A study of ion-solvent interaction in aqueous Al(III), Y(III) and La(III) nitrate solutions

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1. Introduction

Application of acoustics methods have showed extensive possibilities in the field of solution chemistry, particularly on study of structural properties of salts such as their compressibility and volumetric parameters. It is also possible to estimate the hydration numbers of electrolytes from the molar compressibility value at infinite dilution.

The apparent molar compressibilities φ_K of aqueous solutions of aluminum, yttrium, and lanthanum nitrates have been determined from ultrasound velocity and density measurements at $20^{\circ}C$. The measurements were carried out with an ultrasonic interferometer and the density was measured by a capillary pycnometer. All other experimental details were described in our earlier works [1-3]. In the present work the anion is common, so the dependence of variation with concentration of the different parameters of the solutions of these salts can be related to the properties of the cation. Investigated cations are representatives of inert-gas electron configuration, and in this respect it is interesting to compare the Al(III), Y(III), and La(III) in common systems.

2. Results and discussion

The dependence of the apparent molar compressibility φ_K on the square-root of concentration of $Al(NO_3)_3$, $Y(NO_3)_3$ and $La(NO_3)_3$ solutions is shown in Fig.1.

According to the Masson theory [4], φ_K is linear function of $C^{1/2}$ and on is given by

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

where φ_K^0 is the apparent molar compressibility of the infinitely diluted solution and S_K is the slope. S_K can be theoretically calculated for each valency type and for 3-1 electrolytes $S_K = 92.4 \times 10^{-15}\,\mathrm{m^5.l^{1/2}/N\cdot mol^{3/2}}$. 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 φ_K^0
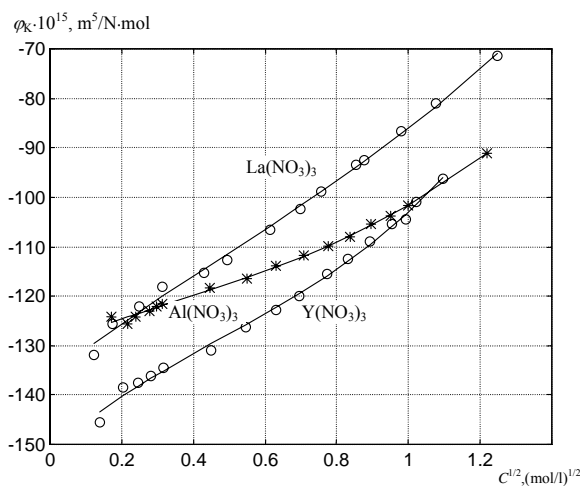

Fig.1. **Variation of apparent molar compressibility**

the total hydration numbers Z_0 for investigated solutions were determined:

$$\varphi_K^0 = Z_0 V_1^0 \beta_0, \tag{2}$$

where V_1^0 is the molar volume and β_0 is the adiabatic water compressibility. Thus the hydration numbers were obtained: $Z_0 = 15,8$, $18,4$ and $16,8$ for aluminum, yttrium, and lanthanum nitrates respectively. Three valency cations not only influence the water molecules in the first hydration sphere, but also reduce 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 the 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: $r_{Al}^{3+} = 53$ pm, $r_Y^{3+} = 90$ pm and $r_{La}^{3+} = 122$ pm [5]. Consequently, the ionic potential and charge density at the surface on these ions decreases substantially on going from Al(III) to La(III). The variation of apparent molar compressibility at concentration 0.4 mol/l versus parameter z^2/r (z-valency of metal, r-radius of cation) is shown in Fig. 2.

The value of z^2/r characterize the ion- dipole interaction between Al^{3+}, Y^{3+}, La^{3+} and water molecules around these cations. As seen, the dependence of apparent molar compressibility against a parameter z^2/r is nonlinear, so the ion-solvent interaction cannot be explained simply by the electric field strength. Fig.3 shows non-monotonically dependence of the $\varphi_K{}^0$ versus an atomic number N of elements in the periodic system. This may be due to individual chemical nature of the investigated cations [2].
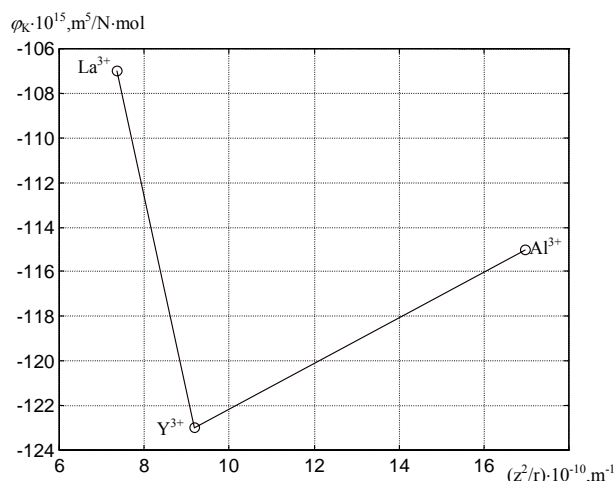

