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Investigation of the Ion-Solvent Interactions in Aqueous Solutions of Some 3-1 Electrolytes by Ultraacoustic Method

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Abstract: The apparent molar compressibilities φ_K of aqueous solutions of aluminium, yttrium and lanthanum nitrates have been determined from ultrasound velocity and density measurement at 20° C. The values of φ_K have been extrapolated to infinite dilution and from the data $\varphi_K{}^o$ the total hydration numbers Zo for investigated solutions were determinated. The partial molar volumes $\overline{V}{}^0{}_{Me(III)}$ were calculated for individual cations. The volume change $\overline{V}{}^0{}_{Me(III)}$ for water caused by ion-solvent interactions are discussed.

Keywords: acoustic and volumetric properties.

NOTATION

φ_K - apparent molar compressibility ($m^5/N{\cdot}mol$);
Z_o – total hydration number;
r – ionic radii (pm);
n – coordination number of the cation;
φ_V – partial molar volume (cm^3/mol);
$\overline{V}{}^0{}_{Me(III)}$ – partial molar volume of the cation (cm^3/mol);
$\Delta V^0{}_{Me(III)}$ – volume change for water caused by the ion-solvent interaction.

1. INTRODUCTION

Application of acoustics methods have showed extensive possibility in the fields 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 the electrolyte 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°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 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.

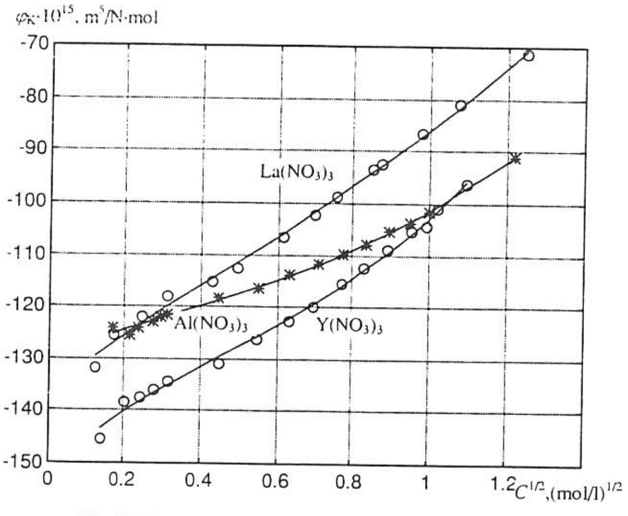

Fig.1. Variation of apparent molar compressibility with square root of concentration.

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

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

where $\varphi_K{}^0$ 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 $S_K=92.4\times10^{-15} m^5.1^{1/2}/N{\cdot}mol^{3/2}$. 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

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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:

$$\varphi_K{}^0 = Z_0 V_1{}^0 \beta_0, \qquad (2)$$

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 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: $r_{Al}{}^{3+}$=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 against parameter z^2/r (z-valency of metal, r-radius of cation) is shown in Fig. 2.

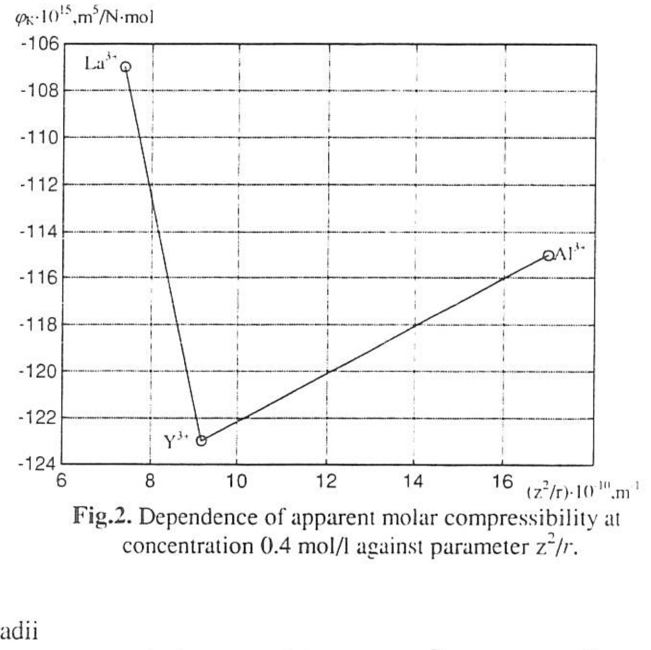

Fig.2. Dependence of apparent molar compressibility at concentration 0.4 mol/l against parameter z^2/r.

