# Structural characteristics of hydration complexes of rubidium chloride in solutions

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The density and the velocity of ultrasound in aqueous solutions of rubidium chloride were measured over a broad range of concentrations and temperatures with the goal of quantitative description of structural features of hydration complexes formed by RbCl in water. The volume compression of the solvent, the hydration numbers, the molar volume, the adiabatic compressibility of water in the hydration shells of ions, and the intrinsic volume of a stoichiometric mixture of $Rb^+$ and $Cl^-$ ions were estimated. The change in the hydration number was found to make the major contribution to the variation of the volumetric properties of hydration complexes with an increase in the electrolyte concentration, while the effect of temperature is exerted *via* the solvent structure.

**Key words:** hydration, compressibility, density, hydration complex, hydration number, rubidium chloride.

Despite the numerous investigations of electrolyte solutions, a satisfactory quantitative description of their volumetric properties based on the molecular nature of ion—solvent interactions over wide ranges of concentrations and temperatures is still missing. Of special interest is the broad concentration range up to the complete solvation where one component (solvent) is in a large excess and the degree of hydration of the solute decreases upon an increase in the concentration due to overlap of the coordination spheres of ions.[1]

Among investigation methods sensitive to structural changes in solution, the acoustic method deserves attention. However, in recent years, the interest in ultrasonic methods has gradually attenuated. In our opinion, this was mainly caused by two facts. One of them is related to the advent of new, selective methods that allow one to evaluate more rigorously the observed processes. The second one is probably the lack of new approaches in interpreting the supersonic data. The Debye[2] or Passynski[3] relations used most often were obtained with the assumption that ion hydrates are incompressible.[4] The incompressibility of hydration complexes formed by electrolyte ions leads to the conclusion that the hydration number does not depend on concentration. However, this assumption is valid only as a rough approximation. The possibility of taking into account the compression of water bound in the hydration shells was demonstrated for infinitely dilute solutions of sugars[5] and for electrolyte solutions[6] up to the full hydration boundary. A series of studies[7—9] present an attempt to bring supersonic studies to a molecular level using a more advanced model, regarding the physical meaning. Data on the velocity of sound and the density at different temperatures and concentrations were employed to derive information on the volume compression caused by ion—water interactions, concentration-dependent hydration numbers, water compressibility and density in hydration shells, *etc.* The present work is an attempt to use this approach to study volumetric properties of aqueous solutions of rubidium chloride under adiabatic compression and thermal expansion conditions.

## Experimental

Reagent grade rubidium chloride was purified by recrystallization, doubly distilled water was degassed before preparation of solutions, and measurements were carried out immediately after the preparation of solutions.

The density of RbCl solutions was measured on an A.Paar, DMA 602 vibrating densimeter (Austria) with a total maximum error not exceeding $5 \cdot 10^{-2}$ kg m$^{-3}$. The method is based on the measurement of the intrinsic vibration frequency of a measuring cell placed in an electromagnetic vibration generator. The densimeter was calibrated against doubly distilled water and dried air at a constant pressure. To ensure the above-mentioned accuracy, double-circuit thermostating with an error of $4 \cdot 10^{-3}$ K was done.

The sound velocity ($u$) was measured using a specially designed variable-length ultrasonic laser interferometer at a frequency of 6 MHz with an error of $2.5 \cdot 10^{-3}$% (Fig. 1).[10,11] The design of the setup makes it possible to maintain also the rod with the reflector at a constant temperature.[12] The temperature

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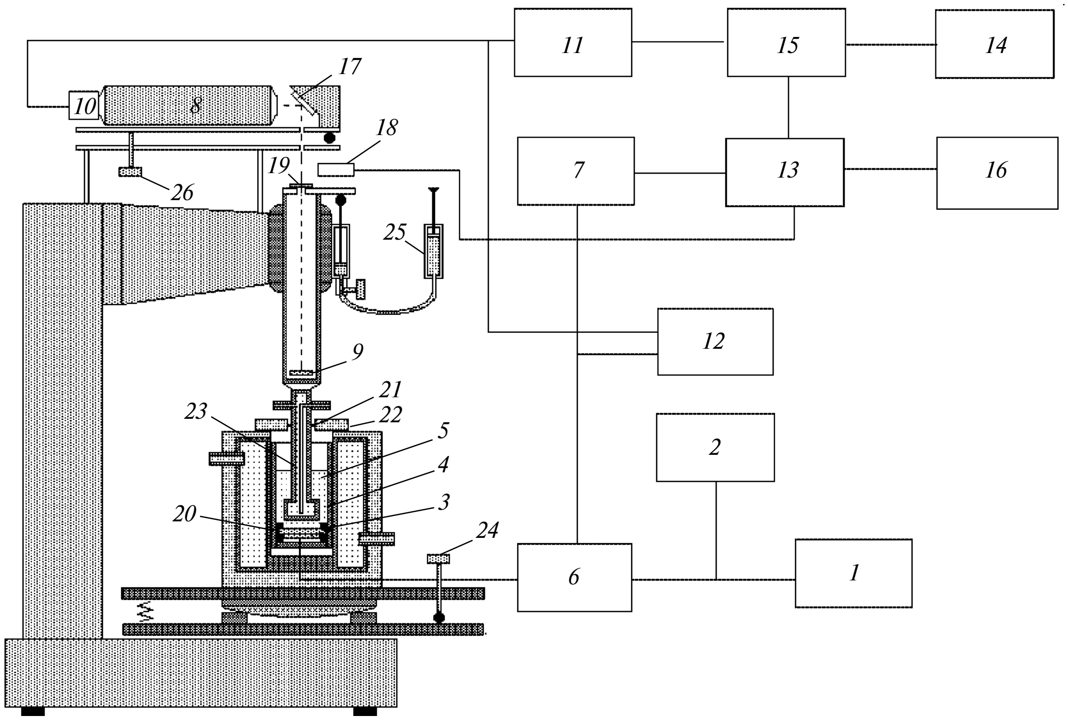

