# Solvation of Electrolytes and Nonelectrolytes in Aqueous Solutions

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ABSTRACT: A new theory of electrolyte and nonelectrolyte solutions has been developed which, unlike the Debye—Hückel method applicable for small concentrations only, makes it possible to estimate thermodynamic properties of a solution in a wide range of state parameters. One of the main novelties of the proposed theory is that it takes into account the dependence of solvation numbers upon the concentration of solution, and all changes occurring in the solution are connected with solvation of the stoichiometric mixture of electrolyte ions or molecules. The present paper proposes a rigorous thermodynamic analysis of hydration parameters of solutions. Ultrasound and densimetric measurements in combination with data on isobaric heat capacity have been used to study aqueous solutions of electrolytes $NaNO_3$, KI, NaCl, KCl, $MgCl_2$, and $MgSO_4$ and of nonelectrolytes urea, urotropine, and acetonitrile. Structural characteristics of hydration complexes have been analyzed: hydration numbers h, the proper volume of the stoichiometric mixture of ions without hydration shells V_{2h}, compressibility β_{1h}, and the molar volume of water in hydration shells V_{1h}, their dependencies on concentration and temperature. It has been shown that for aqueous solutions the electric field of ions and molecules of nonelectrolytes has a greater influence on the temperature dependence of the molar volume of solution in hydration shells than a simple change of pressure. The cause of this effect may be due to the change in the dielectric permeability of water in the immediate vicinity of hydrated ions or molecules. The most studied compounds (NaCl, KCl, KI, $MgCl_2$) have been studied in a wider range of solute concentrations of up to 4—5 mol/kg. Up to the complete solvation limit (CSL), the functions $V_{1h} = f(T)$ and $\beta_{1h} = f(T)$ are linear with a high correlation factor, and the dependence $Y_{K,S} = f(\beta_1 V_1^*)$ at all investigated concentrations of electrolytes and nonelectrolytes up to the CSL enables h and $\beta_h V_h$ to be determined on the basis of relationships obtained in the study. The behavior of nonelectrolyte solutions is no different from that of electrolyte solutions, although it is possible to trace the difference between hydrophobic and hydrophilic interactions.
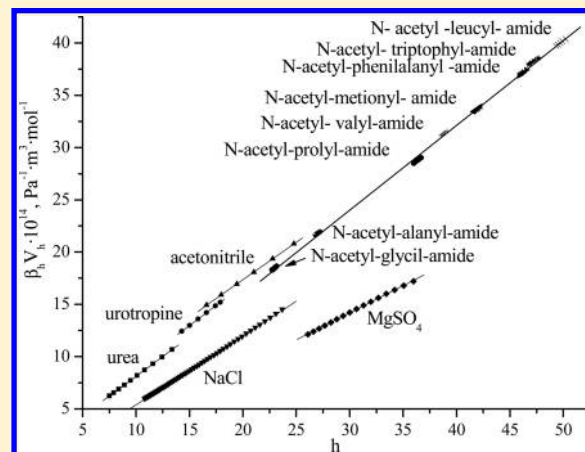
I. INTRODUCTION

In spite of there being a large number of both experimental and theoretical studies of solvation, there is still no rigorously substantiated model of the structure of solutions.[1] Of special interest are aqueous electrolyte and nonelectrolyte solutions in which at different concentrations there occur significant structural changes in hydration shells due to the specific structure of water. At present, there is quite a number of different approaches aimed at obtaining information on hydration processes, though data obtained using these are rather contradictory.[2] The solvation process has been investigated using various theoretical and experimental methods such as X-ray and neutron diffraction, quantum-chemical methods, computer modeling and NMR relaxation, calorimetric and densimetric measurements, and various modifications of the Debye—Hückel method[3] and Pitzer method.[4,5] All of these methods relate a change of some property of the solution to the solvation processes.

Unfortunately, it is not quite correct to compare these data with the results obtained using ultrasound methods. First, the given studies are based on the assumption that hydration numbers are independent of the concentration of the electrolyte. Second, the methods used by the authors of the given studies enable one to

determine hydration numbers only for the closest environment of the ions or molecules. Our studies[6,7] of the adiabatic compressibility of solutions clearly show that hydration numbers are a function of the solute concentrations. Besides, rather high hydration numbers in our studies are due to the fact that they include not only the first but also the subsequent solvation shells. In one of the first papers,[8] it was shown that solvation numbers obtained by the adiabatic compressibility method may be in good agreement with the data of papers on neutron and X-ray scattering, but only if the measurements are made at comparable concentrations. An attempt has been made[9,10] to carry out ultrasound investigations at the molecular level and from the data on the speed of propagation of ultrasound, heat capacity, and density at different temperatures and concentrations to obtain information on volumetric compression caused by the ion—solvent interaction, hydration numbers dependent on the concentration, compressibility, and density of water in hydration shells, etc. The most complete list of data on the determination of hydration parameters of different
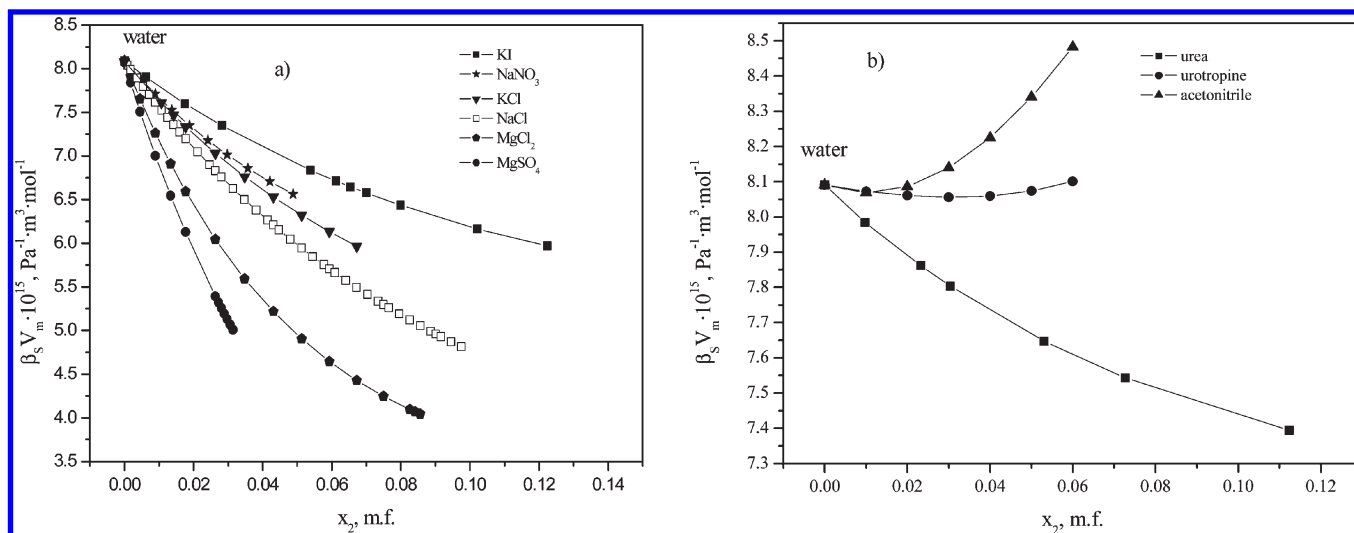
Figure 1. Concentration dependence of the molar adiabatic compressibility of electrolytes and nonelectrolytes in aqueous solutions at 298.15 K: (a) potassium iodide, sodium nitrate, potassium and sodium chlorides, magnesium chloride, and sulfate; (b) urea, urotropin, and acetonitrile.

salts using the adiabatic compressibility method is given in ref 10. Many different systems have been investigated by this method, including nonorganic electrolytes, acids and alkalis, amino acids, dipeptides of the glycil series, and nonelectrolytes, though in a limited temperature range, and similar regularities have been confirmed in all cases up to the complete solvation level.

The present paper presents the most important results obtained recently in the solvation theory of aqueous solutions of electrolytes ($NaNO_3$, KI, NaCl, $MgCl_2$, $MgSO_4$) and nonelectrolytes (urea, urotropin, and acetylnitrile) (Figure 1a,b). Figure 2 shows that electrolyte solutions include different systems whose characteristics of the speed of ultrasound propagation are significantly different from those in solutions of, say, potassium iodide and sodium chloride. However, all of them have a common feature of temperature dependencies of molar adiabatic compressibility $\beta_S V_m = f(x_2)$ intersecting at one point depending on the mole fraction of the electrolyte. The behavior of nonelectrolyte solutions does not differ from that of electrolyte solutions, though in these aqueous systems it is possible to trace the difference of hydrophobic and hydrophilic interactions.

II. ION−DIPOLE INTERACTIONS IN THE GIBBS FREE ENERGY

To create a theory of electrolytes that would enable one to correctly describe their thermodynamic properties in a wide range of concentrations is a very challenging task nowadays. At small concentrations, the method proposed by Debye and Hückel still remains the most reliable one.[11] However, as has been shown in numerous works, its application is limited to concentrations in the range of about 0.01 mol/kg; this is considerably lower than the concentration range at which different solutions exist.

In a recent review,[12] methods have been considered which should extend the concentration range by obtaining a more exact solution of the Poisson equation, taking into account the influence of dipole and quadripole moments of the particles, and using the method of the "mean" field. However, the approaches mentioned in the review do not give a definite answer to the question of how the composition of solvation shells of ions affects thermodynamic functions of the solution. Some studies have made an attempt to answer the question about the contribution of solvation shells of

ions.[13] Unfortunately, the conclusions of the given paper are based on the assumption that hydration numbers are independent of concentration, which runs contrary to our latest research.[14]

To take into account the experimentally observed dependence of solvation numbers, an expression was proposed[15] for that part of the Gibbs energy which is connected with the changes occurring in hydration shells of ions as the concentration of an electrolyte increases

$$\Delta G_2 = \lambda N_2 (\Delta h)^{3/2} \tag{1}$$

where N_2 is the number of electrolyte molecules; Δh is the difference between the solvation number at infinite dilution h_0 and the solvation number h corresponding to the given concentration x_2; and λ is a constant independent of the concentration.

According to the ultrasound investigations of electrolyte solutions, the concentration dependence of solvation numbers should be expressed as follows

$$h = h_0 \exp(-kx_2) \tag{2}$$

This expression at small concentrations is replaced by

$$h = h_0 - Kx_2 \tag{3}$$

Consequently, if formula 1 is used to obtain from the condition of the minimum of the free Gibbs energy the dependence of the dielectric constant of a solvent on the value of Δh, it should have the form of

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0}(1 + \alpha \Delta h) \tag{4}$$

As in the range of big concentrations, the contribution of ΔG_2 to the total free Gibbs energy becomes the dominant one,[16] and it becomes necessary to give a theoretic grounding of relationship 1. According to different estimates, the enthropy contribution to ΔG_2 is much less than the energy one, and consequently, the problem of finding the dependence of ΔG_2 on Δh is reduced to finding the dependence of the energy of solvation shell on the number of dipoles in it. Dipoles are known to create around each ion a shell of the opposite sign. The energy of electrostatic interaction of an ion with the dipoles of the solvation shell is
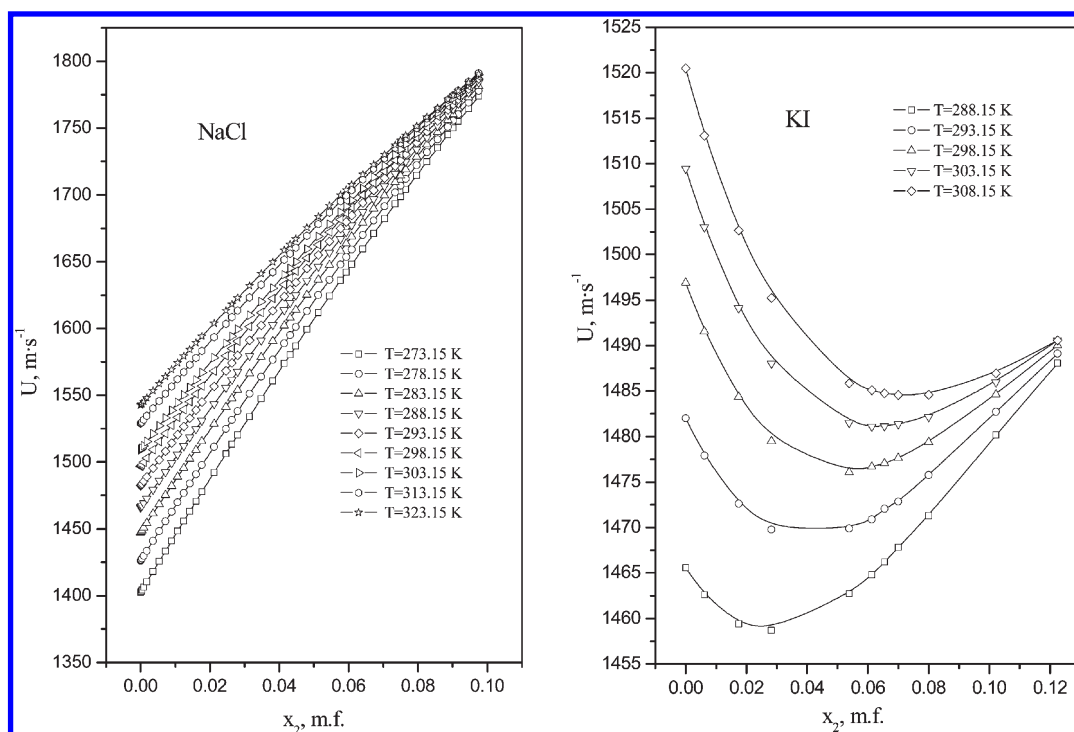
Figure 2. Concentration dependence of the speed of ultrasound at various temperatures in aqueous solutions of NaCl and KI.

proportional to h. Besides, the energy of electrostatic repulsion of the dipoles, which must be proportional to h^2, should be taken into account. Another contribution to ΔG_2 is made by the nonelectrostatic part of the energy of particle interaction in the solvation shell. This contribution is proved by the ultrasound studies of electrolytes which showed that the density and compressibility of the solvent in solvation shells of ions are different from the density and compressibility of the solvent outside the solvation shells. Depending on whether nonelectrostatic forces are short-range or long-range their energy must be proportional to h or h^2. Thus, if both the electrostatic and nonelectrostatic contributions are taken into account, the expression for the energy of solvation shell of a biatomic molecule will contain terms proportional to both h and h^2. Hence, according to the above considerations, the general form of the expression for ΔG_2 can be written as

$$\Delta G_2 = (\delta h + \lambda h^2 - \delta h_0 - \lambda h_0^2)N_2 \qquad (5)$$

where δ and λ are constants characteristic of a given solution and N_2 is the number of electrolyte molecules.