The value of z^2/r describes 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.

In the region of diluted solutions the apparent molar volume has proved to be useful in the 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 cations Me^{3+} and 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]. 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]:

$\overline{V}{}^0_{abs.} = 2.523\times10^{-6}(r+238.7)^3 - 18.07\times n - 417.5\times z^2/r+238.7$,(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 1 mole of the ions in the solution. The dependence of $\Delta V^0_{Me(III)}$ against an atomic number N in the periodic elements system is shown in Fig. 3.

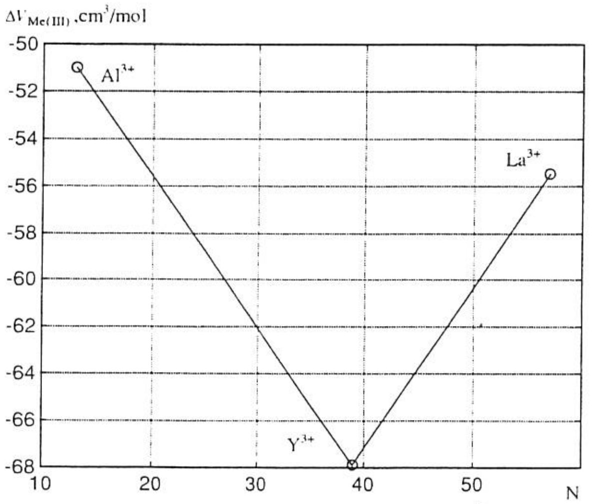

Fig.3. Dependence of the volume change $\Delta V^0_{Me(III)}$ against an atomic number N of element in the periodic system.

Nonlinear dependence $\Delta V^0_{Me(III)}$ against an atomic number of element may be caused by various reasons. One of 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 a 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 rate constant k_{ex} and on its hydrolysed form with rate constant k_{OH}. The difference between both exchange paths may be due to the strong electron donating capability of HO^{-1}. The strong bonding between the metal center and this group will weaken the remaining metal – water bonds. The aqua complex thus 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 low value of $\Delta V^0_{Y(III)}$ is obtained (Fig. 3). 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_a 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 associative A for Y^{3+}, and I_a mechanism is proposed for La^{3+}.

REFERENCES

1. **Илгунас В., Руткунене Д.**. Исследование парциальных мольных сжимаемостей ионов в водных растворах многовалентных электролитов. Акустический журнал, т.31, вып.1. 1985. С.58-61.
2. **Rutkūnienė D, Voleišienė B., Miglinienė** G. III grupės metalų nitratų vandeninių tirpalų makrosavybių analizė. Ultragarsas. Kaunas: Technologija. Nr. 2(32). 1999. P. 13-16.
3. **Miglinienė G., Voleišienė B**. Acoustical and volumetric properties of aqueuos solutions of ytrium and lanthanum nitrates. Chemija. Vilnius: Academia, 1999 (spaudoje).
4. **Stuehr J. and Yeager E.** in "Physicheskaya akustika", (Ed. By I. G. Michailov), 2(A), p.371, Moscow, 1968.
5. **Marcus Y.** Ionic radii in aqueous solutions. Chem. Rev. No. 88, pp. 1475-1498, 1988.
6. **Millero F. J.** in "Water and aqueous solutions", (Ed. By R. A. Horne), chapter 13, Willey-Interscience, New York, 1972.
7. **Swaddle T. W.** A model of the prediction of the molar volume effects accompanying changes in the primary ccrdination number of aqueous metal ions. Inorg. Chem. No. 22, pp. 2663-2665, 1983.
8. **Laurenczy G., Merbach A. E.** The reaction volume for the equilibrium between lanthanide (III) ennea-and octaaqua ions as a diagnostic aid for their water-exchange mechanisms. Helv. Chim. Acta. Vol. 71, pp. 1971-1973, 1988.
9. **Merbach A. E.** Use of high pressure kinetic studies in determining inorganic substitution mechanisms. Pure & Appl. Chem. Vol. 59, No. 2, pp.161-172, 1987.
10. **Helm L. and Merbach A. E.** Structure and dynamics of lanthanide (III) ions in solution: a neutron scattering contribution. Eur. J. Solid State. T. 28, pp. 245-250, 1991.