Partial molar compressibility of ions in aqueous solutions of some rare Earth chlorides and nitrates

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Introduction

For some time investigations of the state hydration of ions in water solvent have been concerned with the specific they exhibit in their interactions with water and the corresponding structural reaction the water in response to the presence of the ion. These structure changes are associated with electrostriction around the ion and changes of H-bonding equilibrium among water molecules.

Specifities in ion-solvent interaction can only be examined if the individual ionic contribution to the property can be evaluated. In the present paper we report measurement of the apparent molar compressibility φ_K^0 of some rare Earth chloride and nitrate in aqueous solutions and explore the dependence φ_K^0 of ionic charge and radius. The individual ionic contribution in the partial molar compressibility $\bar{K}_2^0$ of rare Earth chlorides in aqueous solutions has been estimated.

Results and discussion

The apparent molar compressibilities φ_K of aqueous solutions of some rare Earth nitrates and chlorides have been determined from ultrasound velocity and density measurements at 20^0C [1-2]. All measurements were made at the frequency of 6 MHz. The error of absolute ultrasound velocity measurements amounts to 0.001%. The density was measured by a capillary pycnometer of 0.01% accuracy. The concentration of cations was determined by EDTA titration using Xylenol Orange as the end-point indicator with deviation less than 1%. The structural properties of the solutions (the coefficient of adiabatic compressibility β and the apparent molar compressibility φ_K) have been calculated by means of the following relations [3]:

$$\beta = 1/\rho c^2, \qquad (1)$$

$$\varphi_K^0 = 1000/C\rho_0 \times (\rho_0\beta - \rho\beta_0) + \beta_0 \times M_2/\rho_0, \qquad (2)$$

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

Absolute errors of these calculated parameters are: $\Delta\beta = \pm 0.005 \cdot 10^{-11}$ m^2/N, and $\Delta\varphi_K^0 = \pm 0.1 \cdot 10^{-15}$ m^5/N·mol.

According to the Masson theory [3], φ_K is linear function of $C^{1/2}$ and is given by:

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

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 $S_K = 92.4 \cdot 10^{-15}$ m^5·l$^{1/2}$/N·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. The values of φ_K^0 for investigated solutions are listed in Table 1.

Table 1. **The data of φ_K^0 for studied 3-1 electrolyte solutions**

Electrolyte	$\varphi_K^0 \cdot 10^{15}$, m^5/N·mol
$La(NO)_3$	-140
$Ce(NO)_3$	-138
$Pr(NO)_3$	-132
$Nd(NO)_3$	-126
$Sm(NO)_3$	-184
$Gd(NO)_3$	-142
$Er(NO)_3$	-170
$LaCl_3$	-168
$Sm\ Cl_3$	-155
$GdCl_3$	-158
$TbCl_3$	-163
$LuCl_3$	-175

Compressibilities φ_K^0 and $\bar{K}_2^0$ (partial molar compressibility) may be expressed as the sum of the compressibility $K_{Me^{3+}}$ and the change of compressibility of water ΔK after the dissolution of one mole of the electrolyte is

$$\varphi_K^0 = \bar{K}_2^0 + \Delta K. \qquad (4)$$

In the region of diluted solutions $\varphi_K^0 \approx \bar{K}_2^0$. The partial molar compressibility $\bar{K}_2^0$ of electrolytes can be usefully interpreted in terms of hydration and electrostriction. Four different solvent-structure regions in the neighborhood of ion exist according to the model of ion-solvent interactions. The primary hydration shell of the cation (region A)-it contains the water molecules that interact directly with the cation. In the region of secondary hydration (region B) the cation has an influence over water molecules. Its electron withdrawing effect on the primary waters of hydration encourages them to hydrogen bond to secondary waters of hydration. The volume of this region depends on the cation. It's large for small highly charged ions. Disordered region (C)-the magnitude of this region again depends on the cation, and bulk water (region D). The water molecules in regions (A) and (B) are already compressed on account of the tension produced by the ionic field and are less compressible than those in the bulk. It is suggesting that ions themselves do not contribute to the measured solution compressibilities. Thus $\bar{K}_2^0$ reflects compressibility changes occuring in regions (A) and (B).

In order to compare the structural effects of various ions we examined how $\bar{K}_2^0$ varies with parameter z^2/r (z-valency of metal, r-radius of cation). The variation of partial molar compressibility of rare Earth nitrates and chlorides in aqueous solutions $\bar{K}_2^0$ versus parameter z^2/r (r-radius of cation against Pauling) is shown in Fig. 1a)-for the lanthanide nitrate solutions, b)-for the lanthanide chloride solutions.