Since for the case of infinite dilution $\Delta G = \Delta G_2$ and $h = h_0$, the expression for the minimum of the free Gibbs energy will have the form

$$\frac{\partial G_2}{\partial h} = 0 \text{ when } h = h_0 \qquad (6)$$

Differentiating 5 with respect to h, with $h = h_0$, we obtain

$$\left(\frac{\partial \Delta G_2}{\partial h}\right)_{h=h_0} = \left(\frac{\partial N_2}{\partial h}\right)_{h=h_0} (\delta h + \lambda h^2 - \delta h_0 - \lambda h_0^2)$$

$$+ \left(\frac{\partial \delta h}{\partial h} + \frac{\partial \lambda h^2}{\partial h} - \frac{\partial \delta h_0}{\partial h} - \frac{\partial \lambda h_0^2}{\partial h}\right)_{h=h_0}$$

$$N_2 = 0 \qquad (6a)$$

Since h_0 is a constant, the derivatives $-((\partial \delta h_0)/(\partial h))$ and $-((\partial \lambda h_0^2)/(\partial h))$ will equal zero; the derivative $((\partial \delta h)/(\partial h))_{h=h_0}$ equals δ; and the derivative $((\partial \lambda h^2)/(\partial h))_{h=h_0}$ equals $2\lambda h_0$, then the expression 6a will have the form

$$\left(\frac{\partial \Delta G_2}{\partial h}\right)_{h=h_0} = \left(\frac{\partial N_2}{\partial h}\right)_{h=h_0} (\delta h + \lambda h^2 - \delta h_0 - \lambda h_0^2)_{h=h_0}$$

$$= 0 \qquad (6b)$$

It follows from 6b that condition 7 is met.

$$\delta + 2\lambda h_0 = 0 \qquad (7)$$

Finding δ from relationship 7 and inserting it into 5, we obtain a theoretically grounded dependence of ΔG_2 on Δh

$$\Delta G_2 = N_2(-2\lambda h_0 h + \lambda h^2 + 2\lambda h_0^2 - \lambda h_0^2) \qquad (7a)$$

Grouping like terms and factoring out λ, we may bring expression 7a to the form

$$\Delta G_2 = \lambda N_2(h^2 + h_0^2 - 2h_0 h) \qquad (8)$$

and show that $(h^2 + h_0^2 - 2h_0 h) = (h_0 - h)^2$. Therefore, the final form of the dependence of ΔG_2 on Δh can be written as

$$\Delta G_2 = \lambda N_2(\Delta h)^2 \qquad (9)$$

It is to be noted that one can differentiate with respect to variable Δh as well. Indeed, this derivative can be expressed as

$$\left(\frac{\partial \Delta G_2}{\partial \Delta h}\right)_{h=h_0} = \left(\frac{\partial \Delta G_2}{\partial h}\right)_{h=h_0} \left(\frac{\partial h}{\partial \Delta h}\right)_{h=h_0} \qquad (9a)$$

As has been shown above, derivative $((\partial \Delta G_2)/(\partial h))_{h=h_0}$ will be equal to zero, and derivative $((\partial h)/(\partial \Delta h))_{h=h_0}$ will be equal to unity, and therefore the following condition is met: $((\partial \Delta G_2)/(\partial \Delta h))_{h=h_0} = 0$. It should be shown that the theoretically grounded formula 9 is different
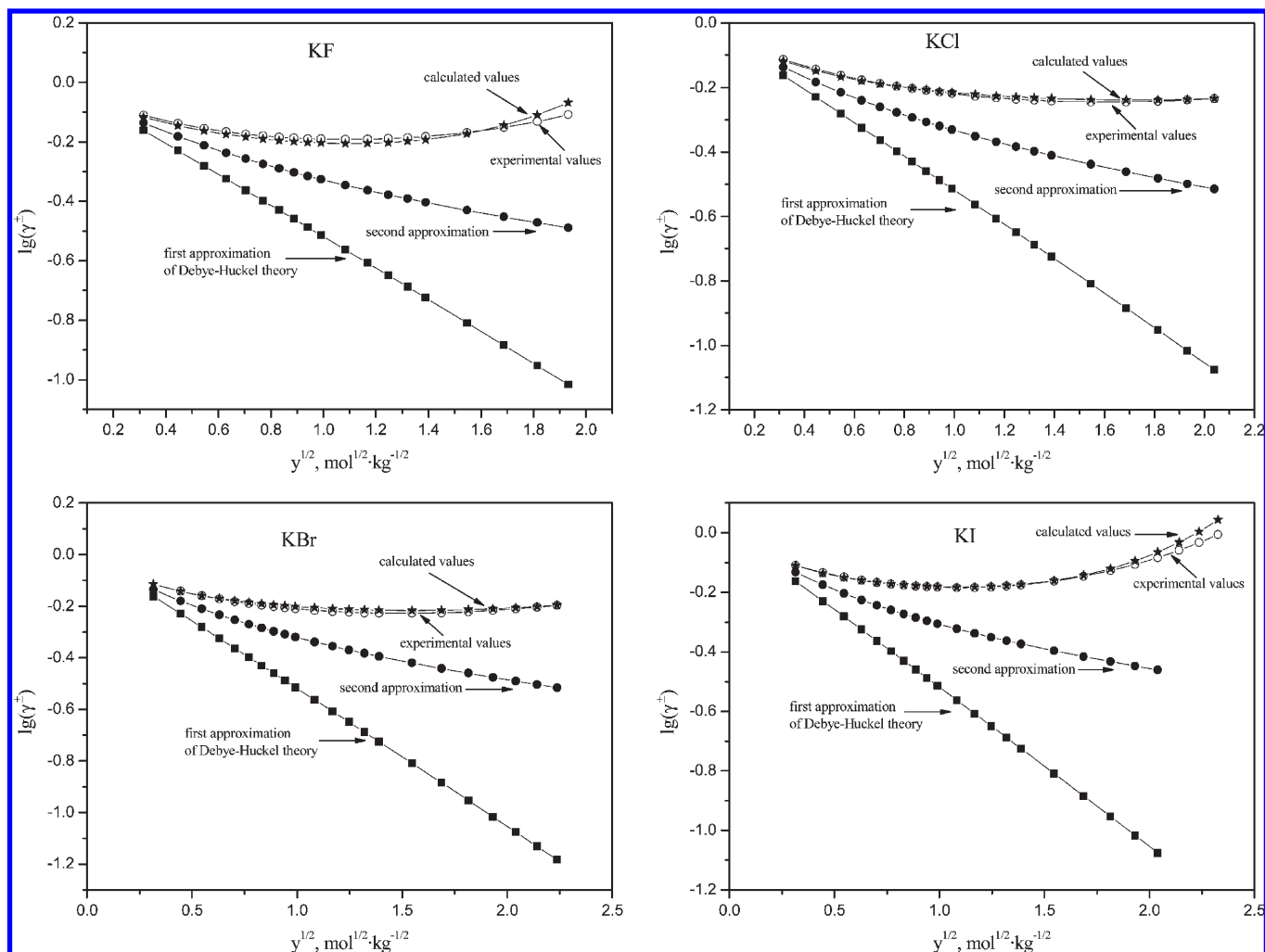
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Figure 3. Dependence of the activity coefficient of salt in aqueous solutions of KF, KCl, KBr, and KI on the variable $y = m/(1 + 0.018m)$, where m is the molality.

from expression 1 used previously.[16] In this connection, we compared the experimental and estimated activity coefficients for halogenous potassium salts: KF, KCl, KBr, and KI. It turned out that selecting a suitable coefficient one can obtain a rather good fit between the estimated and experimental curves.

Since, in this case as well, relationship 3 must be obeyed, the dependence of the dielectric constant 4 should be replaced by expression 10

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0}(1 + \alpha(\Delta h)^{3/2}) \tag{10}$$

Using a technique for estimating activity coefficients similar to the one used by us previously,[16] we obtain an expression for a logarithm of activity coefficient

$$\lg f^{\pm} = -\frac{e^3(1 + \alpha(K \cdot 0.018y)^{3/2})^{3/2}\sqrt{0.018 \cdot \frac{2\pi}{V_0 kT}}}{\varepsilon_0^{3/2}kT(1 + r_0\chi_0(1 + \alpha(K \cdot 0.018y)^{3/2})^{1/2})^2 \cdot 2.303}$$
$$+ \frac{4e^3\alpha}{3\varepsilon_0^{3/2}kT \cdot 2.303}K^{3/2} \cdot (0.018)^{1/2}y^2 \tag{11}$$

in which K and α are constants introduced in eqs 3 and 10, and coefficient λ is excluded when the condition of minimum free

energy is used

$$\chi_0 = \left(\frac{4\pi e}{\varepsilon_0 kT}(\sum\rho_a Z_a^2)\right)^{1/2} \tag{12}$$

where ρ_a is the density of the number of ions of a-type; Z_a is the charge in atomic units; V_0 is the molar volume of the solvent; $y = m/(1 + 0.018m)$; r_0 is the radius of ion in angstroms; and m is molality.

Introducing quantities A, B, and b which depend only on the nature of the solvent and temperature, as well as parameter $\varphi = \alpha(0.018K)^{3/2}$, one can write relationship 11 as

$$\lg f^{\pm} = -\frac{Ay^{1/2}(1 + y^{3/2}\varphi)^{3/2}}{(1 + r_0By^{1/2}(1 + y^{3/2}\varphi)^{1/2})^2} + b\varphi y^2 \tag{13}$$

The values of A, B, and b for aqueous solutions at 25 °C are given in the book by K.S. Krasnov;[11] therefore, when going to the activity coefficient expressed in the molar scale $\gamma^{\pm} = f^{\pm}/(1 + 0.018m)$, we obtain the relation

$$\lg \gamma^{\pm} = -\frac{0.507y^{1/2}(1 + y^{3/2}\varphi)^{3/2}}{(1 + r_00.3287y^{1/2}(1 + y^{3/2}\varphi)^{1/2})^2} + 0.383\varphi y^2$$
$$- \lg(1 + 0.018m) \tag{14}$$

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The data derived using formula 14 as compared to the experimental data for aqueous solutions of KF, KCl, KBr, and KI are given in Figures 3a–d. In eq 14, variation parameters r_0 and φ were used; the best fit for estimated and experimental data is ensured by the following values of these quantities: $r_0 = 0.046$ Å, $\varphi = 1.81$ for KF; $r_0 = 1.74$ Å, $\varphi = 0.005$ for KCl; $r_0 = 1.91$ Å, $\varphi = 0.006$ for KBr; $r_0 = 2.15$ Å, $\varphi = 0.0145$ for KI. It should be noted that r_0 decreases from KF to KCl but increases for KCl, KBr, and KI; however, φ decreases from KI to KCl, whereas φ constants increase in the set KCl, KBr, and KI. It turned out that both expressions 1 and 9 are in good agreement with experiment. However, since only eq 9 is theoretically grounded, it should to be used in further calculations.

To calculate chemical processes occurring in solutions, one must know characteristics of individual ions, but λ from eq 9 refers to their stoichiometric mixture. However, for electrolyte molecules dissociating into ions A and B, one can find a relationship between λ and the coefficients characterizing individual ions λ_A and λ_B. Relation 9 will be considered to be applicable to both type of ions. Therefore, an expression for a biatomic molecule can be written as

$$\Delta G_2 = N_2 \lambda (\Delta h)^2 = N_2 \lambda_A (\Delta h_A)^2 + N_2 \lambda_B (\Delta h_B)^2 \quad (15)$$

where $\Delta h = \Delta h_A + \Delta h_B$. The correlation between the changes in solvation numbers Δh_A and Δh_B can be found from the condition of minimum ΔG_2 with respect to the redistribution of solvent molecules in hydration shells of ions at constant Δh.

Therefore, the right-hand side of eq 15 can be written in the form

$$\Delta G_2 = N_2 \lambda_A (\Delta h_A)^2 + N_2 \lambda_B (\Delta h - \Delta h_A)^2 \quad (16)$$

and differentiating relation 16 with respect to Δh_A we obtain

$$\left(\frac{\partial(\Delta G_2)}{\partial(\Delta h_A)} \right)_{h=h_0} = N_2 \left(\frac{\partial \lambda_A (\Delta h_A)^2}{\partial(\Delta h_A)} + \frac{\partial \lambda_B (\Delta h - \Delta h_A)^2}{\partial(\Delta h_A)} \right)_{h=h_0}$$
$$+ \left(\frac{\partial N_2}{\partial(\Delta h_A)} \right)_{h=h_0} (\lambda_A (\Delta h_A)^2$$
$$+ \lambda_B (\Delta h - \Delta h_A)^2)_{h=h_0} = 0 \quad (16a)$$

The derivative $((\partial \lambda_A (\Delta h_A)^2)/(\partial(\Delta h_A)))$ will be equal to $2\lambda_A \Delta h_A$, and the derivative $(\partial \lambda_B (\Delta h - \Delta h_A)^2)/(\partial(\Delta h_A))$ will be determined by the expression

$$\frac{\partial \lambda_B (\Delta h - \Delta h_A)^2}{\partial(\Delta h_A)} = 2\lambda_B (\Delta h - \Delta h_A) \cdot \frac{\partial(\Delta h - \Delta h_A)}{\partial(\Delta h_A)}$$
$$= -2\lambda_B (\Delta h - \Delta h_A) \quad (16b)$$

Substituting the obtained values for the derivatives into 16a, we obtain the equation

$$(\Delta h_A)^2 (\lambda_A + \lambda_B) - 2\lambda_B \Delta h \Delta h_A + \lambda_B (\Delta h)^2 = 0 \quad (17)$$

and

$$\frac{1}{\lambda} = \frac{1}{2\lambda_A} + \frac{1}{2\lambda_B} \quad (18)$$

It is expression 18 that is the formula relating the coefficients λ_A, λ_B, and λ.

It is evident that the energy of solvation shells must be taken into account when calculating the solvation energy, which is essentially a gain in the free energy obtained when a mole of the

investigated ions is transferred to solvent at a given dilution. According to Born, the estimation of solvation energy is reduced to the calculation of the difference between the energy of the electric field of ions in vacuum and in solution with a dielectric constant ε, which must lead to the relation

$$-\Delta G_S = N_A \frac{Z_i e^2}{8\pi \varepsilon_0 r_i} \left(1 - \frac{1}{\varepsilon} \right) \quad (19)$$

where Z_i and r_i are the charge and radius of ion i.

The relation for solvation enthalpy ΔH_S obtained from 19 (the Born–Bjorum formula) can be compared to the experimental data, and it is seen that the values of ΔH_S calculated using the Born formula considerably exceed the experimental data. To get a better agreement between the experimental and theoretical data, a dielectric constant ε_{0h} for solvation shell is introduced assuming that it allows one to take into account the changes occurring in the solution close to ion. Such an approach gives the following relation

$$-\Delta G_S = \frac{Z_i e^2}{8\pi \varepsilon_0 r_i} \left(\frac{1}{r_i} \left(1 - \frac{1}{\varepsilon_{0h}} \right) + \frac{1}{\rho_{0h}} \left(\frac{1}{\varepsilon_{0h}} - \frac{1}{\varepsilon} \right) \right) N_A \quad (20)$$

where ρ_{0h} is the radius within which $\varepsilon = \varepsilon_{0h}$. A disadvantage of such an approach is the uncertainty of parameters ε_{0h} and ρ_{0h}. Making use of formula 5 makes it possible to obtain the change in the free energy of the nearest to ion solvation shell after introduction to the solvent of ions in the form

$$\Delta G_{2,0} = -\lambda h_1^2 N_2 \quad (21)$$

where h_1 is the solvation number for the first solvation shell. Then, considering that outside the nearest solvation shell of ion with the radius of the solvation shell ρ_i, one can use the Born method and obtain the expression

$$-\Delta G_{S,i} = \left(\lambda_i h_{1,i}^2 + \frac{Z_i e^2}{4\pi \varepsilon_0 \rho_i} \left(1 - \frac{1}{\varepsilon} \right) \right) N_A \quad (22)$$

in which the values of radii of the solvation ionic shells can be obtained from ultrasonic measurements.[17]

Assessment made by us of the sum ΔG_S of sodium and chlorine ions in aqueous solutions showed a satisfactory feasibility of the given approach. However, the values $\lambda_{1,i}$ and $h_{1,i}$ have to be known to calculate exactly the hydration energies of separate ions, whereas ultrasound experiments give only parameters λ_0 and h_0 referring to their stoichiometric mixture.

III. ION–DIPOLE AND DIPOLE–DIPOLE SOLVATION

Further research of the solvation and properties of electrolytes and nonelectrolytes was made using the approach described in a paper[7] based on the classical thermodynamic treatment of two states of water. One includes free molecules of water outside the hydration shell and the other the bound molecules of water within the hydration environments of ions or molecules. It was suggested that the volume of the solution obeys the equation

$$V_m = (x_1 - h x_2) \cdot V_1^* + x_2 V_h \quad (23)$$

where V_m is the molar volume of the solution; V_1^* is the volume of a mole of "free" solution (which did not enter the hydration shells of the stoichiometric mixture of ions); V_h is the volume of a mole of hydration complexes; x_1 and x_2 are the molar

fractions of the solvent and the solute, respectively; and h is the hydration number. Hydration number in this case means the number of water molecules per one molecule of the solute whose density and compressibility is considerably different from the density and compressibility of the pure solvent. As is seen from eq 23 the theory used by us does not assume the solution to be ideal since in the ideal solution its volume is the sum of the volumes of the solvent and the solute. The method is based on the adiabatic compressibility of aqueous solutions of electrolytes and nonelectrolytes which presumes that compressibility is decreased with the increase of the concentration of the solute. In the given equation, the main assumption is connected with the fact that all the properties of the solvent not involved in the hydration shell are the same as those of the pure solvent. Differentiating expression 23 with respect to pressure p at constant entropy of solution S_m, and assuming that in an acoustic experiment h is but little dependent on pressure, we obtain the expression for the molar adiabatic compressibility of the solution

$$(\partial V_m/\partial p)_{S_m} = (x_1 - h x_2)\cdot(\partial V_1^*/\partial p)_{S_m} + x_2\cdot(\partial V_h/\partial p)_{S_m} \quad (24)$$

In this expression, the quantity $(\partial V_1^*/\partial p)_{S_m}$ characterizes the molar compressibility of the "free" solvent in solution, and its amount is determined by the number of moles $(x_1 - h x_2)$ of the solvent left over after hydration.