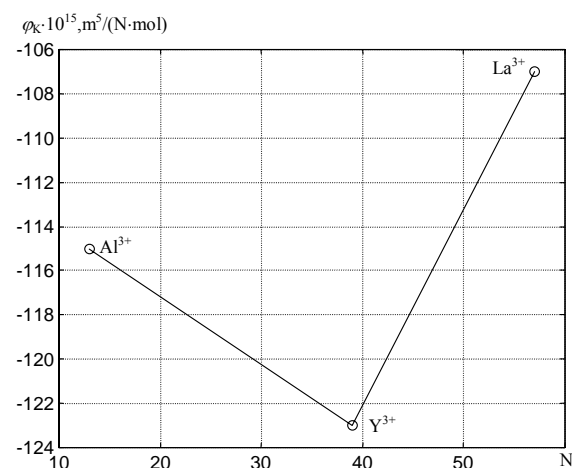Fig.2. **Dependence of apparent molar compressibility at concentration 0.4 mol/l versus parameter z^2/r**

Fig.3. **Variation of apparent molar compressibility at infinite dilution versus an atomic number N of element in the periodic system**

In the region of diluted solutions the apparent molar volume has proved to be useful in studying the ion-solvent interactions. At infinite dilution $\varphi_V = \varphi_V{}^0 = \overline{V}_2{}^0$, where $\overline{V}_2{}^0$ is the partial molar volume. The partial molar volume for 3-1 electrolyte solutions may be given by the expression:

$$\varphi_V{}^0 = \overline{V}_2{}^0(Me(NO_3)_3) = \overline{V}_2{}^0(Me^{3+}) + 3\overline{V}_2{}^0(NO_3)^{-1}, \qquad (3)$$

where $\overline{V}_2{}^0(Me^{3+})$ and $\overline{V}_2{}^0(NO_3)_3$ are the ionic partial molar volumes of the cations Me^{3+} and the anion NO_3^{-1} respectively. From our experiments $\varphi_V{}^0 = 43.0$ cm³/mole for $Al(NO_3)_3$ [1], $\varphi_V{}^0 = 34.2$ cm³/mole for $Y(NO_3)_3$ and $\varphi_V{}^0 = 48.9$ cm³/mole for $La(NO_3)_3$ [3]. The partial molar volume for NO_3^{-1} is 34.4 cm³/mol [6]. Using these values, the partial molar volumes were calculated for investigated ions: $\overline{V}^0{}_{Al(III)} = -38.9$ cm³/mole, $\overline{V}^0{}_{Y(III)} = -69.0$ cm³/mole and $\overline{V}^0{}_{La(III)} = -54.3$ cm³/mole. The absolute partial molar volume of aqua ions in solution, in relation with their coordination number and their ionic radii, can be estimated using a semi-empirical model developed by Swaddle [7]:

$$\overline{V}^0{}_{abs.} = 2.523 \times 10^{-6}(r+238.7)^3 - 18.07 \times n - 417.5 \times z^2/r + 238.7, \qquad (4)$$

where r is the effective ionic radius in *pm* and n is the coordination number of M^{z+} (n is known from NMR or X-ray diffraction studies of solutions). The number of solvent molecules bound in the inner hydration shell is not exactly known, but is likely to be 9 for La(III), 8 for Y(III) and 6 for Al(III). Thus, the absolute partial molar volumes are: $\overline{V}^0{}_{abs.Al(III)} = -58.68$ cm³/mol, $\overline{V}^0{}_{abs.Y(III)} = -66.4$ cm³/mol and $\overline{V}^0{}_{abs.La(III)} = -54.6$ cm³/mol.

The volume change $\Delta V^0{}_{Me(III)}$ for water caused by the ion-solvent interactions can be expressed as $\Delta V^0{}_{Me(III)} = \overline{V}^0{}_{Me(III)} - V_{int}$, where V_{int} is the intrinsic volume occupied by one mole of the ions in the solution. The dependence of $\Delta V^0{}_{Me(III)}$ versus an atomic number N in the periodic elements system is shown in Fig. 4.

The nonlinear dependence $\Delta V^0{}_{Me(III)}$ versus an atomic number of element may be caused by various reasons. One of
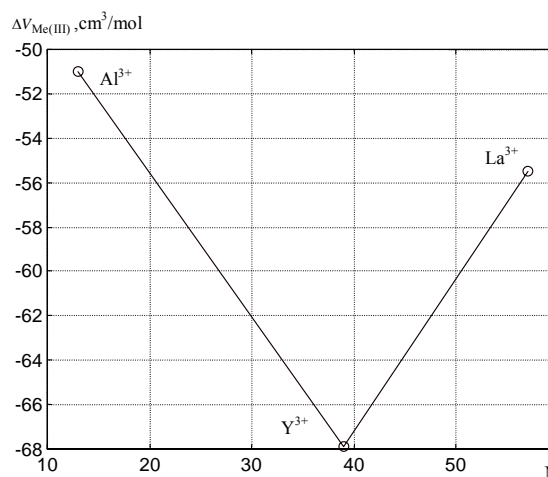