**Fig. 1.** Functional diagram of the variable-length laser ultrasonic interferometer: (*1*) generator of high-frequency vibrations (S46-31 frequency synthesizer), (*2*) digital frequency meter (F5041), (*3*) thermostatic shell of the measuring unit, (*4*) reflecting rod for ultrasonic vibrations, (*5*) the cell with the sample liquid, (*6*) filter for the ultrasonic signal, (*7*) holder for the resonance peak extrema, (*8*) laser (He—Ne, LG-78 type), (*9*) reflector for laser radiation, (*10*) photodiode, (*11*) migration mark former, (*12*) oscillograph, (*13*) electronic counter of the number of half waves, (*14*) migration mark counter, (*15*) counting trigger, (*16*) half-wave number controller, (*17*) reflector lens, (*18*) sensor for the zero point of half-waves, (*19*) polarization filter for laser radiation, (*20*) quartz membrane, (*21*) silicone stuffing-box, (*22*) fluoroplastic cover, (*23*) rod thermostating system, (*24*) adjusting microscrews of the acoustic tract, (*25*) hydraulic reducing gear, (*26*) adjusting microscrews of the laser tract.

**Table 1.** Density ($\rho$/kg m$^{-3}$) and ultrasound velocity ($u$/m s$^{-1}$) for aqueous solutions of RbCl at different temperatures and concentrations ($X_2$/mole fr.)

| $X_2 \cdot 10^2$ | $\rho \cdot 10^3$ | $u$ | $\rho \cdot 10^3$ | $u$ | $\rho \cdot 10^3$ | $u$ |
|---|---|---|---|---|---|---|
| | 15 °C | | 20 °C | | 25 °C | |
| 1.461 | 1.06956 | 1485.78 | 1.06822 | 1500.78 | 1.06667 | 1512.54 |
| 1.754 | 1.08329 | 1489.73 | 1.08186 | 1503.61 | 1.08025 | 1515.63 |
| 2.950 | 1.13805 | 1504.04 | 1.13634 | 1516.30 | 1.13446 | 1527.02 |
| 3.621 | 1.16791 | 1511.60 | 1.16606 | 1523.12 | 1.16406 | 1533.14 |
| 3.789 | 1.17530 | 1513.40 | 1.17341 | 1524.72 | 1.17138 | 1534.59 |
| 4.117 | 1.19205 | 1517.53 | 1.19008 | 1528.37 | 1.18798 | 1537.89 |
| 5.021 | 1.22837 | 1526.26 | 1.22623 | 1536.27 | 1.22398 | 1545.01 |
| 5.213 | 1.23647 | 1528.47 | 1.23429 | 1538.31 | 1.23201 | 1546.91 |
| 5.952 | 1.26724 | 1535.61 | 1.26493 | 1545.02 | 1.26252 | 1552.68 |
| | 30 °C | | 35 °C | | 45 °C | |
| 1.461 | 1.06495 | 1523.48 | 1.06305 | 1532.92 | 1.05880 | 1547.27 |
| 1.754 | 1.07846 | 1525.97 | 1.07652 | 1535.31 | 1.07218 | 1549.17 |
| 2.950 | 1.13245 | 1536.32 | 1.13032 | 1544.50 | 1.12566 | 1556.63 |
| 3.621 | 1.16193 | 1541.80 | 1.15970 | 1549.50 | 1.15488 | 1561.26 |
| 3.789 | 1.16923 | 1543.20 | 1.16698 | 1550.73 | 1.16211 | 1562.07 |
| 4.117 | 1.18577 | 1546.17 | 1.18347 | 1553.52 | 1.17852 | 1564.52 |
| 5.021 | 1.22165 | 1552.60 | 1.21924 | 1559.31 | 1.21413 | 1569.48 |
| 5.213 | 1.22965 | 1554.24 | 1.22723 | 1560.61 | 1.22208 | 1570.73 |
| 5.952 | 1.26006 | 1559.62 | 1.25756 | 1565.65 | 1.25228 | 1574.74 |

was measured with a calibrated uniform thermometer using a cathetometer with a error of $3 \cdot 10^{-3}$ K.