An assumption was made in ref 5 about the equality of the pressure derivatives of the molar volume of the solvent at constant entropy of the solution S_m and the solvent S_1^*: $(\partial V_1^*/\partial p)_{S_m} = (\partial V_1^*/\partial p)_{S_1^*}$. However, it is evident that the adiabatic compressibilities of the solvent in these cases are determined under different conditions. For the quantity $(\partial V_1^*/\partial p)_{S_m}$, the condition of the constant entropy of the solution is met S_m = const, while for the quantity $(\partial V_1^*/\partial p)_{S_1^*}$ it is the condition of the constant entropy of the solvent S_1^* = const. Since the equilibrium state of the system is determined by a set of independent variables (T, p, x_2) and the solution entropy is a function of these variables, it is evident that every solution composition will have its own entropy. All of the above casts some doubt on the possibility to replace the compressibility of the solvent outside hydration shells by the compressibility of pure water. This, in its turn, makes the results obtained by the method of adiabatic compressibility rather questionable. The fallacy of the relationship $(\partial V_1^*/\partial p)_{S_m} = (\partial V_1^*/\partial p)_{S_1^*}$ was pointed out by Blandamer when he was investigating the apparent molar compressibility of the solute[18] $\varphi_{K,S}$. Therefore, to obtain correct results, one must solve the problem of determining the quantity $(\partial V_1^*/\partial p)_{S_m}$. The calculation of this derivative presents some difficulties since it can not be determined directly from "experimental" data using the method of Newton—Laplace. It is our opinion that the best solution would be to obtain an expression relating the pressure derivative of the molar volume of pure solvent at constant entropy of the solution S_m with the derivative of the molar volume of pure solvent at constant entropy of the solvent S_1^*.[19]

Let us demonstrate the simplest and the most consistent method of obtaining an expression relating the adiabatic compressibility of the "free" solvent to the adiabatic compressibility of a pure solvent. In our opinion, the most correct solution to this problem would be to obtain an equation relating the molar adiabatic compressibility of the "free" solvent at constant entropy of solution to the molar adiabatic compressibility of the pure solvent. The first term in the right-hand part of this equation will denote the compressibility of the pure solvent, while the rest of

the terms will be responsible for the change in its compressibility when the entropy of the solution is changed. When using the Jacobinian method, one presumes that all the quantities in the derivative $-(\partial V_1^*/\partial p)_{S_m}$ must be functions of the new variables p and S_1^* at constant electrolyte concentration. While there is no doubt that the quantities V_1^* and p are related to the new variables p and S_1^*, the answer to the question whether the entropy of solution is a function of the entropy of the pure solvent is not so evident. To avoid an incorrect application of the Jacobinians method, we perform a two-stage changeover from the variables p and S_m. At the first stage we go from the adiabatic compressibility of the solvent at constant solution entropy to its molar isothermic compressibility $-(\partial V_1^*/\partial p)_T$ at constant electrolyte concentration. It is evident that in this case all the quantities in the derivative $((\partial V_1^*)/(\partial p))_{S_m}$ are functions of temperature and pressure only (at x_2 = const), and hence, the Jacobinians method can be used

$$(\partial V_1^*/\partial p)_{S_m} = \frac{\partial(V_1^*, S_m)}{\partial(P, S_m)} = \frac{\dfrac{\partial(V_1^*, S_m)}{\partial(p, T)}}{\dfrac{\partial(p, S_m)}{\partial(p, T)}}$$

$$= \frac{\begin{vmatrix} (\partial V_1^*/\partial p)_T & (\partial V_1^*/\partial T)_p \\ (\partial S_m/\partial p)_T & (\partial S_m/\partial T)_p \end{vmatrix}}{\begin{vmatrix} (\partial p/\partial p)_T & (\partial p/\partial T)_p \\ (\partial S_m/\partial p)_T & (\partial S_m/\partial T)_p \end{vmatrix}}$$

$$= \frac{(\partial V_1^*/\partial p)_T\cdot(\partial S_m/\partial T)_p - (\partial V_1^*/\partial T)_p\cdot(\partial S/\partial p)_T}{(\partial p/\partial p)_T\cdot(\partial S_m/\partial T)_p - (\partial p/\partial T)_p\cdot(\partial S_m/\partial p)_T}$$

$$(25)$$

The expression 25 can be essentially simplified. Since the free Gibbs energy G is a function of state and its differential for a closed system (i.e., a system that does not exchange matter with its environment), $dG = -S dT + V dp$ is a total differential, and one of the Maxwell relationships must be met $-(\partial S_m/\partial p)_T = (\partial V_m/\partial T)_p$. Moreover, it is evident that the quantity $(\partial p/\partial p)_T$ equals unity, and the quantity $(\partial p/\partial T)_p$ equals zero. In view of these remarks, the relationship 25 can be written as

$$(\partial V_1^*/\partial p)_{S_m} = (\partial V_1^*/\partial p)_T + \frac{(\partial V_1^*/\partial T)_p\cdot(\partial V_m/\partial T)_p}{(\partial S_m/\partial T)_p} \quad (26)$$

The quantity $-(\partial V_1^*/\partial p)_T$ in eq 26 is the molar isothermic compressibility of the "free" solvent, but since all the quantities included in it (volume V_1^*, pressure p, and temperature T) are the same as for the pure solvent, it can be considered equal to the molar isothermic compressibility of the pure solvent.

At the second stage, we again use the Jacobenians method to obtain an expression relating partial derivatives of the pure solvent $(\partial V_1^*/\partial p)_T$ and $(\partial V_1^*/\partial p)_{S_1^*}$

$$(\partial V_1^*/\partial p)_{S_1^*} = \frac{\partial(V_1^*, S_1^*)}{\partial(p, S_1^*)} = \frac{\dfrac{\partial(V_1^*, S_1^*)}{\partial(p, T)}}{\dfrac{\partial(p, S_1^*)}{\partial(p, T)}} = \frac{\begin{vmatrix} (\partial V_1^*/\partial p)_T & (\partial V_1^*/\partial T)_p \\ (\partial S_1^*/\partial p)_T & (\partial S_1^*/\partial T)_p \end{vmatrix}}{\begin{vmatrix} (\partial p/\partial p)_T & (\partial p/\partial T)_p \\ (\partial S_1^*/\partial p)_T & (\partial S_1^*/\partial T)_p \end{vmatrix}}$$

$$= \frac{(\partial V_1^*/\partial p)_T\cdot(\partial S_1^*/\partial T)_p - (\partial V_1^*/\partial T)_p\cdot(\partial S_1^*/\partial p)_T}{(\partial p/\partial p)_T\cdot(\partial S_1^*/\partial T)_p - (\partial p/\partial T)_p\cdot(\partial S_1^*/\partial p)_T} \quad (27)$$

The expression 27 can also be simplified taking into the account the condition of total differential, as well as the fact that some of

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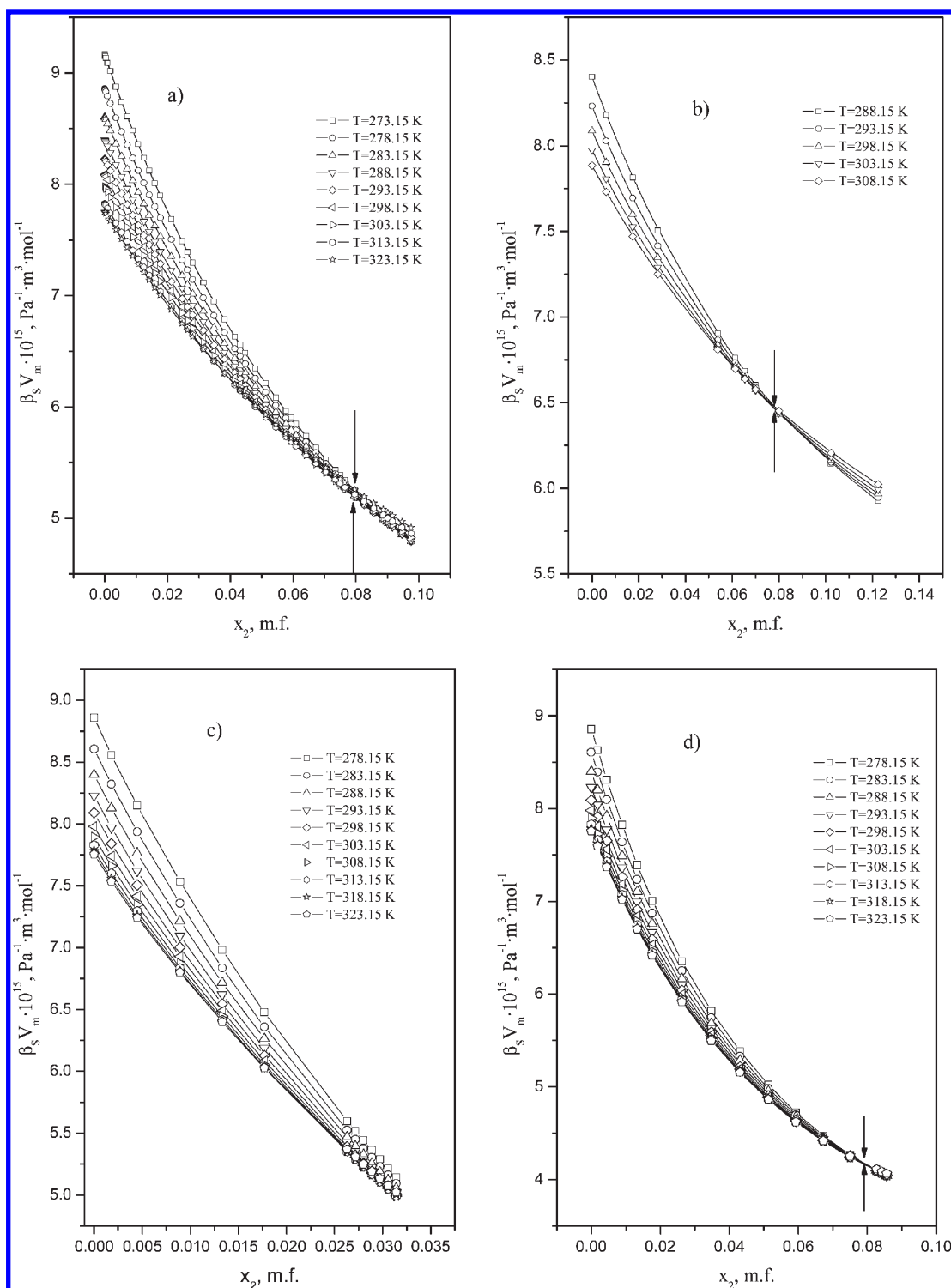
Figure 4. Concentration dependence of the molar adiabatic compressibility at various temperatures in aqueous solutions of: (a) NaCl; (b) KI; (c) MgSO$_4$; and (d) MgCl$_2$.

the partial derivatives equal zero or unity.

$$(\partial V_1^*/\partial p)_T = (\partial V_1^*/\partial p)_{S_1^*} - \frac{(\partial V_1^*/\partial T)_p^2}{(\partial S_1^*/\partial T)_p} \quad (28)$$

The expression relating the molar adiabatic compressibility of the free solvent $-(\partial V_1^*/\partial p)_{S_m}$ to the compressibility of pure water $-(\partial V_1^*/\partial p)_{S_1^*}$ is obtained by substituting the relationship

28 into eq 26

$$-(\partial V_1^*/\partial p)_{S_m} = -(\partial V_1^*/\partial p)_{S_1^*}$$
$$+ (\partial V_1^*/\partial T)_p \cdot \left[\frac{(\partial V_1^*/\partial T)_p}{(\partial S_1^*/\partial T)_p} - \frac{(\partial V_m/\partial T)_p}{(\partial S_m/\partial T)_p} \right]$$
$$(29)$$

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If partial derivatives from eq 29 can be interpreted as quantities experimentally determined $(\alpha_1^* = [1/(V_1^*)](\partial V_1^*/\partial T)_p$, the thermal expansion coefficient of the solvent; $\alpha_m = [1/(V_m)](\partial V_m/\partial T)_p$, the thermal expansion coefficient of the solution determined from the temperature dependencies of the solvent and solution; $C_{1,P}^* = T \cdot (\partial S_1^*/\partial T)_p$, the isobar heat capacity of the solvent; $C_{m,p} = T \cdot (\partial S_m/\partial T)_p$, the isobar heat capacity of the solution determined by calorimetric studies; and $\beta_1^* = -[1/(V_1^*)]((\partial V_1^*)/(\partial P))_{S_1^*}$, the coefficient of adiabatic compressibility of the pure solvent obtained using the Newton—Laplace equation $\beta_S = (1/(\rho U^2))$, where U is the speed of ultrasound propagation and ρ is density), then eq 29 can be written as

$$\beta_1 V_1^* = \beta_1^* V_1^* + \alpha_1^* V_1^* T \cdot \left[\frac{\alpha_1^*}{\sigma_1^*} - \frac{\alpha_m}{\sigma_m}\right] \qquad (29a)$$

In view of the above, expression 24 can be rewritten as

$$\beta_S V_m = (x_1 - hx_2) \cdot \beta_1^* V_1^* + (x_1 - hx_2) \cdot \alpha_1^* V_1^* T \cdot \left[\frac{\alpha_1^*}{\sigma_1^*} - \frac{\alpha_m}{\sigma_m}\right]$$
$$+ x_2 \cdot \beta_h V_h \qquad (30)$$

where $\beta_S V_m = -(\partial V_m/\partial p)_{S_{aq}}$ is the molar adiabatic compressibility of the solution; $\beta_1^* V_1^*$ is the molar adiabatic compressibility of the pure solvent; $\beta_h V_h = -(\partial V_h/\partial p)_{S_{aq}}$ is the molar adiabatic compressibility of hydration complexes; and the ratio of heat capacity to molar volume for the pure solvent and solution is $\sigma_1^* = C_{1,p}^*/V_1^*$ and $\sigma_m = C_{m,p}/V_m$. Substituting expression 30 into the equation $\varphi_{K,S} = [\beta_S V_m - x_1 \cdot \beta_1^* V_1^*]/x_2$ and introducing a new variable $Y_{K,S}$, one obtains an equation to determine the hydration number of electrolyte ions or nonelectrolyte molecules (h), as well as the adiabatic compressibility of hydration complexes ($\beta_h V_h$)

$$Y_{K,S} = -h\left(\beta_1^* V_1^* + \alpha_1^* V_1^* T \cdot \left[\frac{\alpha_1^*}{\sigma_1^*} - \frac{\alpha_m}{\sigma_m}\right]\right) + \beta_h V_h \qquad (31)$$

where $Y_{K,S} = \varphi_{K,S} - (x_1/x_2)\alpha_1^* V_1^* T \cdot ((\alpha_1^*/\sigma_1^*) - (\alpha_m/\sigma_m))$ or as a linear dependence

$$Y_{K,S} = -h \cdot \beta_1 V_1^* + \beta_h V_h \qquad (32)$$

where $\beta_1 V_1^* = \beta_1^* V_1^* + \alpha_1^* V_1^* T \cdot [(\alpha_1^*/\sigma_1^*) - (\alpha_m/\sigma_m)]$. Equation 32 is the main one for determining hydration numbers and the molar adiabatic compressibility of hydration complexes of electrolytes and nonelectrolytes. The variable $\beta_1 V_1^*$ in eq 32 is the molar adiabatic compressibility of the "free" solvent at constant entropy of solution, and $Y_{K,S}$ plays the part similar to the apparent molar compressibility with correction $(x_1/x_2) \cdot \alpha_1^* V_1^* T \cdot [(\alpha_1^*/\sigma_1^*) - (\alpha_m/\sigma_m)]$. It can be shown that $Y_{K,S}$ is a derivative of the apparent molar volume of the solute with respect to pressure at constant entropy of solution. Differentiating with respect to pressure of the known expression for the apparent volume of the solute enables one to write the quantity $-(\partial \varphi_V/\partial p)_{S_m}$ as

$$-(\partial \varphi_V/\partial p)_{S_m} = -\frac{1}{x_2}(\partial V_m/\partial p)_{S_m} + \frac{x_1}{x_2}(\partial V_1^*/\partial p)_{S_m} \qquad (33)$$

The expression for the apparent adiabatic compressibility written in partial derivatives has the form

$$\varphi_{K,S} = -\frac{1}{x_2}(\partial V_m/\partial p)_{S_m} + \frac{x_1}{x_2}(\partial V_1^*/\partial p)_{S_1^*} \qquad (34)$$

When eq 33 is compared to eq 34, it is apparent that the only difference between the two is that in the right-hand side of eq 33
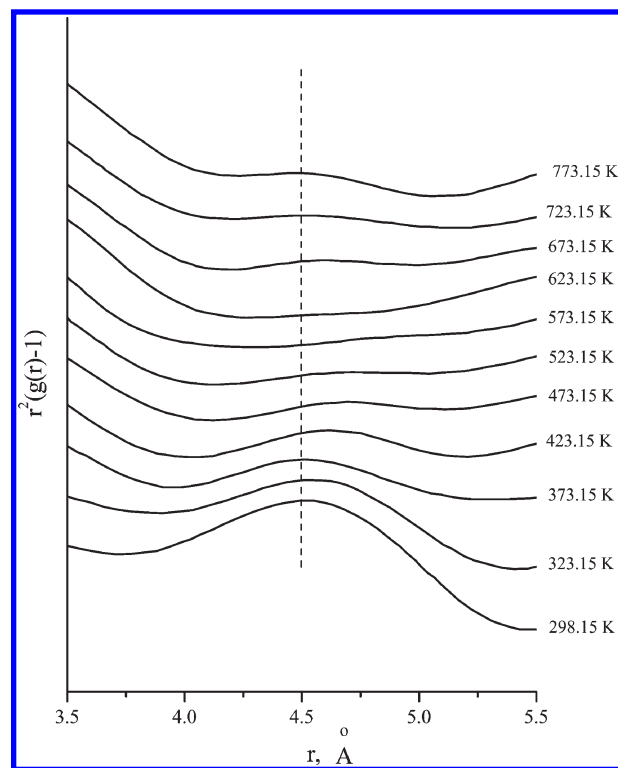

Figure 5. Temperature dependence of the pair correlation functions of water at 1000 atm.[24]

is the derivative $-(\partial V_1^*/\partial p)_{S_m}$, whereas in the right-hand side of eq 34 is the derivative $-(\partial V_1^*/\partial p)_{S_1^*}$. These quantities, in their turn, were shown in eq 29a to differ by the term $\alpha_1^* V_1^* T \cdot [(\alpha_1^*/\sigma_1^*) - (\alpha_m/\sigma_m)]$.

