization capacity of the cation. The polarization of the cations with the filled outer level np^6 is less than for the cations with the filled level nd^{10}. Ga^{3+} and In^{3+} poliarize water molecules more actively than cations: Al^{3+}, Y^{3+}, La^{3+} and form outer sphere aqua complexes with increasing the relative volume, therefore the adiabatic compressibility of the solution increases and the hytration number of the cations decreases. The location of empty electronic levels also has the influence for the cation-water interaction. The cations with the dense empty levels (Y^{3+}, La^{3+}) can attach more ligands than the cations with rare

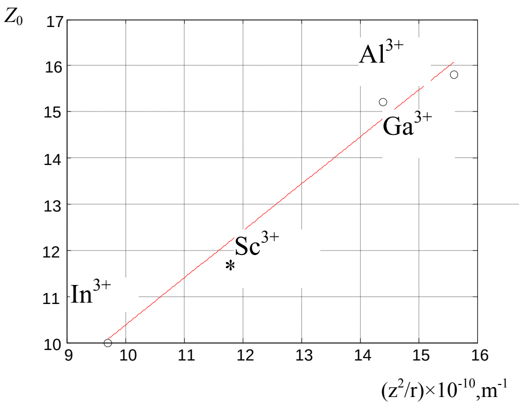

Fig.2. **Dependence of hydration number against parameter z^2/r.**

empty levels (Al^{3+}, Ga^{3+}, and In^{3+}). That causes the magnitude of the coordination number of the element: Al^{3+}, Ga^{3+}, In^{3+} - 6, Y^{3+}-8, La^{3+}-9. Solvent exchange around some diamagnetic trivalent ions has been studies by NMR experiments [14]. The smaller Al^{3+} and Ga^{3+} , being rather crowded, are easily willing to expel a solvent molecule from their first coordination sphere at the transition state, whereas Sc^{3+} and In^{3+}, much larger, will more readily host a seventh molecule around them, at least partially , in forming the activated complex. So, the of water exchange at $Al^{3+}_{(aq)}$, $Ga^{3+}_{(aq)}$, and $Sc^{3+}_{(aq)}$, $In^{3+}_{(aq)}$ is characterized by dissociative **D**, **D**, and associative **A** mechanisms, respectively. Trivalent cation Sc^{3+} exists in a water solution as $[Sc(H_2O)6]^{3+}$ and may be put on the line in Figure 2. The polarization capacity has influence also on hydration of the III B group elements. The deep empty electronic level $3d^{10}$ increases the polarization capacity of cation Sc^{3+} in comparison of La^{3+} and Y^{3+}, and the formation of outer shpere complexes about cation Sc^{3+} decreases its hydration number [15].

Lanthanide nitrate solutions

Elements with an atomic number between 57 (lanthanum) and 71 (lutetium) are included in the lanthanide series. These elements have the gaseous electron configuration of $[Xe]4f^n5d^06s^2$, La($[Xe]4f^05d^16s^2$, Ce($[Xe]4f^15d^16s^2$), Gd($[Xe]4f^75d^16s^2$) and Lu$[Xe]4f^{14}5d^16s^2$ with the electron configuration of Gd reflecting the stability of the half filled shell. The coordination of the Ln^{3+} ions in aqueous solutions is certainly one of the most controversial questions of lanthanide chemistry. It is as yet still unclear whether a coordination change occurs along the series or not, despite the large number of studies devoted to that problem. Our studies on the hydration of lanthanide nitrates in aqueous solutions indicate a change of hydration number across the series. The results of calculated apparent molar compressibility φ_K at infinite solutions for lanthanide nitrates and hydration number Z_0 are given in Table 3.