Fig.4. **Dependence of the volume change $\Delta V^0{}_{Me(III)}$ versus an atomic number N of element in the periodic system**

them is the different coordination number of the investigated ions. The volume difference for the two coordinances, corresponding to the dissociation of one water from $[Ce(H_2O)_9]^{3+}$ to form $[Ce(H_2O)_8]^{3+}$, has been calculated using the model developed by Swaddle [7]. This volume is +12.8 cm^3/mol and agrees well with the reaction volume ΔV^0=10.9 cm^3/mol determined experimentally by variable-pressure UV spectroscopy at 295 nm [8]. Solvent exchange around some diamagnetic trivalent ions has been studied by NMR [9]. The activation volume $\Delta V^{\#}$ for solvent exchange on $Al(H_2O)_6^{3+}$ was determined +5.7 cm^3/mol. The sign of $\Delta V^{\#}$ is a diagnostic of the activation step: positive for bond stretching or negative for bond making. So, water exchange mechanism for Al^{3+} is characterized by dissociative interchange I_d mechanism. Moreover, for Al^{3+} in water the hydrolysis is kinetically important. The overall rate constant will be therefore the sum of contributions from the two reaction paths: the water exchange on the hexaaqua species with the rate constant k_{ex} and on its hydrolysed form with the rate constant k_{OH}. The difference between both exchange paths may be due to strong electron donating capability of HO^{-1}. The strong bonding between the metal center and this group will weaken the remaining metal – water bonds. Hence, the aqua complex become more labile and dissociative activation is favorable (more positive activation volume). Limiting volume of activation for water exchange on aqua Y^{3+} cation is – 12.9 cm^3/mol [7], this is indicative of an associative activation mode. For this reason such a low value of $\Delta V^0{}_{Y(III)}$ is obtained (Fig. 4). The activation volumes $\Delta V^{\#}$ for water exchange on the heavy $Ln(H_2O)_8^{3+}$ ions are all negative and close to - 6 cm^3/mol and associative interchange I_a mechanism is proposed [10]. The $\Delta V^{\#}$ values should be regarded as the difference transfer to the first coordination sphere, and a positive contribution due to the difference in partial molar volume between the larger N+1 coordinated transition state and the N coordinated aqua ion. If this reaction volume is similar along the lanthanide series, then the water exchange on the ion La^{3+} occurs most probably by a I_d mechanism.

Conclusions

The acoustic and volumetric properties of aqueous solutions of aluminium, yttrium and lanthanum nitrates depend on the nature of the cation. The total hydration numbers Z_o were obtained: Z_o=15.8, 18.4 and 16.8 for Al^{3+}, Y^{3+} and La^{3+} nitrates respectively. Ion-solvent interaction cannot be explain simply by the electrostatic field theory. The assumption is made that nonlinear dependence of the volume change $\Delta V^0{}_{Y(III)}$ against an atomic number is conditioned by the different water exchange mechanism for individual

cations, e.g. the dissociative interchange I_d mechanism is for Al^{3+}, associative A for Y^{3+}, and I_d mechanism is proposed for La^{3+}.

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Jonų ir tirpiklio molekulių sąveikos tyrimas Al(III), Y(III) ir La(III) nitratų vandeniniuose tirpaluose

Reziumė

Remiantis ultragarso greičio ir tankio matavimais vandeniniuose aliuminio, itrio ir lantano nitratų tirpaluose, nustatytos tariamo molinio spūdumo φ_K koncentracinès priklausomybės. Ištirta, kad φ_K priklausomybių nuo koncentracijos $C^{1/2}$ polinkio koeficientai yra daug mažesni negu teorinè S_K reikšmė 3-1 elektrolitų tirpalams. Tai aiškinama jonų ir tirpiklio molekulių sąveika. Ekstrapoliavus φ_K, esant begaliniam praskiedimui, apskaičiuoti hidrataciniai skaičiai Z_0. Pateikiamos 0,4 mol/l koncentracijos tyrinètų metalų nitratų vandeninių tirpalų φ_K priklausomybès nuo dydžio z^2/r, apibūdinančio katijono ir vandens molekulių dipolių elektrostatinę sąveiką. Ši priklausomybė nėra tiesinė. Nustatyta taip pat parametrų φ_K ir $\Delta V_{Me(III)}$ (vandens tūrio pokyčio, veikiant katijonui) nemonotoniškas kitimas, didėjant metalo eilès numeriui N periodinèje elementų sistemoje. Išvadoje teigiama, kad $\Delta V_{Me(III)}$ nulemia skirtingi vandens molekulių mainų mechanizmai, vykstantys tarp molekulių, esančių akvakomplekse su išorinėmis.