Therefore, the derivative of the molar adiabatic volume of the solute is related to its apparent adiabatic compressibility by the expression 35

$$-(\partial \varphi_V/\partial p)_{S_m} = \varphi_{K,S} - \frac{x_1}{x_2}\alpha_1^* V_1^* T \cdot \left[\frac{\alpha_1^*}{\sigma_1^*} - \frac{\alpha_m}{\sigma_m}\right] \qquad (35)$$

Comparison of eqs 35 and 31 leads to the conclusion that $Y_{K,S} = -(\partial \varphi_V/\partial p)_{S_m}$ and hence

$$-\left(\frac{\partial \varphi_V}{\partial p}\right)_{S_m} = -h\beta_1 V_1^* + \beta_h V_h \qquad (36)$$

The quantity $\beta_h V_h$, according to the assumptions used, is equal to the sum of two quantities: the molar adiabatic compressibility of a stoichiometric mixture of electrolyte ions without hydration shells ($\beta_{2h} V_{2h}$) and water in hydration shells ($\beta_{1h} V_{1h}$)

$$\beta_h V_h = \beta_{2h} V_{2h} + h \cdot \beta_{1h} V_{1h} \qquad (37)$$

Since the apparent molar volume is determined by the expression

$$\varphi_V = (V_m - x_1 V_1^*)/x_2 \qquad (38)$$

then by substituting eq 23 into 38 we obtain the equation for the apparent molar volume of the hydration complex

$$\varphi_V = -hV_1^* + V_h \qquad (39)$$

Since the molar volume of the hydration complex can be expanded into the molar volume of the stoichiometric mixture

Table 1. Concentration Dependence of the Molar Adiabatic Compressibility of Hydration Complexes $\beta_h V_h$, Hydration Numbers h, and the Coefficients of Linear Correlation $R_{corr.}$ for Aqueous Solutions of NaCl, KI, NaNO$_3$, KI, MgCl$_2$, and MgSO$_4$ up to the Complete Solvation Limit

m, mol kg^{-1}	$\beta_h V_h \cdot 10^{14}$, Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1}	h	$R_{corr.}$
	NaCl		
0.001	15.718	25.28	−0.9996
0.002	15.702	25.26	−0.9996
0.005	15.667	25.21	−0.9996
0.01	15.621	25.14	−0.9996
0.02	15.547	25.04	−0.9997
0.05	15.369	24.78	−0.9997
0.1	15.119	24.42	−0.9998
0.2	14.686	23.80	−0.9998
0.3	14.297	23.24	−0.9998
0.4	13.936	22.72	−0.9999
0.5	13.598	22.23	−0.9999
0.6	13.277	21.77	−0.9999
0.7	12.972	21.33	−0.9999
0.8	12.680	20.90	−0.9999
0.9	12.402	20.49	−0.9999
1.0	12.134	20.10	−0.9998
1.2	11.630	19.36	−0.9998
1.4	11.162	18.67	−0.9998
1.5	10.940	18.34	−0.9997
1.6	10.726	18.02	−0.9997
1.8	10.320	17.42	−0.9996
2.0	9.939	16.85	−0.9996
2.2	9.582	16.31	−0.9995
2.4	9.246	15.80	−0.9995
2.5	9.086	15.56	−0.99934
2.6	8.930	15.32	−0.9993
2.8	8.632	14.87	−0.9993
3.0	8.351	14.43	−0.9992
3.2	8.084	14.03	−0.9991
3.4	7.833	13.64	−0.9990
3.5	7.712	13.45	−0.9990
3.6	7.594	13.27	−0.9990
3.8	7.367	12.91	−0.9989
4.0	7.152	12.58	−0.9988
4.2	6.948	12.25	−0.9987
4.4	6.753	11.95	−0.9987
4.5	6.659	11.80	−0.9987
4.6	6.567	11.65	−0.9986
4.8	6.391	11.37	−0.9986
5.0	6.222	11.10	−0.9985
	KCl		
0.6	11.700	18.83	−0.99935
0.8	11.188	18.08	−0.99948
1	10.678	17.34	−0.99955
1.5	9.582	15.73	−0.99973
2	8.631	14.31	−0.99983
2.5	7.815	13.09	−0.99991
3	7.105	12.00	−0.99995

Table 1. Continued

m, mol kg^{-1}	$\beta_h V_h \cdot 10^{14}$, Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1}	h	$R_{corr.}$
3.5	6.480	11.05	−0.99998
4	5.946	10.22	−1
	KI		
0.343	16.315	22.59	−0.9985
0.987	14.014	19.60	−0.9992
1.613	12.726	17.86	−0.9997
3.161	10.125	14.34	−0.9997
3.622	9.440	13.42	−0.9997
3.887	9.144	13.01	−0.9996
4.181	8.805	12.54	−0.9997
	NaNO$_3$		
0.24011	16.867	25.21	−0.9999
0.49023	15.779	23.67	−0.9998
0.75099	14.701	22.14	−0.9997
1.02308	13.732	20.75	−0.9996
1.30727	12.818	19.43	−0.9995
1.60438	11.969	18.18	−0.9996
1.9153	11.141	16.98	−0.9997
2.24104	10.449	15.93	−0.9998
2.58266	9.768	14.90	−0.9999
	MgCl$_2$		
0.1	16.975	32.35	−0.9991
0.25	16.352	31.15	−0.9993
0.5	15.263	29.22	−0.9996
0.75	14.131	27.32	−0.9998
1.0	13.050	25.52	−1
1.5	11.166	22.36	−1
2.0	9.660	19.78	−1
2.5	8.461	17.66	−1
3.0	7.493	15.91	−1
3.5	6.700	14.43	−1
4.0	6.041	13.18	−1
4.5	5.490	12.11	−1
	MgSO$_4$		
0.25	19.410	38.88	−0.9989
0.5	17.696	35.77	−0.9989
0.75	16.427	33.49	−0.9989
1.0	15.343	31.56	−0.9988
1.5	13.513	28.30	−0.9985
1.55	13.350	28.01	−0.9985
1.6	13.191	27.72	−0.9984
1.65	13.034	27.44	−0.9984
1.7	12.881	27.16	−0.9984
1.75	12.731	26.89	−0.9983
1.8	12.583	26.62	−0.9983

of electrolyte ions without hydration shells (or a nonelectrolyte molecule) V_{2h} and the molar volume of water in hydration shell V_{1h} (with allowance made for h, the number of water molecules in the hydration shell)

$$V_h = V_{2h} + hV_{1h} \qquad (40)$$

then introducing expression 40 into relationship 39 we obtain an equation for the molar volume of the stoichiometric mixture of
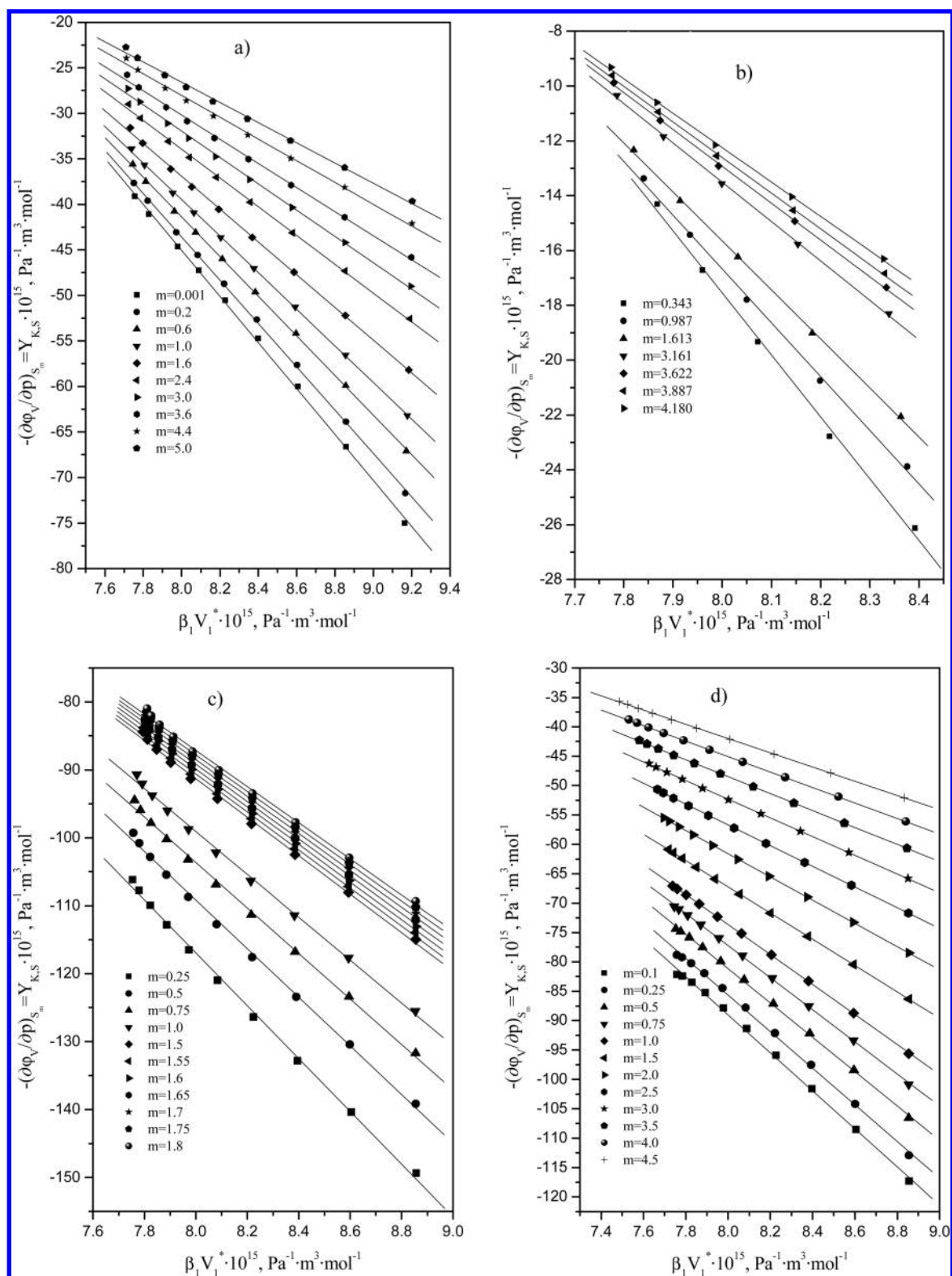
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Figure 6. Linear dependence of the function $Y_{K,S}$ on the molar adiabatic compressibility of the free solvent $\beta_1 V_1^*$ at various concentrations: (a) for aqueous solutions of NaCl; (b) for KI; (c) for MgSO$_4$; and (d) for MgCl$_2$.

ions without hydration shells (or molecules of nonelectrolyte) V_{2h} and the molar volume of hydration water (V_{1h})

$$\varphi_V = V_{2h} - h(V_1^* - V_{1h}) \qquad (41)$$

where $(V_1^* - V_{1h})$ determines the volumetric compression of water in a hydration shell. Thus, the use of eq 37 in combination with eq 41 gives a way of determining the compressibility coefficient of the stochiometric mixture of ions (β_{2h}) and, which
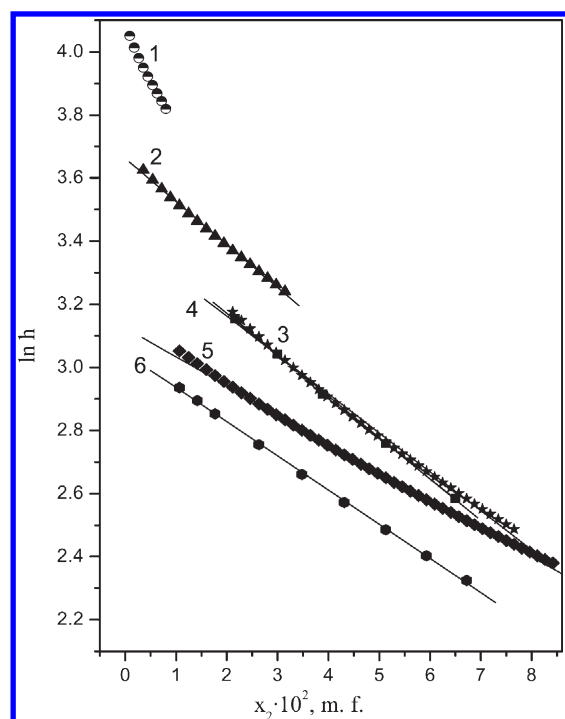
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Figure 7. Concentration dependence of hydration numbers for aqueous solutions of: 1, Na_2SO_4; 2, $MgSO_4$; 3, $MgCl_2$; 4, $CaCl_2$; 5, NaCl; 6, KCl.

Figure 8. Dependence of the molar adiabatic compressibilities of hydration complexes on hydration numbers in aqueous solutions of potassium iodide, sodium nitrate, sodium and potassium chlorides, magnesium chloride, and sulfate.

is especially important, the compressibility coefficient and molar volume of the solvent in hydration shells (β_{1h}, V_{1h}). With the increase of temperature, the change in the molar adiabatic compressibility of a hydration complex $\beta_h V_h$ is negligible compared to the change in the molar adiabatic compressibility of the "free" water $\beta_1 V_1^*$; therefore, it would be appropriate to study the dependence of the apparent molar compressibility $\varphi_{K,S}$ on temperature at constant concentration of the solute rather than the concentration dependence $\beta_S V_m$ at constant temperature. Since in the present paper the function $Y_{K,S}$ is similar to the apparent molar compressibility and variable $\beta_1 V_1^*$ is the molar adiabatic compressibility of the free solvent in solution, the dependence $Y_{K,S} = f(\beta_1 V_1^*)$ was investigated at a fixed concentration of the solute with the purpose of determining h (Figure 6).

IV. INFLUENCE OF THE SOLVENT ON THE PROCESS OF SOLVATION

The application of the present approach over a wider range of conditions and estimation of structural characteristics of the complexes of the solute which are formed require precision experimental measurements. The work involved the measurement of the speed of sound (U), density (ρ),[20,21] and the isobar heat capacity[22] over a wide range of concentrations and temperatures.