Table 3. **The data of φ_K^0 and Z_0 for lanthanide nitrates**

Electrolyte	$\varphi_K^0\cdot10^{15}$, m^5/N·mol	Z_0
$La(NO_3)_3$	-140	17.0
$Ce(NO_3)_3$	-138	16.8
$Pr(NO_3)_3$	-132	16.1
$Nd(NO_3)_3$	-126	15.3
$Sm(NO_3)_3$	-184	22.4
$Gd(NO_3)_3$	-142	17.3
$Dy(NO_3)_3$	-170	20.7
$Er(NO_3)_3$	-190	23.1

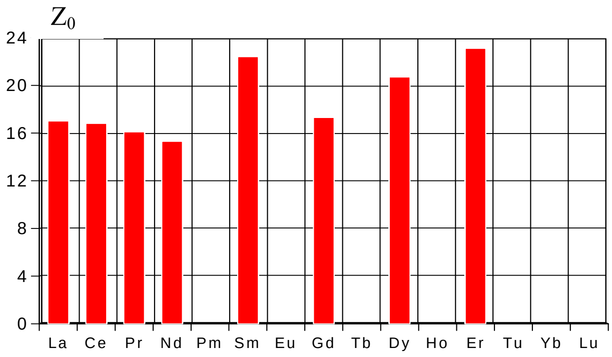

Fig.3. **Hydration numbers for lanthanide nitrate solutions at 20°C across the series**

The variation of the hydration number Z_0 for lanthanide nitrate solutions across the series is shown in Fig. 3. The progressive filling of the 4*f* orbitals from La^{3+} to Lu^{3+} is accompanied by a smooth decrease in ionic radius with increase in atomic number as a consequence of the increasingly strong nuclear attraction for the electrons in the diffuse *f* orbitals. These orbitals are shielded by the surrounding filled 5s and 5*p* orbitals, leading to very small crystal field splitting in the lanthanide complexes. Thus, the coordination properties of the Ln^{3+} ions mainly depend upon the steric and electrostatic nature of the ligands. Hence, for solvents without covalent bonding like water, ion-solvent forces can be well represented by simple Coulomb and van der Waals terms. The radii of the lanthanide ions decrease from La to Lu (lanthanide contraction). As a consequence, the surface change density on the lanthanide ion increases from La to Lu, and this should give rise to an increase in the extent of the ion-dipole interactions between the Ln^{3+} and water molecules around the lanthanide ions. The primary hydration sphere number for the lighter ions (La^{3+}-Nd^{3+}) is nine, and the heavier ions (Gd^{3+}-Lu^{3+}) are predominantly eight-coordinate species. The ions Sm^{3+}-Eu^{3+} exist in equilibrium between nine-and eight-coordinate [16]. Our results also show a change of the hydration number in the lanthanide series: e.g. from La to Nd the hydration numbers are almost constant and in Gd-Lu range the hydration number increases. These results indicate that the increase in the number of water molecules affected by the increasing electric field of the cation exceeds the decrease of the amount of the coordinated water molecules. The inner-sphere hydration number change is probably the main factor explaining the discontinuity (the so-called ”gadolinium break”) observed in the middle of the series (in fact, the break occurs at Sm^{3+}, Eu^{3+} or Gd^{3+}, depending which property is examined) [17].

The difference of ultrasound velocity values $c\text{-}c_{water}$ also describes nonlinear dependence across the series and shows minimum in the solutions of $Sm(NO_3)_3$ (Fig.4).

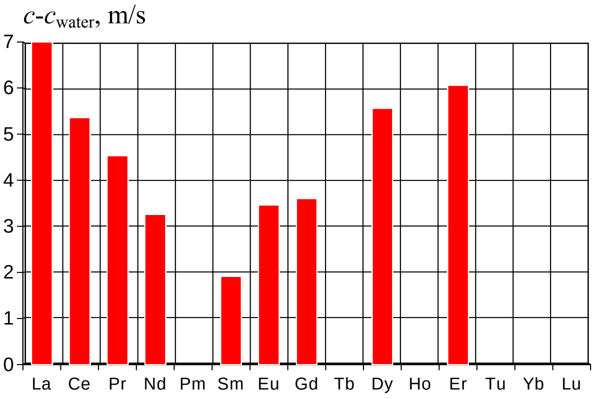

Fig.4. **Dependence of ultrasound velocity differencies $c\text{-}c_{water}$ against of atomic number** .