The results of measurements of the ultrasound velocity and the density of aqueous solutions of RbCl at different temperatures and concentrations are listed in Table 1.

## Results and Discussion

### Solution model

The dissolution of an electrolyte in water is known to be accompanied by volume compression and by a decrease in the solution compressibility due to dissociation and solvation of the electrolyte. The variations of these values serve as a measure of ion hydration for acoustic measurements.

The ion—dipole interactions in the hydration complexes of electrolytes are described using a simple model according to which each ion is located at the center of a shell consisting of water molecules. The shell includes water molecules whose density and compressibility differ from those of the pure solvent. The hydrated ions and the free solvent are assumed to form an ideal solution. Thus, the additivity principle can be applied to the solution volume

$$V_m = X_1^{fr}V_1 + X_2V_h, \quad (1)$$

where $V_m = (X_1M_1 + X_2M_2)/\rho$ is the molar volume of the solution, $M_1$ and $M_2$ are the molecular masses of water and the electrolyte, $X_1$ and $X_2$ are the initial mole fractions of water and the salt, respectively, $X_1^{fr} = (X_1 - hX_2)$ is the mole fraction of free water, $V_1$ and $V_h$ are the volumes of one mole of water not included in the hydration shell and one mole of the hydrated salt, respectively, and $h$ is the hydration number. In terms of this model, this number refers to the water molecules subject to the overall influence of the electrostatic field of the cation and the anion, which induces the change in the molar compressibility of the hydration water compared to the free water in the solution bulk.

By differentiating Eq. (1) with respect to pressure at a constant entropy ($S$ = const) or with respect to temperature (for $P$ = const) and taking into account the fact that $\beta_SV = (\partial V/\partial P)_S$ and $\alpha V = (\partial V/\partial T)_P$, we obtain the following relations:

$$\beta_SV_m = (X_1 - h_uX_2)\beta_{S,1}V_1 + X_2\beta_{S,h}V_h, \quad (2)$$

$$\alpha V_m = (X_1 - h_\alpha X_2)\alpha_1V_1 + X_2\alpha_hV_h, \quad (3)$$

where $\beta_{S,1}V_1$ and $\alpha_1V_1$ are the molar adiabatic compressibility and expansibility of pure water, $\beta_{S,h}V_h$ and $\alpha_hV_h$ are the molar compressibility and expansibility of the hydration complex of the solute, $h_u$ and $h_\alpha$ are the hydration numbers determined from compressibility and from thermal expansion, respectively. The acoustic wavelengths used most often in practice are great compared to the size of the solvation shell, *i.e.*, the region in which the arrangement of molecules obeys a certain order. In other words, the acoustic frequency is rather low compared to the frequencies of intermolecular vibrations in the liquid phase. In addition, the pressure amplitude ($\delta P$), related to the density amplitude ($\delta\rho$) in an acoustic wave as $\delta P = (1/\beta_S)(\delta\rho/\rho)$, does not exceed $2.02 \cdot 10^5$ Pa at a frequency of 1 MHz.[4] Hence, under ambient conditions, it is possible to neglect the dependence of the hydration number in the hydration complex on this pressure variation. By substituting Eqs. (2) and (3) into the expressions determining the apparent molar compressibility and expansibility of a salt dissolved in water, one can obtain the relations

$$\phi_{k,S} = -h_u\beta_{S,1}V_1 + \beta_{S,h}V_h, \quad (4)$$

$$\phi_E = -h_\alpha\alpha_1V_1 + \alpha_hV_h. \quad (5)$$

As the electrolyte concentration increases, the hydration shells of ions start to overlap, which leads to a decrease in the volume of the hydrated salt; in this case, $V_h$ can be expressed as

$$V_h = hV_{1h} + V_{2h}, \quad (6)$$

where $V_{2h}$ is the volume occupied by a stoichiometric mixture of electrolyte ions in the solution except for the hydration sphere, $V_{1h}$ is the molar volume of water in the hydration sphere. By differentiating Eq. (6) with respect to pressure and temperature, respectively, we obtain

$$\beta_{S,h}V_h = h_u\beta_{S,1h}V_{1h} + \beta_{S,2h}V_{2h}, \quad (7)$$

$$\alpha_hV_h = h_\alpha\alpha_{1h}V_{1h} + \alpha_{2h}V_{2h}, \quad (8)$$

where $\beta_{2h}$ and $\alpha_{2h}$ are the compressibility and the expansibility of the volume of the stoichiometric mixture of ions, $\beta_{1h}$ and $\alpha_{1h}$ are the compressibility and the expansibility of the hydration water.