The experimentally derived data were used to calculate molar coefficients of adiabatic compressibility ($\beta_S V_m$) which, according to the terminology introduced in our works, are rational parameters. The molar adiabatic compressibility ($\beta_S V_m$) of aqueous solutions of $NaNO_3$, KI, NaCl, KaCl, $MgCl_2$, and $MgSO_4$ in water was shown to decrease up to the complete solvation limit as the temperature and electrolyte concentration increases (Figure 4). The way these factors affect the compressibility of
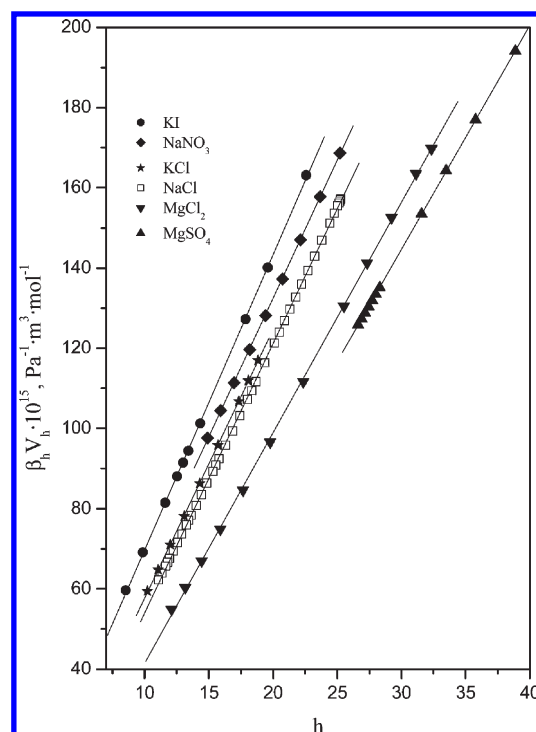
the solution can be expressed in terms of the vibrational and configurational contributions similar to the temperature dependence of the compressibility of water

$$\beta_S V_m = (\beta_S V_m)_{vib} + (\beta_S V_m)_{conf} \qquad (42)$$

where $(\beta_S V_m)_{vib}$ is the vibrational contribution due to intermolecular thermal vibrations, and $(\beta_S V_m)_{conf}$ is the configurational contribution which, according to the bistructural Hall's model, is due to the equilibrium shift between the spatial structure of water (with tetrahedral coordination) and the close-packed phase. As the temperature rises, the vibrational contribution to $\beta_S V_m$ increases due to thermal expansion, which causes the increased compressibility, whereas the configurational one decreases due to the equilibrium shift toward closer packing, which leads to decreased compressibility. At low temperatures, the second process plays the main part. Therefore, up to the complete solvation limit, the decrease of the molar compressibility of the solution in the temperature range studied is attributed to the dominant role of the configurational contribution.[23] Figure 4 shows that the complete solvation limit for aqueous solutions of NaCl, KI, and $MgCl_2$ is reached at the concentration of about $x_2 = 0.08$ where dependencies $\beta_S V_m = f(x_2)$ at different temperatures intersect at one point.

It is to be noted that compressibility of water has some peculiarities due to structural transformations of the net of hydrogen bonds affecting the compressibility of hydration shells of ions. One of them is the temperature dependence of the compressibility coefficient of water having a minimum at 338.15K (β_S), and another is related to the minimum of the molar adiabatic compressibility at 329.15 K ($\beta_S V_m$). The last one manifests itself when studying the temperature dependence of
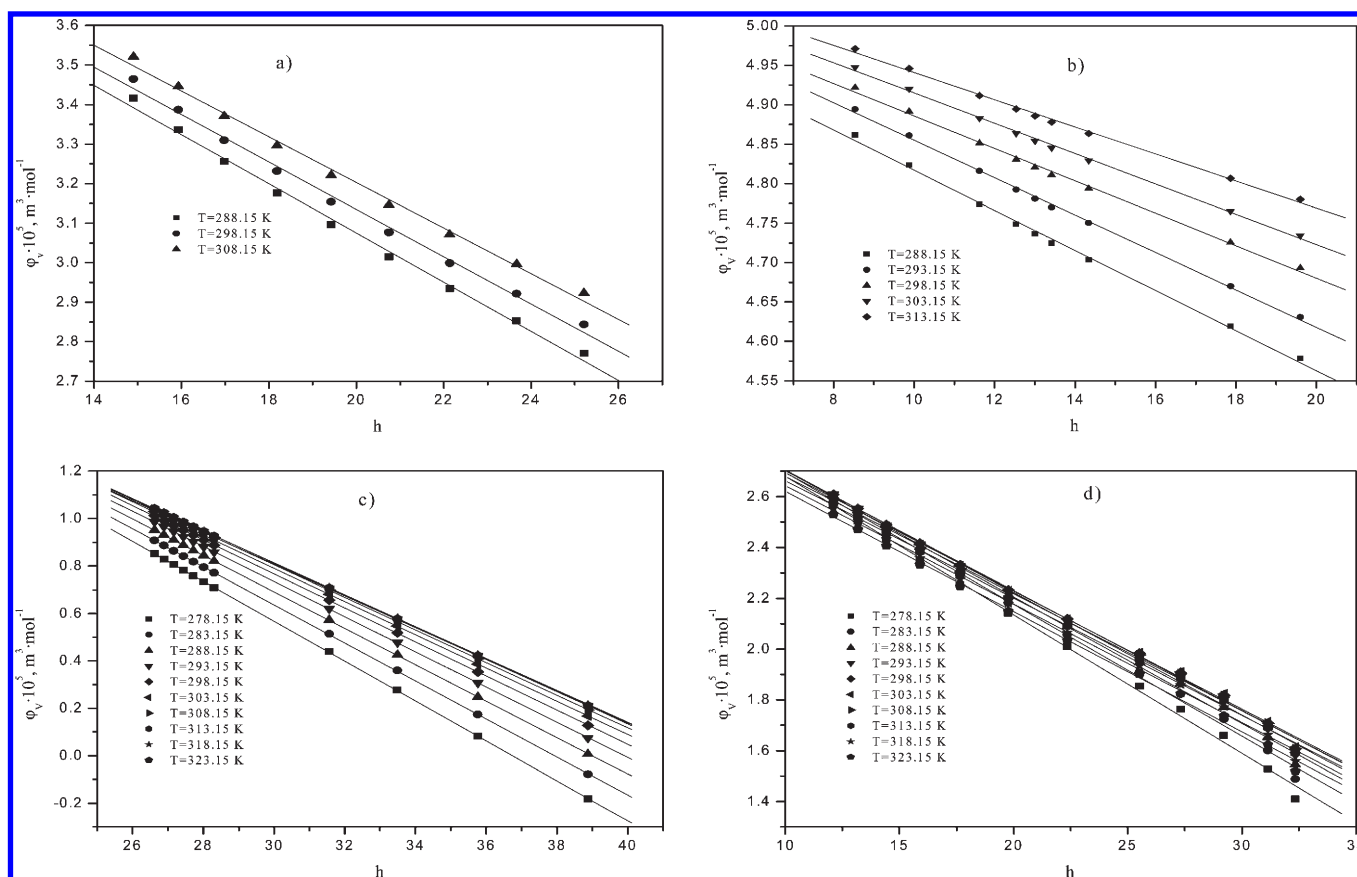
Figure 9. Dependence of the apparent molar volume of the solute φ_V on the hydration number h in aqueous solutions of: (a) $NaNO_3$; (b) KI; (c) $MgSO_4$; and (d) $MgCl_2$.

the function of radial distribution at high pressures (Figure 5) when the destruction of the tetrahedral structure of water (the decreased peak 4.5 A) is replaced by its stabilization (the increased peak at $T > 573.15$ K)[24] as the temperature is increased.

We believe that this effect might be exhibited not just in supercritical conditions. It may occur in hydration shells of ions close to normal temperatures as well. Electrostriction producing high pressure around an ion reduces the possibility of forming tetrahedral structure of water, and a considerable increase of the kinetic energy of the solvent molecules is required for the tetrahedral structure to be achieved again. This may be accompanied by an additional increase of the molar volume of water in a hydration shell with the increase of temperature, which is observed in the dependence $V_{1h} = f(T)$ in aqueous solutions of halogenides, nitrates, and sulfates of alkali and even alkaline-earth metals (Figures 8 and 11).

Water in solution up to the complete solvation limit can be considered both as a free solvent not bound to an ion or molecule of the solute and as hydration water in electrostriction solvated state of electrolytes and nonelectrolytes.

Pure water is itself quite a complex structure, having increased dielectric properties, a high dissolving capacity, and low-frequency vibration of H_2O molecules in gaseous and in liquid phases. Of special interest is the recently discovered effect of selective solvation of water with respect to the solute due to the rotational moment of its ortho-isomers that have a greater mobility than para-isomers favoring complex formation.[25] Thus, up to the complete solvation level, water is in two states, in a free

state and bound to an ion or molecule of nonelectrolyte, and in this case, a thermodynamic analysis enables one to determine the solvation numbers and molar compressibility of its hydration complexes.

As the concentration of electrolytes or nonelectrolytes is increased, the dependencies of adiabatic compressibility $\beta_S V_m = f(x_2)$ at various temperatures approach each other, and at the point of intersection quantities $\beta_S V_m$ become independent of the temperature (Figure 4). The relation $x_1 = h \cdot x_2$ is the complete solvation limit: $V_h = (V_m/x_2)$, $\beta_S V_m = x_2 \cdot \beta_h V_h \rightarrow \beta_S = \beta_h$. The interval of permissible concentrations turns out to be quite wide —from diluted solution to quite considerable molal concentrations (e.g., NaCl, 5.1 m; KI, 4.18 m; $MgCl_2$, 4.5 m, etc.)—and considerably exceeds the range evaluated by the Debye−Hückel method even with semiempirical assumptions. It should be noted that at this point the value of β_S coincides with the compressibility of the solute β_h, and thus the compressibility of the hydration complex formed can be estimated. In this case of greatest interest is the increased range of concentrations of the solute from zero to the complete solvation limit (the concentration range of, e.g., NaCl is increased at least 5000 times) where it becomes possible to calculate the solvation numbers and compressibilities of the hydration complex.[26] Table 1 lists the results for NaCl, KCl, $NaNO_3$, KI, and $MgCl_2$ up to the complete solvation limit, the concentration of $MgSO_4$ unfortunately not reaching this limit. After the complete solvation limit, when the solute is completely solvated by the solvent ($x_1 = h \cdot x_2$) and water, which acts as a solvent, and is still in the hydration shell of

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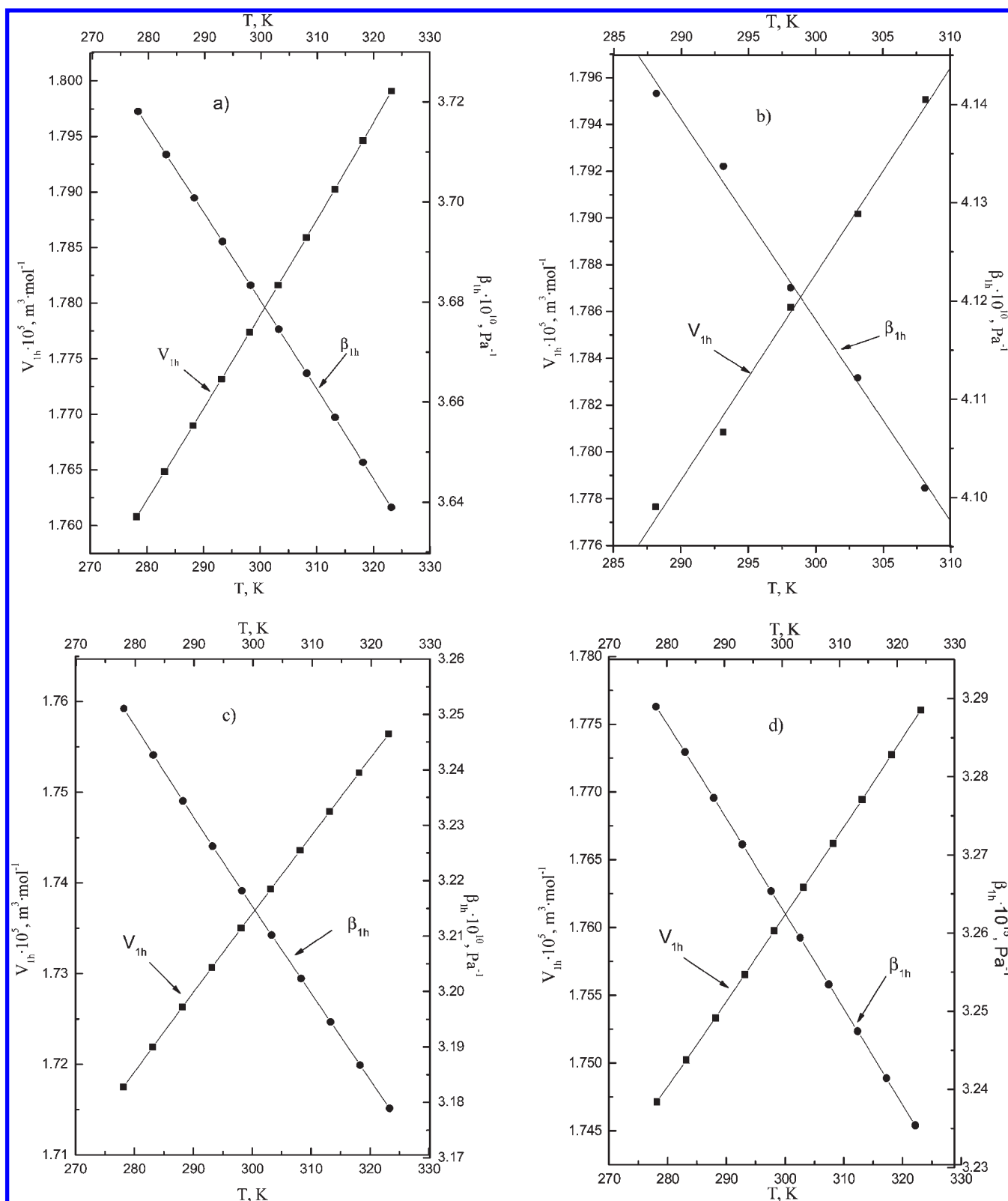
Figure 10. Temperature dependence of the molar volume V_{1h} and compressibility coefficient β_{1h} of water in hydration complexes of: (a) NaCl; (b) KI; (c) MgSO$_4$; and (d) MgCl$_2$.

the electrolyte or nonelectrolyte, the solvation number is gradually decreased with concentration because the ion or molecule no longer retains water in its inner sphere. The latter effect takes place even when the additional electrolyte or nonelectrolyte is added to the aqueous solution after the complete solvation limit is reached: $(C_{CLS})/(C_{CLS} + C_{ADD})$.

Table 2. Volumetric Compression $(V_1^* - V_{1h})$, Volume V_{1h}, and Compressibility β_{1h} of Water in Hydration Shells and Volume V_{2h} and Compressibility β_{2h} of the Stoichiometric Mixture of Ions without Hydration Shells

T, K	$(V_1^* - V_{1h}) \cdot 10^7$, m^3/mol	$V_{1h} \cdot 10^5$, m^3/mol	$\beta_{1h} \cdot 10^{10}$, Pa^{-1}	$V_{2h} \cdot 10^5$, m^3/mol	$\beta_{2h} \cdot 10^{10}$, Pa^{-1}
		NaCl			
273.15	4.345	1.758	3.821	2.408	5.495
278.15	3.923	1.762	3.812	2.407	5.496
283.15	3.562	1.766	3.803	2.406	5.499
288.15	3.254	1.771	3.794	2.405	5.501
293.15	3.000	1.775	3.785	2.404	5.504
298.15	2.781	1.779	3.776	2.403	5.505
303.15	2.607	1.783	3.767	2.403	5.505
313.15	2.366	1.792	3.749	2.407	5.498
323.15	2.242	1.801	3.730	2.414	5.482
		KCl			
283.15	3.459	1.767	3.787	3.365	2.748
288.15	3.182	1.771	3.778	3.372	2.742
293.15	2.946	1.775	3.770	3.376	2.739
298.15	2.743	1.779	3.761	3.377	2.738
303.15	2.593	1.783	3.753	3.379	2.737
308.15	2.481	1.787	3.744	3.380	2.736
		KI			
288.15	2.539	1.778	4.141	5.071	6.850
293.15	2.372	1.781	4.134	5.092	6.822
298.15	2.056	1.786	4.121	5.091	6.823
303.15	1.920	1.790	4.112	5.107	6.802
308.15	1.720	1.795	4.101	5.113	6.794
		NaNO$_3$			
288.15	8.232	1.723	3.695	4.596	3.779
298.15	7.928	1.730	3.680	4.600	3.776
308.15	7.649	1.738	3.664	4.616	3.762
		MgCl$_2$			
278.15	5.212	1.749	3.327	3.224	4.958
283.15	4.964	1.752	3.321	3.214	4.974
288.15	4.765	1.756	3.315	3.201	4.994
293.15	4.612	1.758	3.309	3.187	5.015
298.15	4.501	1.762	3.303	3.172	5.039
303.15	4.429	1.765	3.297	3.157	5.064
308.15	4.393	1.768	3.291	3.141	5.090
		MgSO$_4$			
278.15	9.241	1.709	3.127	3.091	7.390
283.15	8.801	1.714	3.118	3.041	7.511
288.15	8.431	1.719	3.109	2.997	7.623
293.15	8.127	1.724	3.101	2.957	7.724
298.15	7.880	1.728	3.093	2.923	7.815
303.15	7.687	1.733	3.085	2.893	7.895
308.15	7.543	1.737	3.077	2.868	7.965