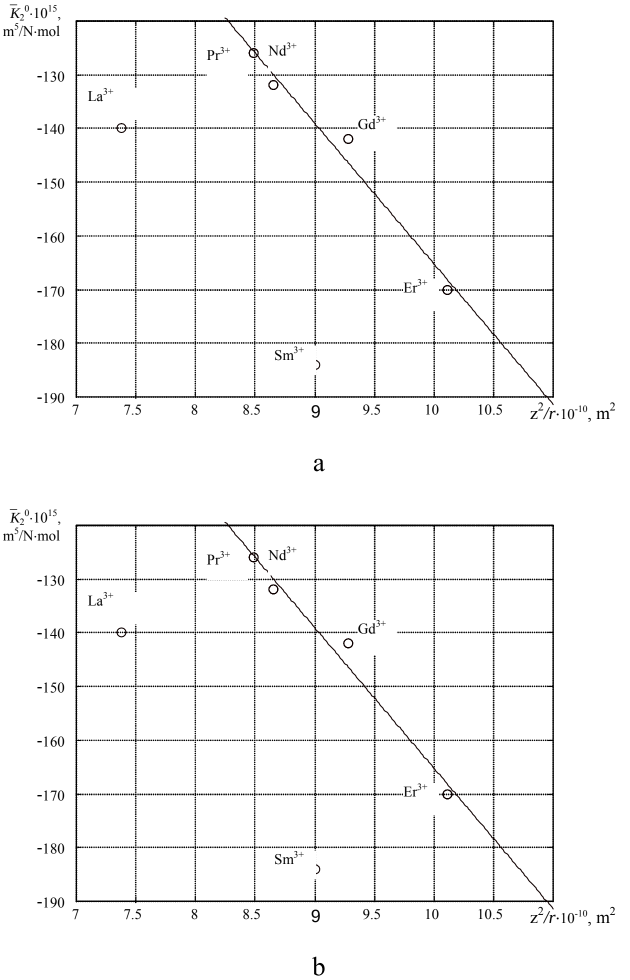

Fig. 1. **Dependence of partial molar compressibility versus parameter z^2/r: a)-rare Earth nitrate solutions, b)- rare Earth chloride solutions**

The rare earth ions behave very similarly in solutions since they all exist in the trivalent state. Furthermore, the ionic radius of the rare Earth ion decrease in a regular way across the series owing to the lanthanide contraction forming an ideal group of ions for studying ion-solvent interactions. The value of parameter z^2/r characterizes the ion-dipole interaction between cations and water molecules around these ions. As seen, the dependence of partial molar compressibility $\bar{K}_2^0$ against the parameter z^2/r is nonlinear, except for some electrolytes in a series of rare Earth nitrates (Fig. 1 a) and rare Earth chlorides (Fig. 1 b). This observation implies that ion-solvent interaction cannot be explained only by the electric field strength. Since the radius of the rare Earth ions decrease regularly across the series from La to Lu, the charge density of the ion increases. The size of water affected by the rare Earth ion region also increases across the rare Earth series. In other words, both the strength and the extent of the rare Earth ion-water interaction increases across the series. This increase of total hydration is reflected in decreasing of the partial molar compressibility $\bar{K}_2^0$ from Nd to Er in aqueous nitrate solutions (Fig. 1 a) and from Sm to Lu in aqueous chloride solutions (Fig. 1 b).

The displacement of partial molar compressibility data for $La(NO_3)_3$, $Ce(NO_3)_3$, $Sm(NO_3)_3$, and $LaCl_3$ has been attributed to a structural change in the inner hydration sphere where the coordination number is thought to decrease from 9 (La to Nd) to 8 (Tb to Lu) [4,5]. Between Nd and Tb intermediate forms exist between the two coordinated forms that is displaced from the higher to the lower coordination. The decrease in inner sphere hydration will result in the loss of the electrostriction of this water molecule, and will increase partial molar compressibility of ions Nd^{3+}, Gd^{3+}, Er^{3+} compare with La^{3+}, Sm^{3+} (Fig.1 a).

Assignment of individual ionic values of partial molar compressibility $\bar{K}_2^0$ is more difficult problem, but is important if compressibility studies of ionic solutions are to be useful in indicating specifities in ionic solvation. For the evaluation of the individual ionic compressibility the method, recommended by the authors [6] has been employed. If $\bar{K}_2^0$ is determined by both the extent and local intensity of ion-solvent interaction, it should be related to the electrostrostriction $\bar{V}_e$ which can be defined as the volume change in the ionic hydration co-sphere associated with charge-dipole attraction.