By combining Eq. (1) and Eq. (6) with the equation expressing the apparent molar volume of the electrolyte in water ($\phi_V$), it is possible to determine the intrinsic volume of the stoichiometric mixture of ions, the volume compression caused by the ion—solvent interaction, and the molar volume of water in the hydration shell. Thus, the apparent molar volume can be represented by the equation

$$\phi_V = V_{2h} - h(V_1 - V_{1h}), \quad (9)$$

where $(V_1 - V_{1h})$ is the volume compression, $V_{2h}$ is the intrinsic volume of the cavity of the stoichiometric mixture of ions. Thus, in terms of the considered model,[7—9] the molar compressibility of the hydration complex of electrolyte ions ($\beta_{S,h}V_h$) with temperature variation is negligibly small compared to that of pure water ($\beta_{S,1}V_1$). Thus, it is expedient to study the temperature dependences of the apparent molar compressibility ($\phi_{k,S}$) and the apparent molar expansibility ($\phi_E$) of an electrolyte solution at a constant concentration of the solute.

In order to use this approach in an extended range of conditions and estimate structural characteristics of the hydration complexes formed by the solute, precision experimental measurements of the density and ultrasound velocity are required. In this study, data on the ultrasound velocity ($u$) in aqueous solutions of RbCl and the density ($\rho$) over a concentration range of (0.8—3.5) mol kg$^{-1}$ and a temperature range of 288.150—318.15 K were obtained for the first time.

The results were used to determine the molar expansion ($\alpha V_m$) and adiabatic compression ($\beta_SV_m$) coefficients, which are rational parameters according to a proposed terminology,[13,14] and the apparent molar expansibility ($\phi_E$) and adiabatic compressibility ($\phi_{k,S}$). Our experiments demonstrated that the molar adiabatic compressibility ($\beta_SV_m$) of an aqueous solution of RbCl decreases with an increase in the temperature or the electrolyte concentration and that the temperature dependence of $\beta_S V_m$ for the solution follows this dependence of $\beta_{S,1} V_1$ for pure water. The effect of the temperature and concentration on the solution compressibility includes vibrational and configurational contributions:

$$\beta_S V_m = (\beta_S V_m)_{vib} + (\beta_S V_m)_{conf}, \tag{10}$$

where $(\beta_S V_m)_{vib}$ is the vibrational contribution caused by intermolecular thermal vibrations and $(\beta_S V_m)_{conf}$ is the configurational contribution related to the shift of equilibrium between a three-dimensional tetrahedral network of H-bonds and a denser structure arising due to the deformation and cleavage of H-bonds. As the temperature increases, the vibrational contribution to the $\beta_S V_m$ grows due to thermal expansion, resulting in a higher compressibility, while the configurational contribution decreases due to the equilibrium shift toward the denser structure. Thus, the decrease in the molar compressibility in the temperature range studied is caused by the predominant role of the configurational contribution.[15]

The introduction of ions in water gives rise to more compact structures resulting in lower $\beta_S$ and lower $V_m$ of the solution due to electrostriction of water in the hydration shells. For electrolyte concentrations near the full hydration boundary, the concentration of free water decreases, together with the configurational contribution to the compressibility, and $\beta_S V_m$ gradually increases with an increase in the concentration after the minimum.

The molar volume expansion coefficients ($\alpha V_m$) of aqueous solutions of RbCl increase with an increase in the temperature and the concentration; the rate of their variation slows down at higher concentrations due to the decrease in the amount of free solvent in the solution.

Figure 2, *a* shows the dependences of $\phi_{k,S}$ on the molar adiabatic compressibility of pure water ($\beta_{S,1} V_1$) for the solutions under study; in accordance with Eq. (4), the plots are linear ($R > 0.999$). This indicates that $h$ and $\beta_{S,h} V_h$ do not depend on the temperature over the studied range of state variables.

Determination of exact thermodynamic values for apparent molar expansion ($\phi_E$) requires the knowledge of precision values for the density ρ (g cm$^{-3}$) measured with an error not exceeding one or two units in the sixth decimal place. Nevertheless, we are able to analyze the main trends in the variation of the molar expansion parameters and quantities derived from them following the change in the temperature for aqueous solutions of RbCl over a broad range of concentrations. Thus, the dependence of the apparent molar expansibility ($\phi_E$) of rubidium chloride solutions on the molar thermal expansion of pure water ($\alpha_1 V_1$) in the region of 288.15—308.15 K is linear ($R > 0.995$) according to Eq. (5) (see Fig. 2, *b*).

Table 2 presents the $h$ values and molar parameters of the hydration complex determined using Eqs. (4) and (5).