At the same time, hydration water can also be differentiated into two forms: (1) close to and (2) distant from the ion or molecule. If hydration water is close to the solvated ion (or molecule), it is to be considered as being directly in the field of particles, and it is quite likely to move with them in the liquid phase reactions, at least until the complete solvation limit is reached. Such hydration water would be quite rigidly bound to ion which implies that it forms a single chemical basis with the solvatizing ion or nonelectrolyte molecule (with a known dipole moment) determining their interaction in the solution. This interaction accounts for the main part of ion—dipole, electrostriction action, and dielectric saturation. Besides the water rigidly bound to an ion, there is other water in the solvation sphere of the solvent which is not so strongly bound to the ion. It is this water, overall bound to the far-away
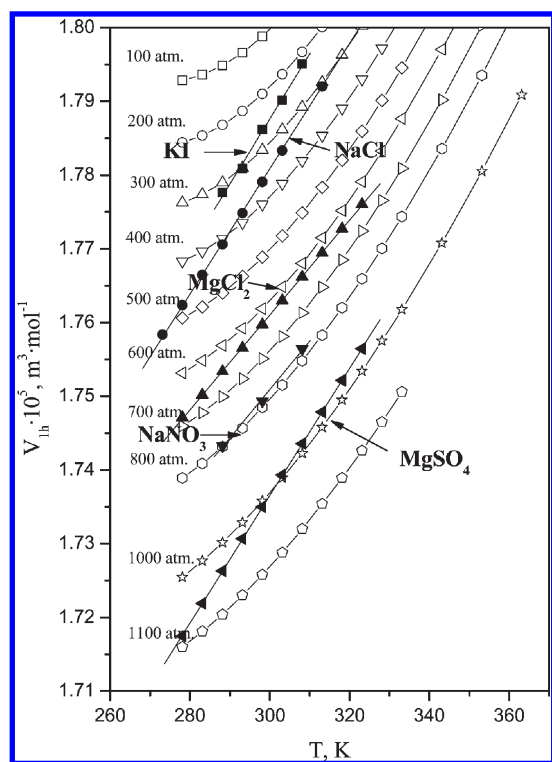
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Figure 11. Temperature dependence of the molar volume of hydration water in solutions of KI, NaCl, MgCl₂, NaNO₃, and MgSO₄ and the molar volume of pure water at various pressures.

environment of ions or molecules in the solvation sphere, that was investigated by us for its bond with ions or molecules of the solvent.[7,14]

The separation of water in the hydration shell of an ion or molecule of nonelectrolyte looks quite definite, but theoretical predictions make it even more convincing. Thus, Zaitsev developed an improved theory for calculating the contributions to thermodynamic functions of the nearest environment of ions in solution. According to this theory, the term ΔG_2 consists of two parts: the entropy part $\Delta G'_2$ characterizing the first solvation sphere of ion and not changing with concentration and the energy part $\Delta G''_2$ defined by the change in the total solvation number $h = h_1 + h_2$. It was demonstrated that the possibility of developing a theory correctly describing the concentration dependence of the solvation number ΔG_2 may be proportional to $(\Delta h)^{3/2}$ or $(\Delta h)^2$. It was uniquely established that the dependence proportional to the square of Δh is more preferable. This enabled us to correctly describe the dependence of activity coefficients of strong electrolyte solutions at quite high concentrations, and it was possible to obtain the relationship for the solvation energy of electrolytes which is a refinement of the known Born formula with two new parameters introduced, $\rho_{o,h}$ and $\varepsilon_{o,h}$[27] (eq 20).

V. INVESTIGATION OF ELECTROLYTES UP TO THE COMPLETE SOLVATION LIMIT

Careful analysis of the literature data[20−22] on density, heat capacity, and speed of ultrasound in aqueous solutions of chloride and nitrate of sodium, chloride and iodide of potassium, and chloride and sulfate of magnesium has shown that the dependence $-((\partial\varphi_V)/(\partial p))_{S_m} = Y_{K,S} = f(\beta_1 V_1^*)$ is linear up to the CSL, the coefficient of correlation being $R_{corr.} \geq -0.9998$

(Figure 6). These findings suggest that the linearity of these dependencies enables the hydration numbers h and the molar adiabatic compressibility $\beta_h V_h$ to be determined in this range of compositions which are independent of temperature[26,27] up to the complete solvation limit. Hence, hydration numbers can be defined using the expression

$$h = \frac{d(\partial\varphi_V/\partial p)_{S_m}}{d(\beta_1 V_1^*)} \qquad (43)$$

Hydration numbers, the adiabatic compressibility of hydration complexes, and the coefficient of linear correlation calculated using this equation are given in Table 1. As seen from the findings, the values of h and $\beta_h V_h$ decrease monotonously with the increase of the electrolyte concentration. Such behavior of the stated quantities is presumably caused by the overlapping of hydration shells of ions with the increase of the salt concentration.[7,9,10] The dependence of hydration numbers on the solute concentration is described by an exponential function

$$h = h_0 \cdot \exp(-kx_2) \qquad (44)$$

where h_0 is the hydration number at infinite dilution, and k is a constant defining the dependence of hydration numbers on the electrolyte concentration. The following values were obtained: $h_0 = 24.43$, $k = 9.99$ for NaCl; $h_0 = 21.01$, $k = 10.85$ for KCl; $h_0 = 26.14$, $k = 11.85$ for NaNO₃; $h_0 = 22.71$, $k = 8.26$ for KI; $h_0 = 32.43$, $k = 13.60$ for MgCl₂; $h_0 = 39.16$, $k = 13.89$ for MgSO₄. As may be seen from the experimental dependencies of the logarithm of hydration numbers on the molar fraction of the solute (Figure 7), the choice of the exponential function to describe the concentration dependencies of hydration numbers was quite justified, $R_{corr.} = -0.9985$. It is to be noted that the approximating function for eq 44 was determined by selecting the best fit of the estimated and experimental data. The molar adiabatic compressibility of the stoichiometric mixture of ions without hydration shells $\beta_{2h} V_{2h}$ and the adiabatic compressibility of water in hydration shells $\beta_{1h} V_{1h}$ were determined by eq 37. From the processing of the experimental data, it follows that the quantities $\beta_{2h} V_{2h}$ and $\beta_{1h} V_{1h}$ are independent of concentration, and all changes in the adiabatic compressibility of hydration complexes with the increase of the solute concentration $\beta_h V_h$ are determined by the concentration dependence of hydration numbers h. Figure 8 demonstrates linear dependence of the function $\beta_h V_h$ on the hydration number h with the linear correlation coefficient $R_{corr.} \geq 0.9997$ for sodium and potassium chlorides, potassium iodide, sodium nitrate, magnesuium chloride, and sulfate, which again supports our assumption that $\beta_{2h} V_{2h}$ and $\beta_{1h} V_{1h}$ are independent of concentration.

The isotherms of the apparent molar volume $\varphi_V = f(h)$ shown in Figure 9 correspond to eq 41 in which the quantity $(V_1^* - V_{1h})$ is the change of the volumetric compression of water in a hydration shell; V_{2h} is the molar volume of the stoichiometric mixture of ions without hydration environment; and V_{1h} is the molar volume of water in the hydration shell. As is seen from Figure 9, the apparent molar volume of electrolytes φ_V is linelly dependent on h ($R_{corr.} \geq 0.999$) up to the complete solvation limit.

On the strength of this fact, one can draw the conclusion that the quantities V_{1h} and V_{2h} are independent of the electrolyte concentration, and the concentration dependence of the apparent molar volume of stoichiometric mixture of ions φ_V is determined by the change in the hydration numbers as the salt concentration changes (Figure 9).
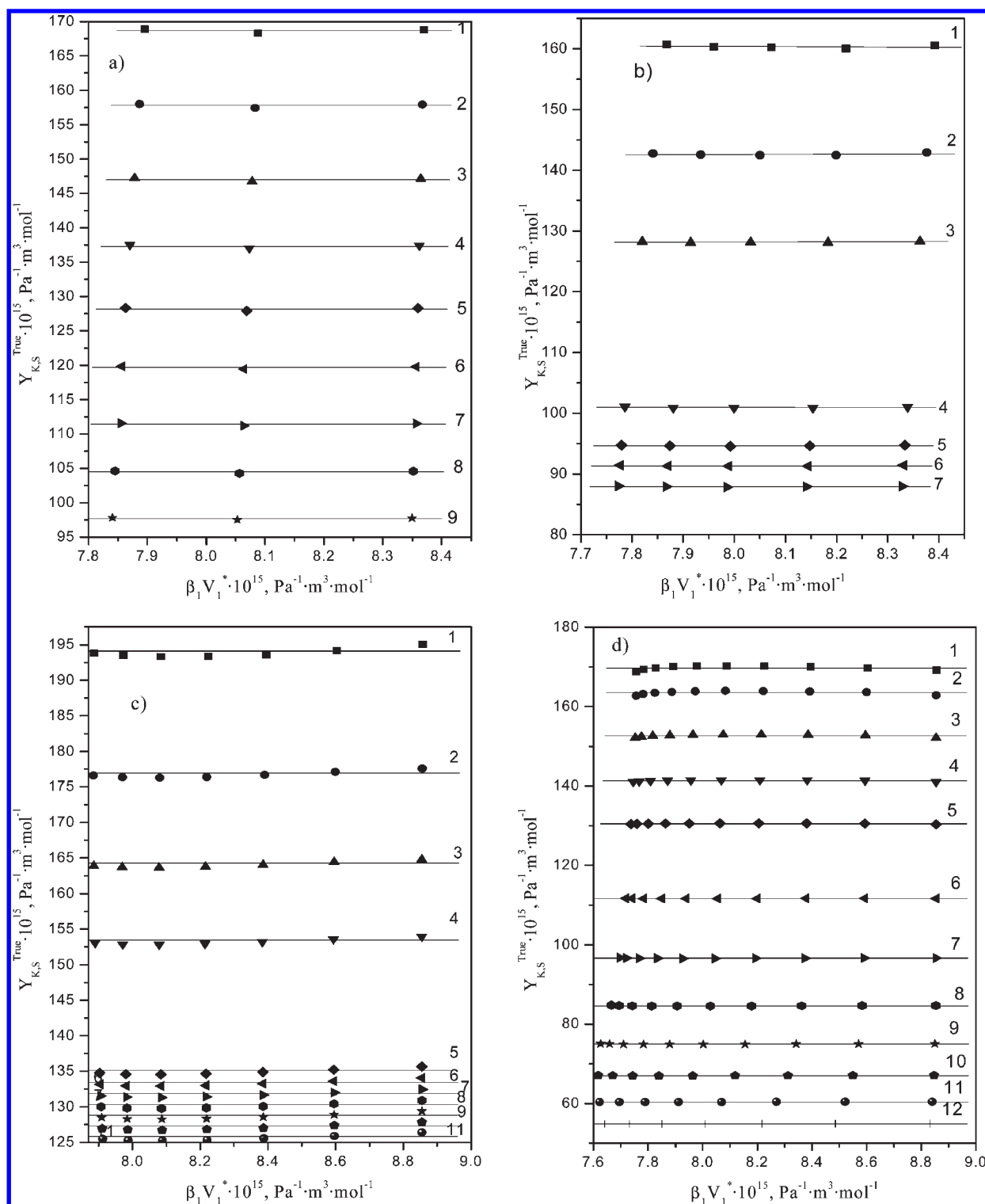
Figure 12. Relationship between the function $Y_{K,S}$ and the molar adiabatic compressibility of the free solvent $\beta_1 V_1^*$ for aqueous solutions of: (a) NaNO$_3$ (1, 0.240 m; 2, 0.490 m; 3, 0.751 m; 4, 1.023 m; 5, 1.307 m; 6, 1.604 m; 7, 1.915 m; 8, 2.241 m; 9, 2.583 m; (b) KI (1, 0.344 m; 2, 0.987 m; 3, 1.613 m; 4, 3.161 m; 5, 3.622 m; 6, 3.887 m; 7, 4.180 m); (c) MgSO$_4$ (1, 0.25 m; 2, 0.5 m; 3, 0.75 m; 4, 1.0 m; 5, 1.5 m; 6, 1.55 m; 7, 1.6 m; 8, 1.65 m; 9, 1.7 m; 10, 1.75 m; 11, 1.8 m); (d) MgCl$_2$ (1, 0.1 m; 2, 0.25 m; 3, 0.5 m; 4, 0.75 m; 5, 1.0 m; 6, 1.5 m; 7, 2.0 m; 8, 2.5 m; 9, 3.0 m; 10, 3.5 m; 11, 4.0 m; 12, 4.5 m).

The increase of temperature brings about the increase of the molar volume of hydration water V_{1h} (Figure 10) which is due to the greater temperature dependence of V_{1h} as compared to the temperature dependence of the molar volume of "free" solvent V_1^*. The use of both eq 37 and eq 41 permits the calculation of such quantitative solvation parameters as compressibilities of the stoichiometric mixture of ions β_{2h} and, which is especially important, compressibilities β_{1h} and molar volumes of the solvent in

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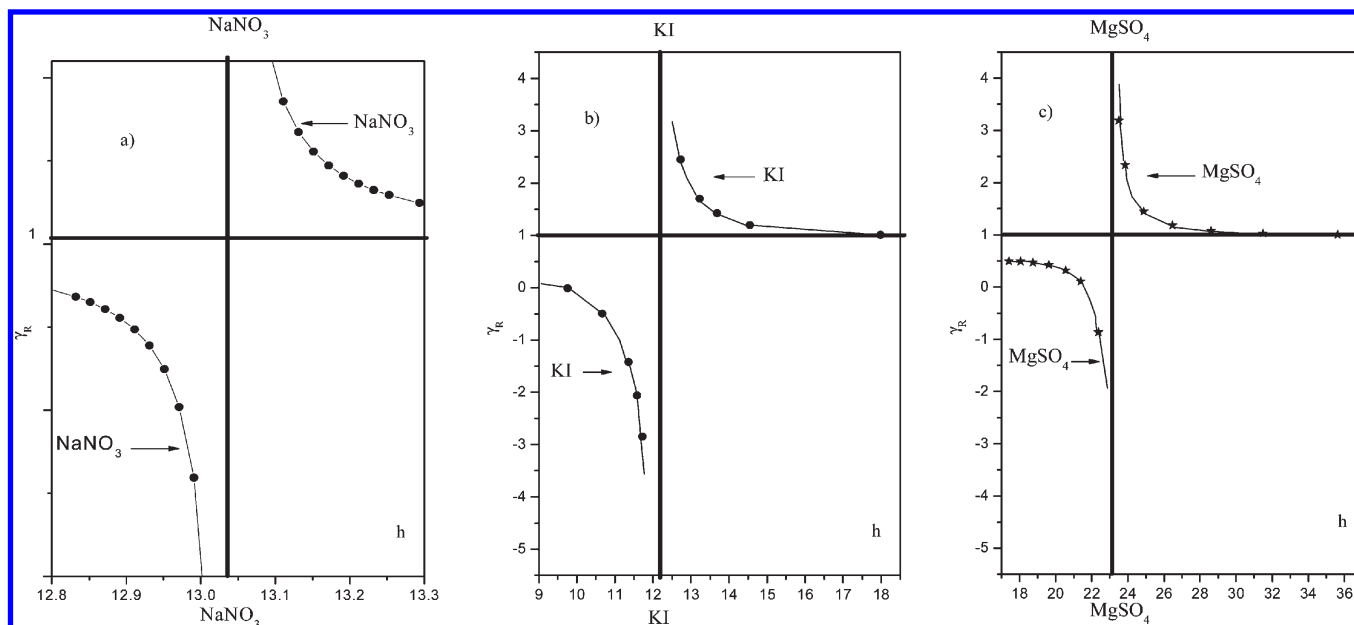dx.doi.org/10.1021/jp1108834 |*J. Phys. Chem. B* 2011, 115, 6541–6563

Figure 13. Dependence of the verified activity coefficient of the solvent for aqueous solutions of sodium nitrate, potassium iodide, and magnesium sulfate on hydration numbers.

hydration shells V_{1h}. Temperature dependencies of V_{1h} and β_{1h} are given in Figure 10, and numerical values of their main volumetric properties are given in Table 2. It is significant that the molar volume V_{1h} and compressibility β_{1h} of liquid water are linearly dependent on temperature up to the complete solvation limit.