From simple geometrical considerations it also follows that change in the lanthanide aqua-ion structure can occur 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 [12.] Then:

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

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

Now the minimum radii ratio is 0,732 and this is observed at Sm^{3+} according to Ahrens or at Tb^{3+} according to Pauling. So, ultrasound velocity measurements in lanthanide nitrate solutions indicate the structural properties of these solutions and the result for Sm^{3+} corresponds indeed to an equilibrium between nine-and eight-coordinate.

Scandium, Yttrium and Lanthanum chloride solutions

Fig. 5 shows the dependence of the apparent molar compressibility on the square root of concentration in $ScCl_3$, YCl_3 and $LaCl_3$ solutions. The values of φ_K^0 and Z_0 for investigated chlorides solutions are presented in Table 4. As seen, the hydration numbers are higher for chloride solutions as compared with nitrates respectively. As mentioned previously [10], this is due to the formation of inner-sphere complexes by the nitrate ion which reduces the number of water molecules in the first hydration layer and which at the same time reduces the electric field of the cation, thereby reducing also the influence of the cation on further water molecules. In outer sphere the complexes of metal and ligand are separated by one or more water molecules but no hydration separating the cation and anion exists in inner sphere complexes. The existence of both outer and inner sphere complexes in polyvalent electrolyte salts solutions has been determined by different techniques, for example, Choppin using NMR method [18] has summarized the data on the lanthanide nitrates, concluding that 27% $[LaNO_3^{2+}]_n$ inner sphere complexes exist in $La(NO_3)_3$ water solution.

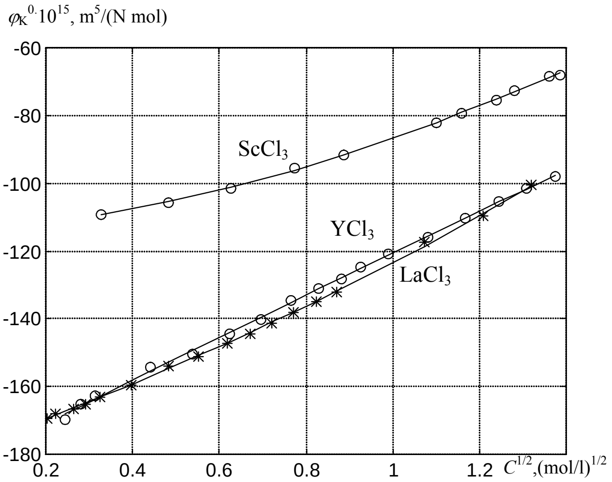

Fig.5. **Dependence of apparent molar compressibility on the square root of concentration in $ScCl_3$, YCl_3 and $LaCl_3$ solutions**

Table 4. **The data of φ_K^0 and Z_0 for investigated chlorides**

Electrolyte	$\varphi_K^0\cdot10^{15}$, m^5/N·mol	Z_0
$ScCl_3$	-113.4	14.3
YCl_3	-151,6	22.4
$LaCl_3$	-168.0	20.8

In the case of $ScCl_3$ solution the smaller value of hydration number Z_0 has been determined. This allow us to draw the conclusion that the small amounts of the inner-sphere chloride complex may occur.

Lanthanum bromide solution

To obtain a more detailed insight into the hydration phenomenon of lanthanum we have studied also the $LaBr_3$ solutions. Fig. 6 shows the dependence of apparent molar compressibility on the square root of concentration in $LaBr_3$ solution. The hydration number for lanthanum bromide was obtained Z_0=20.1, i.e. is larger than for lanthanum nitrate solution (Table 3). No dispersion was found for solutions of $LaBr_3$ and $LaCl_3$ in the frequency