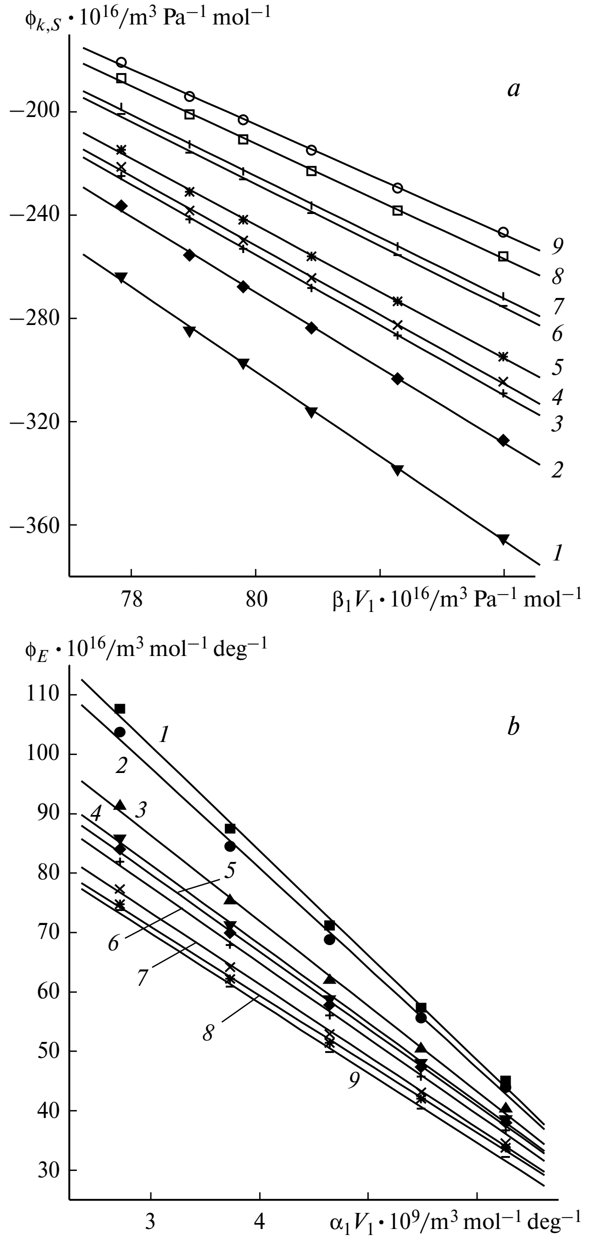

**Fig. 2.** Apparent molar adiabatic compressibility $\phi_{k,S}$ (*a*) and apparent molar expansibility $\phi_E$ (*b*) of RbCl in water *vs.* the molar compressibility and expansibility of pure water at concentrations ($X_2 \cdot 10^2$/mole fr.): 1.461 (*1*), 1.754 (*2*), 2.950 (*3*), 3.621 (*4*), 3.789 (*5*), 4.117 (*6*), 5.021 (*7*), 5.213 (*8*), and 5.952 (*9*).

The $h$, $\beta_{S,h} V_h$, and $\alpha_h V_h$ values decrease with an increase in the electrolyte concentration. It is noteworthy that the hydration numbers determined from the adiabatic compressibility ($h_u$) are in good agreement with those found using thermal expansion ($h_\alpha$). In view of the obtained results, one can consider the hydration number ($h$) to be the major component in the concentrationdependence of solvation, while temperature can be considered as a factor

**Table 2.** Hydration numbers ($h_u$, $h_\alpha$), molar compressibility ($\beta_h V_h$), and molar thermal expansion ($\alpha_h V_h$) of the hydration complex of rubidium chloride (Eqs. (4), (5))

| $X_2 \cdot 10^2$ /mole fr. | $h_u$ | $\beta_h V_h \cdot 10^{15}$ /m$^3$ Pa$^{-1}$ mol$^{-1}$ | $h_\alpha$ | $\alpha_h V_h \cdot 10^8$ /m$^3$ mol$^{-1}$ deg$^{-1}$ |
|---|---|---|---|---|
| 1.461 | 16.7 | 103.2 | 17.6 | 15.4 |
| 1.754 | 16.3 | 100.9 | 16.8 | 14.8 |
| 2.950 | 14.6 | 89.9 | 14.3 | 12.9 |
| 3.621 | 13.6 | 83.2 | 13.3 | 12.1 |
| 3.789 | 13.4 | 82.0 | 12.9 | 11.8 |
| 4.117 | 12.9 | 78.8 | 12.7 | 11.5 |
| 5.021 | 11.9 | 73.1 | 12.0 | 10.9 |
| 5.213 | 11.8 | 72.4 | 11.6 | 10.6 |
| 5.952 | 11.2 | 68.1 | 11.6 | 10.5 |

affecting this dependence through the change in the solvent structure.

The decrease in the hydration numbers of RbCl with an increase in concentration is due, first of all, to the overlap of the hydration shells of ions. The dependence of the overlap mechanism and, hence, the change in $h$ on the salt concentration follows a complex pattern. We attempted to describe this dependence quantitatively without considering the difference between the hydration water in the cation and anion shells. Moreover, we neglected the possible effects of ion—ion interactions. Despite this, rather imperfect approximation, we obtained a hyperbolic equation for the concentration dependence of the hydration numbers of RbCl ions