It is known that the change of pressure in the range of up to several hundred atmospheres does not greatly affect the temperature dependence of the molar volume of pure water. Therefore, it was interesting to compare the temperature dependencies of the molar volume of water in the hydration shell with the molar volume of pure water at various pressures. The comparison showed that a greater dependence on temperature was observed for the molar volume of water in hydration shells than for pure water (Figure 11). Such findings indicate that "the electrostriction compression of water" has a greater influence on its structure of the hydrated ion than just an increase of pressure. It may be assumed that this phenomenon is due to the decreased dielectric permeability of water in the immediate vicinity of ions. As is seen from Figure 11, the change of the average pressure at 298.15 K in the hydration shells of chloride sodium ions compared to pure water is of the order of 360 atm, 358 atm for potassium chloride, 270 atm for potassium iodide, 625 atm for magnesium chloride, and 1010 atm for magnesium sulfate.

To make sure that the present approach is valid, in the first place up to the complete solvation limit, an additional check of the method described was made by an independent method which includes the definition of the solvent as a collection of hydration complexes of the solute and solvent. Equation 23 for the molar volume includes only the formal molar fractions (x_1 and x_2) of the solvent and solute. Their true values (Z_1 and Z_2) can be obtained only through the formal ones taking into account the solvation numbers (h) changing with concentration

$$Z_1 = \frac{n_1 - hn_2}{n_1 - hn_2 + n_2} = \frac{x_1 - hx_2}{1 - hx_2},$$
$$Z_2 = \frac{n_2}{n_1 - hn_2 + n_2} = \frac{x_2}{1 - hx_2} \qquad (45)$$

The corrected molar volume (V_m^{True}) and the corrected molar compressibility of the solution ($\beta_S V_m^{True}$) then will take the values

$$V_m^{True} = \frac{Z_1 \cdot M_1 + Z_2(M_2 + hM_1)}{d} \qquad (46)$$

$$\beta_S V_m^{True} = \frac{Z_1 \cdot \beta_1 V_1^* + Z_2 \beta_h V_h}{d} \qquad (47)$$

Then, the quantity $\varphi_{K,S}^{True}$ will be written as

$$\varphi_{K,S}^{True} = \frac{(Z_1 \beta_1 V_1^* + Z_2 \beta_h V_h - Z_1 \beta_1^* V_1^*)}{Z_2} \qquad (48)$$

and the quantity $Y_{K,S}^{True}$ as

$$Y_{K,S}^{True} = \varphi_{K,S}^{True} - (Z_1/Z_2)\alpha_1^* V_1^* T \cdot \left(\frac{\alpha_1^*}{\sigma_1^*} - \frac{\alpha_{aq}}{\sigma_{aq}} \right) = \beta_h V_h$$
$$(49)$$

With the use of the hydration numbers obtained in this study, the "corrected" apparent molar compressibility of the solute ($Y_{K,S}^{True}$) becomes equal to the molar adiabatic compressibility of the hydration complex. This leads to the independence of ($Y_{K,S}^{True}$) on the temperature (expressed through $\beta_1 V_1^*$) under all investigated conditions up to the complete solvation limit. Figure 12 illustrates the stated relationship at different concentrations in the studied range of temperatures.

The rational activity coefficient of water in electrolyte solutions according to Lewis' equation is defined as: $\gamma_R = (a_W)/(x_1)$. However, not all water found in solution must be included when calculating the activity coefficient since part of the solvent is found to be involved in the solvation structure of ions of the stoichiometric mixture. The concentration of pure water decreases with the increase of the solute concentration, and only free water (water

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Table 3. Concentration and Temperature Dependencies of Density (ρ) and the Speed of Ultrasound (U) in Aqueous Solutions of Urea, Urotropine, and Acetonitrile

urea—water						
278.15 K	x_2 m.f.	0.00824	0.01980	0.02856	0.05348	0.07583	0.11031
	ρ, kg/m³	1007.88	1018.49	1026.19	1046.63	1.063.31	1086.60
	U, m/s	1442.83	1464.58	1480.23	1520.96	1553.56	1597.93
283.16 K	x_2 m.f.	0.00739	0.01416	0.01899	0.04317	0.07856	0.12469
	ρ, kg/m³	1006.61	1012.74	1017.01	1037.20	1063.54	1093.31
	U, m/s	1460.84	1472.79	1481.18	1519.55	1568.30	1621.80
288.15 K	x_2 m.f.	0.01033	0.02051	0.02908	0.05636	0.07250	0.11123
	ρ, kg/m³	1008.44	1017.27	1024.44	1045.72	1057.38	1082.81
	U, m/s	1483.25	1499.39	1512.35	1550.19	1570.50	1614.14
293.15 K	x_2 m.f.	0.01481	0.04977	0.07622	0.10617	0.13334	—
	ρ, kg/m³	1011.18	1039.06	1057.93	1077.37	1093.42	—
	U, m/s	1504.88	1552.08	1583.33	1614.92	1640.69	—
298.15 K	x_2 m.f.	0.00979	0.02322	0.03044	0.05308	0.07272	0.11234
	ρ, kg/m³	1005.49	1016.64	1022.39	1039.61	1053.41	1078.68
	U, m/s	1510.94	1528.80	1538.05	1565.22	1586.73	1625.71
303.15 K	x_2 m.f.	0.01195	0.01954	0.03834	0.06136	0.08147	0.09945
	ρ, kg/m³	1005.77	1011.99	1026.67	1043.40	1056.96	1068.34
	U, m/s	1524.70	1534.25	1556.38	1581.37	1601.49	1618.10
308.15 K	x_2 m.f.	0.01296	0.01999	0.03042	0.04845	0.06644	0.10810
	ρ, kg/m³	1004.82	1010.48	1018.61	1031.99	1044.55	1070.98
	U, m/s	1535.49	1543.65	1555.30	1574.24	1591.91	1628.72

urotropine—water						
278.15 K	x_2 m.f.	0.00949	0.01992	0.02915	0.03470	0.04938	0.05978
	ρ, kg/m³	1015.81	1031.80	1044.89	1052.31	1070.49	1082.16
	U, m/s	1460.67	1497.53	1529.06	1547.33	1593.30	1623.33
283.16 K	x_2 m.f.	0.01037	0.02034	0.03095	0.03430	0.04872	0.06817
	ρ, kg/m³	1016.68	1031.63	1046.29	1050.68	1068.29	1089.14
	U, m/s	1482.12	1514.78	1548.36	1558.53	1600.76	1651.52
288.15 K	x_2 m.f.	0.00841	0.01812	0.02744	0.03732	0.05092	0.06658
	ρ, kg/m³	1012.79	1027.43	1040.41	1053.15	1069.18	1085.66
	U, m/s	1492.35	1522.21	1550.01	1578.03	1614.47	1652.40
293.15 K	x_2 m.f.	0.01041	0.01927	0.02878	0.03068	0.04335	0.06238
	ρ, kg/m³	1014.82	1027.85	1040.80	1043.24	1058.81	1079.45
	U, m/s	1512.75	1538.04	1564.20	1569.36	1602.23	1647.06
298.15 K	x_2 m.f.	0.00881	0.01967	0.02765	0.03498	0.04182	0.06457
	ρ, kg/m³	1011.08	1026.97	1037.73	1047.04	1055.25	1079.57
	U, m/s	1520.87	1549.82	1570.32	1588.57	1605.07	1654.79
303.15 K	x_2 m.f.	0.00949	0.02074	0.02684	0.03633	0.04888	0.07150
	ρ, kg/m³	1010.60	1026.79	1034.93	1046.83	1061.24	1083.81
	U, m/s	1533.45	1561.53	1576.15	1598.16	1625.61	1669.25
308.15 K	x_2 m.f.	0.00993	0.01799	0.02782	0.03976	0.04488	0.06278
	ρ, kg/m³	1009.58	1021.17	1034.30	1048.85	1054.68	1073.27
	U, m/s	1543.72	1562.54	1584.79	1610.47	1620.97	1654.59

acetonitrile—water					
278.15 K	x_2 m.f.	0.01723	0.03257	0.04896	0.05935	—
	ρ, kg/m³	995.85	992.12	987.88	984.98	—
	U, m/s	1473.29	1504.12	1526.07	1534.63	—
283.15 K	x_2 m.f.	0.00930	0.01741	0.03244	0.05076	0.07295
	ρ, kg/m³	997.21	995.05	990.95	985.69	978.68
	U, m/s	1471.12	1488.83	1514.51	1534.44	1544.38

Table 3. Continued

acetonitrile—water					
288.15 K	x_2 m.f.	0.00953	0.01674	0.03413	0.05083	0.06544
	ρ, kg/m³	996.32	994.21	989.01	983.78	978.94
	U, m/s	1487.17	1500.78	1525.93	1539.96	1545.57
293.15 K	x_2 m.f.	0.00897	0.01680	0.03362	0.04970	0.06366
	ρ, kg/m³	995.40	992.93	987.50	982.12	977.26
	U, m/s	1499.79	1512.31	1532.70	1543.79	1547.78
298.15 K	x_2 m.f.	0.00864	0.01677	0.03373	0.05015	0.06732
	ρ, kg/m³	994.16	991.42	985.60	979.77	973.44
	U, m/s	1511.20	1522.55	1538.98	1547.34	1549.30
303.15 K	x_2 m.f.	0.01001	0.01676	0.03379	0.05123	0.06337
	ρ, kg/m³	992.10	989.69	983.47	976.94	972.27
	U, m/s	1523.11	1530.79	1544.04	1549.82	1550.11
308.15 K	x_2 m.f.	0.00953	0.01639	0.03408	0.04950	0.06545
	ρ, kg/m³	990.47	987.88	981.09	975.03	968.64
	U, m/s	1531.07	1537.38	1547.92	1551.03	1549.48

not involved in hydration) can be considered as an environment and be a true solvent: $\gamma_R = (a_W)/(Z_1) = (a_W(1 - hx_2))/(x_1 - hx_2)$.

Figure 13 shows dependence of the verified activity coefficient of the solvent γ_R on hydration numbers h. Water activities are taken from ref 3. The dependencies $\gamma_R = f(h)$ are a typical example of a discontinuous function describing a discontinuous change of the solvent state in solutions. In the area of discontinuity, an abrupt change in γ_R is observed which is due to the transition of the solvent to a new state in the solvent. In this concentration range, the values of γ_R coincide with the area of temperature inversion of the molar adiabatic compressibility of solution characteristic of the complete solvation limit. At small values of x_2 (at large values of h) the verified coefficient of water activity is observed to rise from unity to a maximum point characteristic of the transition of the free solvent into the coordination spheres of ions; then from the minimum point γ_R begins to rise, which is related to the solvent being removed from hydrated ion states as the salt concentration is increased. After the CSL, the ion—ion interaction brings about a gradual displacement of the solvent from the inner coordination sphere which is used for hydration of further electrolyte portions. It is this process for electrolytes that is characterized by Figure 13. The solution exists both up to the CSL and beyond it. Therefore, $Z_1 = (x_1 - hx_2)/(1 - hx_2)$ is the molar fraction of the noncoordinated water up to the CSL, whereas beyond this limit it is the molar fraction of water displaced from the hydration shells as a result of the ion—ion interaction and subsequent new hydration of electrolyte Z'_1 ($Z_{max} = Z_1 > Z_1'$).

As the concentration increases and the complete solvation limit is approached, the molar fraction of the free solvent tends to zero, while water activity in this range of solvent concentration is still not zero. Thus, the activity coefficient of water at the CSL tends to infinity.[28] It is this range that was used by us for deriving the concentration dependence of hydration numbers of the solvent. At the complete solvation limit $Z_1 = 0$, and therefore an exact experimental estimate of the complete solvation limit becomes possible.

VI. NONELECTROLYTES IN AQUEOUS SOLUTIONS

One of the methods which enables the structural characteristics of solvation complexes of both electrolytes and nonelectrolytes[29,30] to be determined is the method of adiabatic compressibility. This
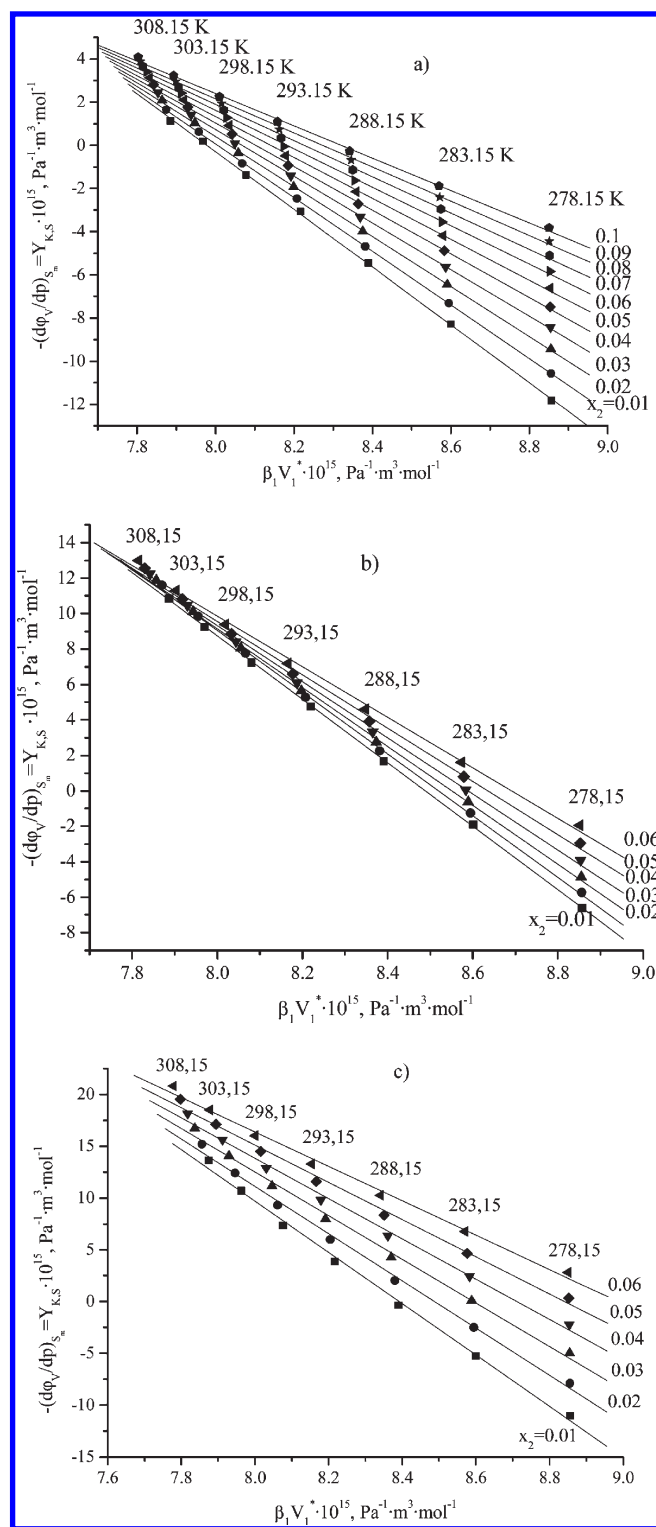
Figure 14. Dependence of the derivative of the apparent molar volume of nonelectrolytes with respect to pressure at constant entropy of solution $Y_{K,S}$ on the compressibility of the free solvent $\beta_1 V_1^*$ at various concentrations: a, urea; b, urotropine; c, acetonitrile.

method is universal because solvation parameters obtained using this method do not refer to the stoichiometric mixture of ions (as in the case of electrolytes) but to nonelectrolyte molecules of the solute. Therefore, it may be interesting to compare hydration parameters of electrolyte systems with the corresponding quantities for various nonelectrolytes.

In the present paper, we report three nonelectrolytes in aqueous solutions: urea (Harnstoff ≥99.5%), urotropine (Sigma-aldrich ≥99%), "chemically pure" acetonitrile. The water content in acetonitrile, determined by the Fisher method, was under 0.04 wt %. The urea and urotropin were dried in a vacuum at 55 °C for two days, and for acetonitrile the temperature did not

Table 4. Concentration Dependencies of Hydration Numbers (h) and Compressibility of Hydration complexes ($\beta_h V_h$) of Urea, Urotropine, and Acetonitrile[a]

urea	x_2 m.f.	0.01	0.03	0.05	0.07	0.09
	h	13.37	11.58	10.11	8.90	6.55
	$\beta_h V_h \cdot 10^{14}$, Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1}	10.67	9.30	8.19	7.28	6.55
	$R_{\mathrm{corr.}}$ eq 32	0.9998	0.9999	0.9996	0.9993	0.9991
urotropine	x_2 m.f.	0.01	0.02	0.03	0.04	0.06
	h	17.90	17.43	16.61	15.82	14.28
	$\beta_h V_h \cdot 10^{14}$, Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1}	15.19	14.85	14.20	13.59	12.41
	$R_{\mathrm{corr.}}$ eq 32	0.9999	0.9996	0.9993	0.9990	0.9983
acetonitrile	x_2 m.f.	0.01	0.02	0.03	0.04	0.06
	h	24.77	22.80	21.04	19.44	16.60
	$\beta_h V_h \cdot 10^{14}$, Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1}	20.79	19.35	18.08	16.94	14.09
	$R_{\mathrm{corr.}}$ eq 32	0.9984	0.9982	0.9980	0.9977	0.9970

[a] $R_{\mathrm{corr.}}$, the correlation coefficient.