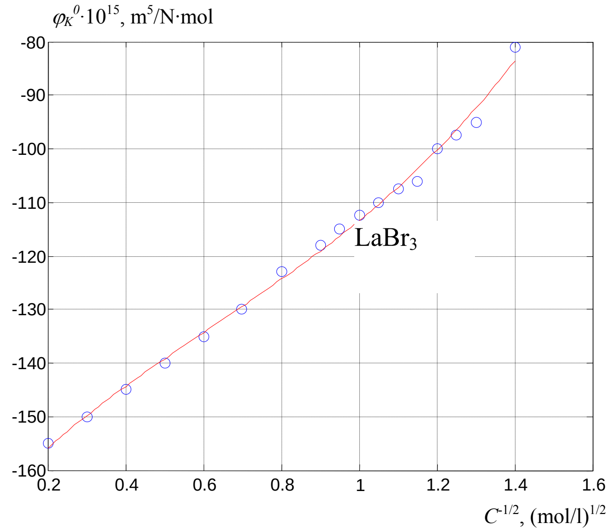

Fig. 6. **Dependence of apparent molar compressibility on the square root of concentration in $LaBr_3$ solution**

range of 1-240 MHz in our earlier investigation. The absence of relaxation for these solutions suggests that in these systems cations La^{3+} and Cl^{-1} or Br^{-1} are separated by solvent molecules. Moreover, the Br^{-1} is a weakly complexing anion, allow us to made the conclusion than compound La-Br does not form any inner sphere complexes in dilution aqueous solutions.

In the work [19] the structure of molten $LaBr_3$ was investigated by X-ray diffraction and molecular dynamics simulations. It was found that short range structure of the molten $LaBr_3$ is very similar to that of molten $LaCl_3$ except for some features such as interionic distances based on the difference of anion size. Concentrated aqueous solutions of lanthanum chloride and bromide were investigated by X-ray, EXAFS and Raman spectroscopy [20]. The results indicate the existence of nine water molecules in the first solvation shell of the lanthanum cation and suggest that only one kind of aggregate is observed in these solutions. Our ultrasonic studies on the hydration of the lanthanum salts indicate the hydration number of lanthanum nitrate is lower than those obtained for chloride and bromide solutions which is due to the formation of inner sphere complexes by nitrate anion.

Conclusions

The results presented above demonstrate the possibility of the ultrasonic method in the study of the hydration phenomenon in electrolyte solutions. The total hydration numbers Z_0 for 3-1 electrolyte solutions have been determined. A correlation between the hydration and the atomic number of elements of the Periodic Table of III group are presented. For the case of nitrates the hydration number Z_0 increases linearly against parameter z^2/r for the elements: Al^{3+}, Ga^{3+}, In^{3+}, and Sc^{3+}, while elements Y^{3+} and La^{3+} behave diverse. No monotonic variation of the hydration number was obtained for lanthanide nitrate solutions across the series. The differences between the hydration numbers of nitrates and chlorides of the elements of III B group are explained by the structural peculiarity of investigated solutions. The lower hydration numbers values for the nitrate solutions, compared with chloride and bromide, are interpreted by the formation of inner sphere complexes $[LnNO_3]^{2+}$.

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Hidratacinių reiškinių tyrimas 3-1 elektrolitų tirpaluose

Reziumė

Pateikiami 3-1 elektrolitų vandeninių tirpalų tariamieji moliniai spūdumai φ_K^o, ekstrapoliuoti begaliniam praskiedimui. Šie duomenys panaudoti tirpalų hidrataciniams skaičiams Z_0 nustatyti. Nagrinėjama hidratacinio skaičiaus priklausomybė nuo elemento eilės numerio periodinėje elementų sistemoje. Nitratų tirpaluose nustatyta tiesinė Z_0 priklausomybė nuo dydžio z^2/r (z - metalo valentingumas, r - katijono kristalografinis spindulys) katijonams Al^{3+}, Ga^{3+}, In^{3+} ir $Sc^{3+.}$. Tirta elementų elektroninės struktūros įtaka katijonų ir tirpiklio molekulių sąveikai. Nustatytas lantanoidų nitratų tirpalų hidratacinio skaičiaus kitimas La-Lu eilėje. Sugretinamos IIIB grupės elementų nitratų ir chloridų vandeninių tirpalų hidratacinės savybės. Konstatuojama, kad nitratų tirpaluose esama vidinių kompleksų, kai anijonas įeina į katijono vidinį hidratacinį apvalkalą.

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