$$1/h = (1/h_0) + kX_2, \quad (11)$$

which is in satisfactory agreement with experimental results ($R = 0.999$; $\sigma = \pm 0.7$) (Fig. 3). The coefficient $k$ characterizes the concentration variation of the hydration number of ions and $h_0$ is the hydration number of rubidium chloride for infinite dilution ($h_0 \approx 20.3$). The presented hydration numbers of the electrolyte exceed the total coordination numbers of ions determined from measured electrical conductivity, activity coefficients, transport numbers, and ε or using NMR, but they are much lower than the values derived from diffusion, refractive index, density, and effective volume measurements.[16,17] This approach, which characterizes the interaction of the ultrasound field with aqueous solutions, allows one to study all sorts of the solute—solvent and solvent—solvent interactions. The hydration numbers found by this method refer not only to water molecules that coordinate the solute (A) but also to molecules that undergo hydrophobic interactions (B) due to stabilization of the hydrogen bond network in water: $h = h_A + h_B$. It has been shown[18] that the coefficient $k$ in Eq. (11) can serve as a measure of hydrophobicity of the electrolyte. In the case of NaCl, $k = 0.51$, while for RbCl, $k = 0.67$, *i.e.*, the change in $h$ with variation of the concentration is more pronounced for Rb$^+$, which is more hydrophobic. The fact that the degree of ordering of the structure of aqueous solutions of RbCl is lower than that for other alkali metal chlorides is also supported by the thermodynamic parameters of hydration $\Delta S°_{hydr}$ and $\Delta H°_{hydr}$ (for example, $\Delta S°_{hydr}$ (J K$^{-1}$ mol$^{-1}$): Li$^+$(−88) < Na$^+$(36.8) < K$^+$(80.3) < < Rb$^+$(99.3) and $\Delta H°_{hydr}$ (kJ mol$^{-1}$): Li$^+$(−522) < < Na$^+$(−407) < K$^+$(−324) < Rb$^+$(−299)).[19]

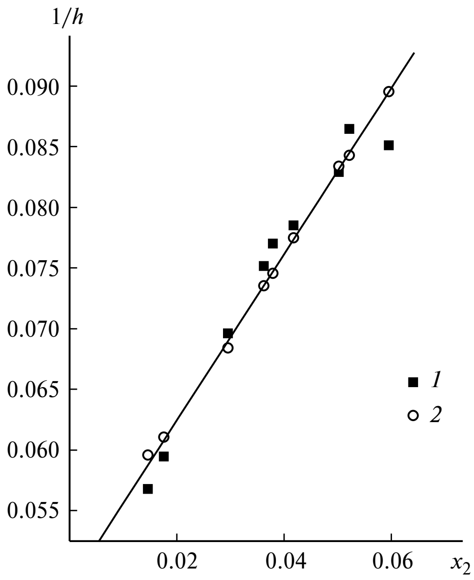

**Fig. 3.** Concentration dependence of the hydration numbers of the RbCl electrolyte ions determined using expansibility (*1*) and adiabatic compressibility (*2*) data.

Analysis of the observed linear dependences $\beta_{S,h}V_h = f(h_u)$ and $\alpha_h V_h = f(h_\alpha)$ showed that their correspondence to Eqs. (7) and (8) proves that the molar adiabatic compressibility and the molar expansibility of water in the hydration shells of ions do not depend on the concentration (Fig. 4). The $\beta_{S,h}V_h$ and $\alpha_h V_h$ values fall in the straight lines with the parameters: $\beta_{S,2h}V_{2h}$ = $(2.5 \pm 0.3) \cdot 10^{-15}$ m$^3$ Pa$^{-1}$ mol$^{-1}$ and $\alpha_{2h}V_{2h}$ = $(9.2 \pm 3) \cdot 10^{-9}$ m$^3$ mol$^{-1}$ deg$^{-1}$, $\beta_{S,1h}V_{1h}$ = $(6.31 \pm 0.02) \cdot 10^{-15}$ m$^3$ Pa$^{-1}$ mol$^{-1}$ and $\alpha_{1h}V_{1h}$ = $(8.3 \pm 0.3) \cdot 10^{-9}$ m$^3$ Pa$^{-1}$ deg$^{-1}$. The compressibility and expansibility of the cavities containing ions such as Rb$^+$ and Cl$^-$ should not be neglected in the temperature and concentration ranges studied. Thus, in addition to the major contribution to the change in the volumetric properties of the electrolyte hydration complexes related to the change in the hydration numbers, there exists apparently a certain contribution of the intrinsic compressibility of the unlike ions of the salt. The $\beta_{S,1h}V_{1h}$ values obtained for the hydration water are lower than those for pure water ($\beta_{S,1}V_1 = 8.09 \cdot 10^{-15}$ m$^3$ Pa$^{-1}$ mol$^{-1}$ at 298.15 K). This confirms once again the occurrence of pronounced interaction in the hydration shells in a stoichiometric mixture of ions.