Table 5. Temperature Dependencies of the Volumetric Compression of the Solvent ($V_1^* - V_{1h}$), the Molar Volume V_{1h}, and the Coefficient of the Adiabatic Compressibility of Hydration Water β_{1h} and the Molar Volume V_{2h} and the Coefficient of the Adiabatic Compressibility of the Solute without Hydration Environment β_{2h} for Urea, Urotropine, and Acetonitrile

	T, K	278.15	283.15	288.15	293.15	298.15	303.15	308.15
$(V_1^* - V_{1h}) \cdot 10^7$, m$^3 \cdot$mol^{-1}	urea	1.73	1.45	1.21	0.97	0.76	0.74	0.65
	urotropine	−1.78	−1.75	−1.67	−1.52	−1.47	−1.29	−1.06
	acetonitrile	0.73	0.78	0.84	0.92	0.96	1.00	1.02
$V_{1h} \cdot 10^6$, m$^3 \cdot$mol^{-1}	urea	17.84	17.88	17.91	17.95	17.99	18.02	18.06
	urotropine	18.19	18.20	18.20	18.20	18.22	18.22	18.23
	acetonitrile	17.94	17.94	17.95	17.96	17.97	17.99	18.02
$V_{2h} \cdot 10^6$, m$^3 \cdot$mol^{-1}	urea	44.89	45.01	45.15	45.25	45.35	45.60	45.77
	urotropine	105.4	106.0	106.6	107.3	107.7	108.4	109.1
	acetonitrile	47.18	47.82	48.47	49.10	49.68	50.22	50.72
$\beta_{1h} \cdot 10^{11}$, Pa^{-1}	urea	42.27	42.20	42.11	42.02	41.92	41.86	41.77
	urotropine	42.44	42.44	42.43	42.43	42.40	42.38	42.36
	acetonitrile	40.03	40.03	40.02	40.00	39.97	39.92	39.86
$\beta_{2h} \cdot 10^{11}$, Pa^{-1}	urea	12.76	12.73	12.69	12.66	12.63	12.56	12.52
	urotropine	13.06	12.99	12.92	12.84	12.78	12.70	12.62
	acetonitrile	63.16	62.31	61.47	60.68	59.98	59.34	58.74

exceed 45 °C. Aqueous solutions of the above-mentioned nonelectrolytes were prepared by the weight method on the Sartorius-ME215S balance. Density ρ was measured by a vibrational densimeter (A.Paar-602) to an accuracy of 10^{-5} g/cm^3. The speed of ultrasound U was measured by a specially designed ultrasound laser interferometer to an accuracy of 1 cm/s. The measurements were carried out in the temperature range of 278.15−308.15 K with a 5 degree step. The temperature was kept accurate within 1.5×10^{-3} K. Data on density and the speed of ultrasound are given in Table 3. Urea and urotropine are solids; therefore, the density of their aqueous solutions increases with concentration, whereas acetonitrile is a liquid whose density is less than that of pure water. Therefore, specific volume of its solution decreases as its concentration is increased.

Relation 36 was used to determine hydration parameters of solutions of urea, urotropine, and acetonitrile. The compressibility of the free water at constant entropy of solution was calculated using relationship 29a; heat capacities of aqueous solutions of urea and urotropine were taken from ref 31 and that of acetonitrile from ref 32. The linear character of the dependence $Y_{K,S} = f(\beta_1 V_1^*)$ ($R_{\mathrm{corr.}} > 0.997$)

for urea, urotropine, and acetonitrile (Figure 14) shows that, according to eq 32, h and $\beta_h V_h$ are independent of temperature in the studied range of concentrations. Concentration dependencies of hydration numbers h and compressibilities of hydration complexes $\beta_h V_h$ are given in Table 4. The decrease in hydration numbers and molar isoentropy compressibilities of hydration complexes with the increase of concentration is observed for all nonelectrolytes investigated. This fact may be due to the greater degree of overlapping of nonelectrolyte hydration shells with the increase of the solute concentration. The solvation numbers and molar isoentropy compressibilities of hydration complexes obtained in this way were used to determine molar adiabatic compressibilities of water in hydration shell β_{1h} and the solute without hydration environment β_{2h}, which both decrease with the increase of temperature according to Table 5, whereas molar volumes of water in hydration shell V_{1h} and solute without hydration environment V_{2h} increase (Table 5).

Since in the solvation shell there are h molecules of water per one molecule of solute, the molar volume of solvation complexes will be written as $V_h = V_{2h} + hV_{1h}$ where V_{1h} and V_{2h} are the molar volumes of water in the solvation sphere and of the
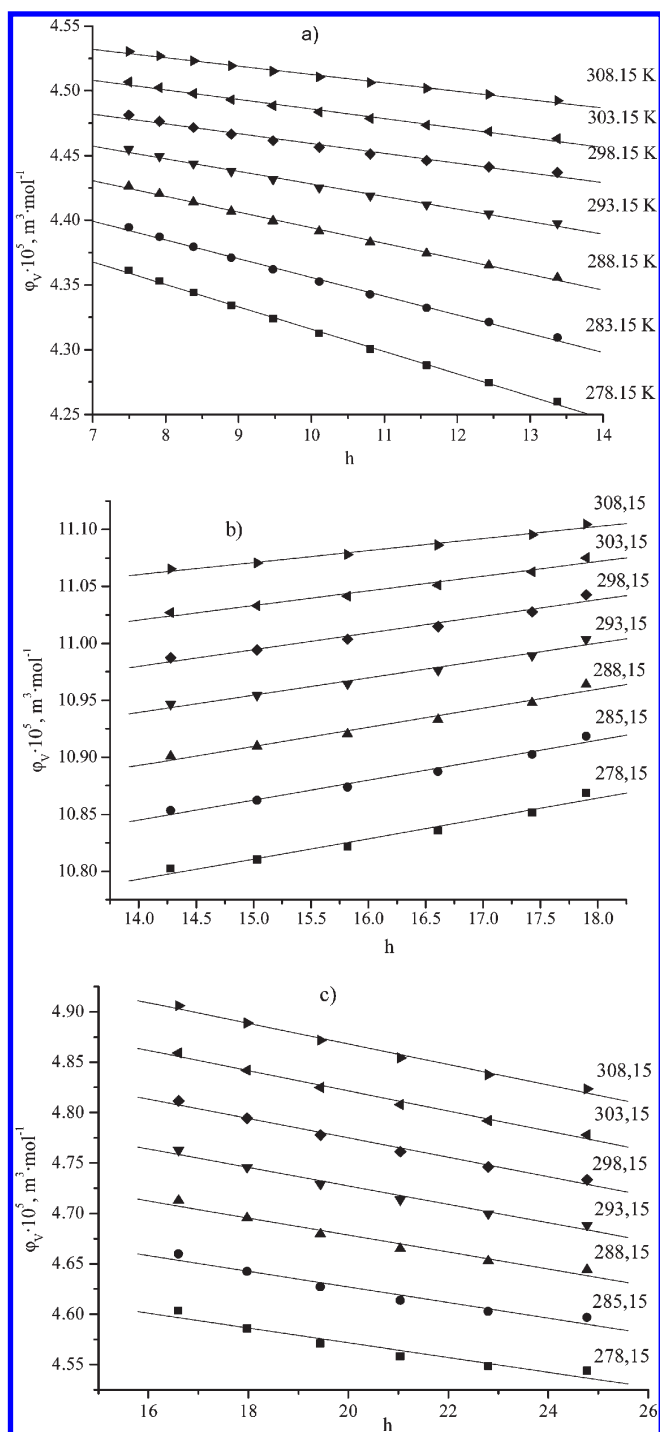
Figure 15. Dependence of the apparent molar volume φ_V on hydration numbers h at various temperatures for: (a) urea, (b) urotropine, and (c) acetonitrile.
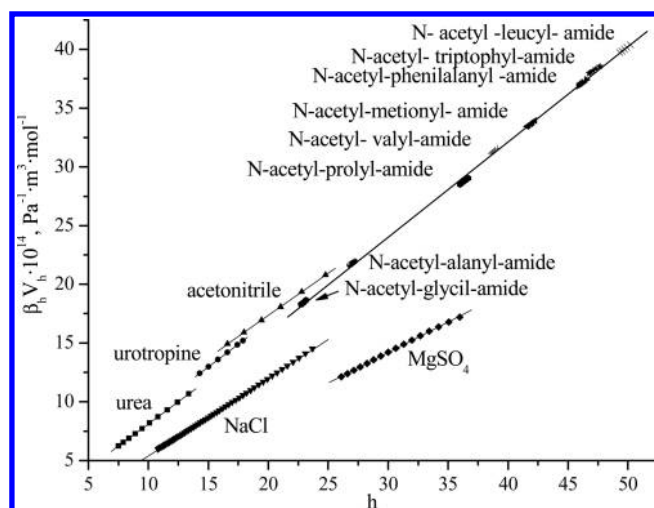

Figure 16. Dependence of the molar adiabatic compressibility of hydration complexes $\beta_h V_h$ on hydration number h for urea, urotropine, acetonitrile, and amides of N-acetyl amino acids.

hydration numbers h, which indicate the independence of the quantities V_{2h} and $(V_1^* - V_{1h})$ on concentration. In contrast to the indicated linear dependencies for urea and acetylnitrile, the linear dependence of the apparent molar volume on hydration numbers $\varphi_V = f(h)$ for urotropine (Figure 15b) has a positive slope $((V_1^* - V_{1h}) > 0)$ which is indicative, according to eq 41, not of the volumetric compression but of the volumetric expansion of the solvent in hydration shells of urotropine. The given relationship, connected with the increase in the apparent molar volume of the solute, suggests that in urotropine there takes place hydrophobic, rather than hydrophilic, solvation, the effect being greater at elevated temperatures.

It should be noted that the change of pressure in the range of up to several atmospheres is known to relatively weakly affect the temperature dependence of the molar volume of pure water, while for the molar volume of water in the hydration shell a stronger temperature dependence is observed. This points to the fact that the influence of the solute on the water molecules in the hydration shell has a stronger specific influence on its structure than a mere change of pressure. Differentiation of expression 40 with respect to pressure at constant solution entropy gives the equation for compressibilities of solvation complexes of nonelectrolytes: $\beta_h V_h = \beta_{2h} V_{2h} + h\beta_{1h} V_{1h}$, where $\beta_{1h} V_{1h}$ is the molar adiabatic compressibility of water molecules in solvation spheres, and $\beta_{2h} V_{2h}$ is the molar adiabatic compressibility of the nonelectrolyte without solvation environment. Figure 16 gives linear dependencies of compressibility of hydration complexes at constant solution entropy on hydration numbers of both electrolytes and nonelectrolytes ($R_{corr.}$ no less than 0.9998). The obtained values for the adiabatic compressibility of water in hydration shells of nonelectrolytes, according to eq 37, are $\beta_{1h} V_{1h} = 7.54 \cdot 10^{15}$ Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1} for urea, $\beta_{1h} V_{1h} = 7.72 \cdot 10^{15}$ Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1} for urotropine, and $\beta_{1h} V_{1h} = 7.18 \cdot 10^{15}$ Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1} for acetylnitrile, which is less than the compressibility of pure water $\beta_1^* V_1^* = -(\partial V_1^*/\partial p)_{S_1^*}$ which is $8.08 \cdot 10^{15}$ Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1} at 25 °C. At the same time, the value of the molar adiabatic compressibility of water in the hydration shell of electrolytes $\beta_{1h} V_{1h}$ is less than the corresponding value for nonelectrolytes. For example, $\beta_{1h} V_{1h} = 6.69 \cdot 10^{-15}$ Pa$^{-1} \cdot$m$^3 \cdot$mol^{-1}

dissolved nonelectrolyte without hydration environment. In view of the previous expression, eq 41 can be written in the form: $\varphi_V = V_{2h} - h(V_1^* - V_{1h})$ where V_{2h} is the molar volume of the nonelectrolyte; $(V_1^* - V_{1h})$ is the difference between the molar volume of the free water and molar volume of water in hydration shell; and $-(\partial \varphi_V/\partial p)_{S_m} = -h\beta_1 V_1^* + \beta_h V_h$.

Figure 15a–c shows linear dependencies of the apparent molar volume φ_V of urea, urotropine, and acetylnitrile on

for KCl, $\beta_{1h}V_{1h} = 6.60 \cdot 10^{-15} \, \text{Pa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ for NaCl, $\beta_{1h}V_{1h} = 6.37 \cdot 10^{-15} \, \text{Pa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ for Na_2SO_4, $\beta_{1h}V_{1h} = 5.82 \cdot 10^{-15} \, \text{Pa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ for $MgCl_2$, $\beta_{1h}V_{1h} = 5.75 \cdot 10^{-15} \, \text{Pa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ for $CaCl_2$, and $\beta_{1h}V_{1h} = 5.19 \cdot 10^{-15} \, \text{Pa}^{-1} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ for $MgSO_4$.[4,7]

The use of both eqs 37 and 41 makes it possible to determine in nonelectrolytes the coefficients of the adiabatic compressibility both of the water in hydration shells β_{1h} and of the dissolved nonelectrolytes without hydration environment in aqueous solutions of urea, urotropine, and acetylnitrile β_{2h} (Table 5). As can be seen, dependencies of the compressibilities of hydration complexes in solutions of amides of N-acetyl amino acids on their hydration numbers lie practically on the same straight line, which points to the closeness of the values of the adiabatic compressibility of water in the hydration shell and the proper adiabatic compressibility of dissolved nonelectrolytes according to the equation $\beta_h V_h = f(h)$ (Figure 16).

VII. CONCLUSIONS

Thus, in the given work, on the basis of rigorous approach to the interpretation of the partial derivatives in eq 24 and the method of adiabatic compression,[26] a thermodynamically correct equation has been suggested for quantitative description of volume-elastic properties of electrolytes and nonelectrolytes when investigating the solvation process. The possibility of its application for aqueous solutions in a wide range of concentrations and temperatures has been shown, which makes it possible to quantitatively estimate the properties of hydration spheres of ions and molecules of nonelectrolytes up to the complete solvation limit: hydration numbers (h), molar compressibility ($\beta_{1h}V_{1h}$), molar volume (V_{1h}), intrinsic compressibility (β_{2h}), the solute volume without hydration shells (V_{2h}), and others. It has been shown that the change in hydration numbers which are part of hydration complexes of electrolytes and nonelectrolytes is due to the change in the concentration of the solute; temperature should be considered as a factor affecting the hydration process, first of all, through the change in the solvent structure of the solvent outside the hydration shell. A correct method of defining the complete solvation limit in aqueous solutions of strong electrolytes and nonelectrolytes has been considered.

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LIST OF SYMBOLS

a_w	water activity
CLS	complete solvation limit
$f^{\pm}$	activity coefficient of solute
h	hydration number
h_0	hydration number at infinite dilution
k	constant characteristic of the given electrolyte
m	molality
p	pressure
$R_{corr.}$	coefficient of linear correlation
S_m	solution entropy
S_1^*	entropy of the pure solvent
T	temperature
V_m	molar volume of the solution
V_1^*	molar volume of the solvent
V_h	molar volume of the hydration complexes
V_{1h}	molar volume of water in hydration shells
V_{2h}	molar volume of the stoichiometric mixture of ions
x_1	mole fraction of the solvent
x_2	mole fraction of the solute
$Y_{K,S}^{True}$	true value of the derivative of the apparent molar solute volume with respect to pressure at constant solution entropy
Z_1	true molar fraction of solvent
Z_2	true molar fraction of hydration complexes

GREEK SYMBOLS

α_1^*	coefficient of thermal expansion of pure solvent
α_m	coefficient of thermal expansion of solution
β_S	coefficient of adiabatic compressibility of solution
β_1	coefficient of adiabatic compressibility of free solvent
β_h	coefficient of adiabatic compressibility of hydration
β_{1h}	coefficient of adiabatic compressibility of water in hydration spheres
β_{2h}	coefficient of adiabatic compressibility of the stoichiometric
β_1^*	coefficient of adiabatic compressibility of pure water
γ_R	rational activity coefficient
$\gamma^{\pm}$	activity coefficient of solute
ρ	solution density
ρ_1^*	density of pure solvent
σ_1^*	isobaric thermal capacity of solvent per its unit volume
σ_m	isobaric thermal capacity of solution per its unit volume
$\varphi_{K,S}$	apparent adiabatic compressibility of solute
φ_V	apparent volume of the solute

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