Drude and Nernst [6] supported that

$$V_e' = B' \times z^2 / r , \qquad (5)$$

partial molar compressibility $\bar{K}_2^0 = . \left(\frac{\partial V^0{}_e}{\partial p} \right)_T$,

and

$$\bar{K}_2^0 = B \times z^2/r, \qquad (6)$$

where B is the derivative of B' with respect to p. Then for an electrolyte M_aX_b:

$$\bar{K}_2^0\ (M_aX_b) = \frac{a z_+{}^2}{r_+} \cdot B_+ + \frac{b z_-{}^2}{r_-} \cdot B_- \qquad (7)$$

Dividing this equation by the parameter $\frac{b z_-^2}{r_-}$ it was obtained:

$$\bar{K}_2^0\ (M_aX_b) \frac{r_-}{b z_-^2} = \frac{a z_+{}^2 r_-}{b z_-{}^2 r_+} \cdot B_+ + B_- . \qquad (8)$$

Thus, by plotting K_2^0 (M_aX_b) $\frac{r_-}{bz_-^2}$ versus a parameter $\frac{az_+^2 r_-}{bz_-^2 r+}$, we should obtain a straight line of slope B_+ and intercept B_-, if Eq.8 is valid. When applied to the experimental data using Pauling radii, non-parallel straight lines are found for $Pr(NO_3)_3$, $Nd(NO_3)_3$, $Gd(NO_3)_3$, $Er(NO_3)_3$ aqueous solutions and for $SmCl_3$, $GdCl_3$, $TbCl_3$, $LuCl_3$ aqueous solutions (Fig. 2 a and Fig. 2 b).

The investigation of Eq. 8 for rare Earth nitrate solutions shows that it is not valid, and the individual ionic values of partial molar compressibility cannot estimate though assignment of individual ionic values of partial molar compressibility for $In(NO_3)_3$, $Fe(NO_3)_3$, $Cr(NO_3)_3$, $Ga(NO_3)_3$ and $Al(NO_3)_3$ in aqueous solutions was successful in our earlier work [7]. This implies that ion-solvent interaction in aqueous rare Earth nitrate solutions cannot be explained simply by an electrostriction of water molecules around rare Earth cations.

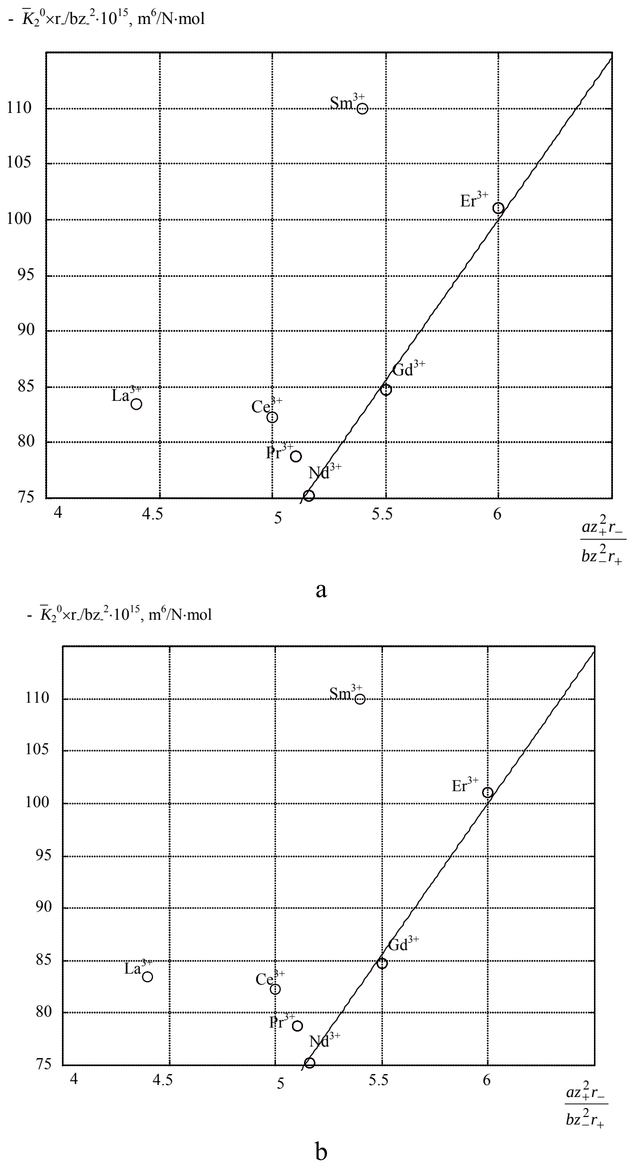

Fig. 2. **Graphic picture of Eq. 8: for rare Earth nitrate solutions, for rare earth chloride solutions**

The investigation of Eq. 8 for rare earth chloride aqueous solutions gives the slope $B_+=12.54\times10^{25}$ $m^6/(N \cdot mol)$ and the intercept $B_-=-75\times10^{-25} m^6/(N \cdot mol)$. This imply that Eq. 6 is valid for cation, but not for anion. Using the value B_+ the partial molar compressibility for each ion (Sm^{3+}, Gd^{3+}, Tb^{3+}, Lu^{3+}) is calculated. The data of $\overline{K}^0{}_{Me}{}^{3+}$ are given in Table 2.