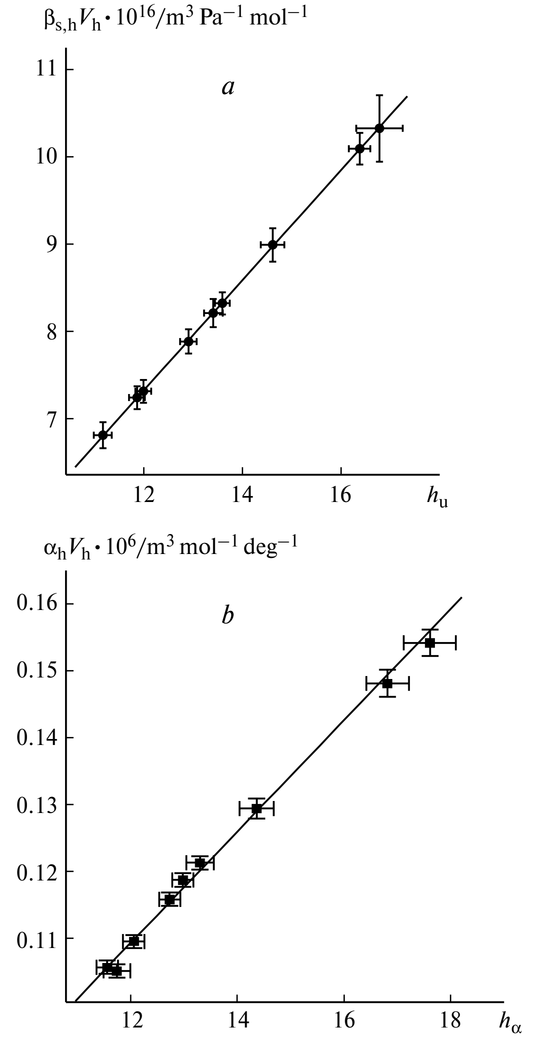

**Fig. 4.** Molar adiabatic compressibility (*a*) and molar thermal expansion (*b*) of the RbCl hydration complex *vs.* hydration number.

Within the framework of our model, the concentration dependence of the apparent molar volume of RbCl in water is described by Eq. (9). It can be seen from Fig. 5 that the dependence $\phi_V = f(h)$ is also linear ($R > 0.998$). Thus, the changes in the volume compression ($V_l - V_{lh}$) and the electrolyte molar volume ($V_{2h}$) do not depend on the concentration, only $h$ being a function of concentration. With an increase in temperature, the compression tends to decrease, while the $V_{2h}$ value remains approximately constant (Table 3). The $V_{2h}$ values found are greater than the intrinsic volumes of electrolytes determined from the crystallographic radii of ions.[20] Thus, $V_{2h}$ can be represented as a volume of a spherical cavity containing a stoichiometric mixture of ions including not only the intrinsic ion volume but also the fluctuation space.

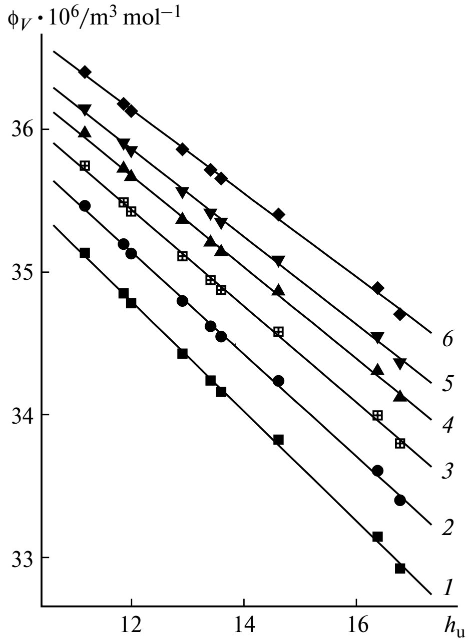

**Fig. 5.** Apparent molar volume ($\phi_V$) of RbCl in water *vs.* hydration number ($h_u$) at temperatures of 288.15 (*1*), 293.15 (*2*), 298.15 (*3*), 303.15 (*4*), 308.15 (*5*), and 318.15 K (*6*).

It should be noted that compressibility of water has a number of specific features related to structural transformations of the hydrogen bond network and affecting the compressibility of the hydration shells of ions. One of these features is the temperature dependence of the compressibility of water, which has a minimum at about 338.15 K and a minimum of the molar adiabatic compressibility in the region of 329.15 K. One more feature is related to the temperature dependence of the high-pressure radial distribution function (Fig. 6) where the destruction of the tetrahedral structure of water upon a temperature rise (a decrease in the peak at 4.5 Å) is replaced by its stabilization (an increase in the peak at $T > 623.15$ K).[21] This phenomenon may be caused by the fact that an increase in pressure not only enhances a hydrogen bond but also destroys a quasi-crystalline structure of water (as in a solid). A temperature rise, which enhances density fluctuations (especially under subcritical conditions), results

**Table 3.** Temperature dependences of the volume compression ($V_l - V_{lh}$), the cavity volume for a stoichiometric mixture of ions ($V_{2h}$), and the molar volume of water in the hydration shells ($V_{lh}$) in a solution of RbCl

| $T$/K | $(V_l - V_{lh}) \cdot 10^6$ | $V_{2h} \cdot 10^6$ | $V_{lh} \cdot 10^6$ |
|---|---|---|---|
| | m$^3$ mol$^{-1}$ | | |
| 288.15 | 0.384 | 39.4 | 17.6 |
| 293.15 | 0.357 | 39.4 | 17.7 |
| 298.15 | 0.337 | 39.4 | 17.7 |
| 303.15 | 0.320 | 39.5 | 17.8 |
| 308.15 | 0.307 | 39.5 | 17.8 |
| 318.15 | 0.293 | 39.5 | 17.9 |

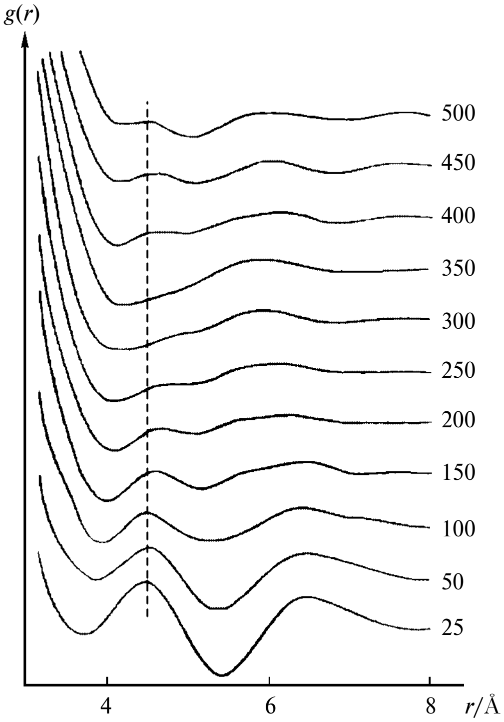

**Fig. 6.** Temperature dependence of the pair correlation functions of water at a pressure of $1 \cdot 10^3$ atm (the numerals at the curves mean $T$/°C).

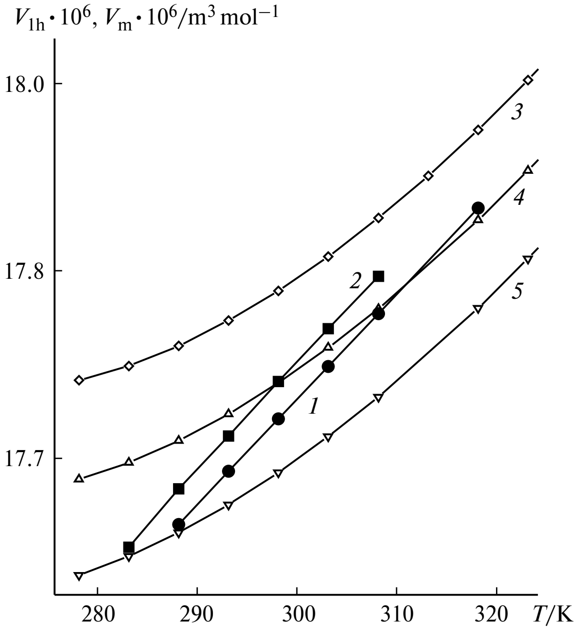

**Fig. 7.** Temperature dependence of the molar volume of water in the hydration shells ($V_{1h}$) in solutions of RbCl (*1*) and KCl (*2*) and isobares of the molar volume of pure water ($V_m$) at pressures of 300 (*3*), 400 (*4*), and 500 atm (*5*).

again in structure stabilization. We believe that this effect can be manifested not only under supercritical conditions. This may also occur in the hydration shells of ions and in the vicinity of normal temperatures. The electrostriction, which ensures high pressure around the ion, destroys the quasi-crystalline structure of the hydrogen bond network; hence, it is necessary to increase the kinetic energy of molecules for the formation of a tetrahedral structure of water around the ion. This may be accompanied by an additional increase in the molar volume of water in the hydration shell following an increase in temperature; this can be seen in the dependence $V_{1h} = f(T)$ for aqueous solutions of KCl [12] and RbCl (Fig. 7). Comparison of the temperature dependences of the molar volume of pure water at pressures from $1.01 \cdot 10^5$ to $1.01 \cdot 10^8$ Pa and the molar volume of the hydration water ($V_{1h}$) demonstrated that the average pressure in the hydration shells of RbCl near the normal temperatures is close to $4.54 \cdot 10^7$ Pa and that for KCl is close to $4.04 \cdot 10^7$ Pa.

Thus, the approach based on the molar parameters of solution compressibility and expansibility made it possible to determine the structural characteristics of the hydration complexes of rubidium chloride ions over a broad range of concentrations and temperatures. The hydrate-bound water was shown to be compressible and to contribute to the change in the volumetric properties of the solutions under study. An increase in the electrolyte concentration entails a decrease in the numbers of hydration of ions, the molar compressibility, and the molar expansibility of the hydration complexes of RbCl; the *h* value does not depend on the temperature over the range of state variables studied. Under these conditions, the results allow the hydration number to be regarded as the key component in the concentration dependence of hydration, and the temperature can be regarded as a factor affecting this dependence through the change in the solvent structure. The molar volume of water in the hydration shell of RbCl ions is lower than that of pure water ($V_{1h} < V_1$).

This model based on the mechanism of overlap of the hydration spheres of ions reproduces quite satisfactorily the volumetric properties of the solution determined experimentally. The structural characteristics of RbCl hydration complexes determined using the molar parameters of adiabatic compressibility and using thermal expansion were shown to be commensurable. The results demonstrate the possibility of extending this approach to other physicochemical properties and reveal the important role of the hydration interactions in electrolyte solutions.

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