Table 2. **Partial molar compressibility and hydration numbers for investigated cations**

Ion	Sm^{3+}	Gd^{3+}	Tb^{3+}	Lu^{3+}	La^{3+}
$K^0{}_{Me}{}^{3+} \cdot 10^{15}$, $m^5/Nmol$	-113	-116	-121	-121	-126
$Z^0{}_{Me}{}^{3+}$	13.7	14.2	14.8	16	15

The values of $\overline{K}_2^0$ are additive properties of individual ions. Using $\overline{K}^0{}_{Me}{}^{3+}$ values to calculate partial molar compressibility for anion Cl^{-1} we obtain that $\overline{K}^0{}_{Cl}{}^{-1}$ = -14×10^{-15} $m^5/N \cdot mol$ at 20 ^{0}C. This value is in good agreement with partial molar compressibility obtained by other authors: Lamberte and Conway [6] $\overline{K}^0{}_{Cl}{}^{-1}$ = -13×10^{-15} $m^5/N \cdot mol$ at 25 ^{0}C and Mathieson and Conway: $\overline{K}^0{}_{Cl}{}^{-1}$ = -17×10^{-15} $m^5/N \cdot mol$ at at 25 ^{0}C from measurements of $\overline{K}_2^0$ for NaCl, KCl, CaCl and RbCl aqueous solutions. Using additivity, the partial molar compressibility of La^{3+} is estimated $\overline{K}^0{}_{La}{}^{3+}$ = -126×10^{-15} $m^5/N \cdot mol$. The total hydration numbers Z_0 are estimated by the relation [3]:

$$\varphi^0{}_K = Z_0 \cdot \overline{V}^0 \cdot \beta_0, \qquad (6)$$

where $\overline{V}^0$ is the molar volume and β_0 is the adiabatic compressibility of water. The values of individual hydration numbers of cations are given in Table 2. The comparison of these values with the calculated value of $Z^0{}_{Cl}{}^{-1}$=2 means that anion is considerable less hydrated as cations. This is physically plausible for two reasons: the dipole orientation of primary hydration water at anion is different from that at cations, the chloride anion is larger than investigated cations. The EXAFS spectroscopy technique was used to study the inner sphere coordination of trivalent lanthanide (Ln) ions in aqueous solutions as a function of increasing chloride concentration [8]. The average chloride coordination numbers N were determined as follows: La^{3+}, N=2.1; Ce^{3+}, N=1.8; Nd^{3+}=1.9. The conclusion was made that the trivalent lanthanide ions have no inner shell chloride complexation at chloride concentrations of ~5 mol/l or less. These data correspond to our investigations, e.g. hydration number of chloride ion $Z^0{}_{Cl}{}^{-1}$=2, and no inner sphere complexation exists in dilute rare earth chloride solutions [1].

Conclusions

The investigation of partial molar compressibility $\overline{K}_2^0$ for rare Earth nitrates in aqueous solutions showed that ion-solvent interaction cannot be explained simply by electrostatic field theory. Moreover the lanthanide nitrates form inner sphere complexes and amount of these complexes nonlinear depends across the series. The individual partial molar compressibility $\overline{K}^0{}_{Me}{}^{3+}$ for cations Sm^{3+}, Gd^{3+}, Tb^{3+}, Lu^{3+} in aqueous chloride solutions can be accounted only in terms of electrostrictive effects. The individual hydration numbers for these cations were calculated.

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Kai kurių Žemės retųjų elementų chloridų ir nitratų vandeninių tirpalų jonų dalinis molinis spūdumas

Reziumė

Analizuojama kai kurių Žemės retųjų elementų chloridų ir nitratų vandeninių tirpalų dalinio molinio spūdumo $\overline{K}_2^0$ priklausomybė nuo dydžio z^2/r (z-metalo valentingumas, r-katijono kristalografinis spindulys). Nitratų tirpaluose vykstančios jonų sąveikos su tirpikliu negalima paaiškinti tik jonų elektrinio lauko sukeliama tirpiklio elektrostrikcija. Netiesinę priklausomybę lemia struktūriniai pokyčiai vidinėje katijono hidratacijos sferoje. Chloridų tirpaluose nustatytas katijonų Sm^{3+}, Gd^{3+}, Tb^{3+} ir Lu^{3+} bei chloro anijono dalinis molinis spūdumas. Nustatyti tyrimų katijonų hidrataciniai skaičiai.

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