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Ultrasonic Study of Volume Characteristics of Hydration of HCl, NaOH, and NaCl

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Abstract—The temperature and concentration dependences of the molar adiabatic compressibility in aqueous solutions of HCl, NaOH, and NaCl are analyzed in terms of the Onori approach and concept of overlap of ion hydration spheres with increasing electrolyte concentration. The structural characteristics of the hydration complexes of the ions are determined. The influence of the temperature and electrolyte concentration on the features of hydration of HCl, NaOH, and NaCl is discussed.

A powerful tool in studying hydration of ions is the ultrasonic method based on measuring the sound velocity in aqueous electrolyte solutions and on determining the adiabatic compressibility of the system [1]. Dissolution of a substance in water is accompanied by compression due to electrostriction of the solvent and to the partial loss of its degrees of freedom under the influence of the electrostatic field of the ion. It was interesting to analyze the concentration and temperature dependences of the adiabatic compressibility of aqueous solutions of HCl, NaOH, and NaCl as typical representatives of different classes of compounds, with the aim to gain insight into the structural features of ion hydration.

All these substances in aqueous solutions are strong electrolytes. The H_3O^- and OH^- ions have similar size (1.33 Å), exhibit abnormally high mobility in water, and are involved in a labile network of hydrogen bonds. Sodium ions are strongly hydrophilic, whereas chloride ions in interaction with water molecules behave as hydrophobic species [2]. In view of these facts, it was interesting to analyze the features of hydration of compounds formed by these ions.

Model of electrolyte solution. Variations in the volume properties of electrolyte solutions were analyzed in terms of a common model [3] assuming that any solution is an ideal mixture of hydrated ions and "free" water. Variation in the compressibility of hydration water contributes to variation in the volume properties of electrolyte solutions. The total volume of a solution containing n_1 moles of solvent, n_{i^+} moles of cations, and n_{i^-} moles of anions ($n_\mathrm{i} = n_{i^+} + n_{i^-}$) is sufficiently accurately described by Eq. (1), and the molar volume, by Eq. (2):

$$V = (n_1 - \Sigma n_i h_i)v_1 + \Sigma n_i v_{ih}, \tag{1}$$

$$V_m = (X_1 - hX_2)V_1 + X_2 V_h, \tag{2}$$

where h is the hydration number of the electrolyte, v_1 and v_{ih} are the partial volumes of free water and hydrated ions, V_1 and V_h are the molar volumes of free water and hydrated ions of the salt, and X_1 and X_2 are the mole fractions of water and the solute. The effect of adiabatic pressure (P) variation on the solution volume is described by the derivative given by Eq. (3), under condition of constant entropy S:

$$(\partial V_m/\partial P)_S = (X_1 - hX_2)(\partial V_1/\partial P)_S + X_2(\partial V_h/\partial P)_S. \tag{3}$$

It should be noted that from the fourth Maxwell relationship $(\partial S/\partial V)_T = (\partial P/\partial T)_V$ follows that $dS = (\partial P/\partial T)_V dV$. Taking into account that $(\partial P/\partial T)_V = -[(\partial V/\partial T)_P/(\partial V/\partial P)_T] = \alpha/\beta$, we obtain at constant temperature $dS = (\alpha/\beta)dV$. In contrast to gases, in the condensed phase $\alpha/\beta \approx 0.1$ and dV is small; therefore, variation of P affects S insignificantly, and this influence can be neglected. By definition, $\beta_S = -(1/V) \times (\partial V/\partial P)_S$, whence follows Eq. (4):

$$\beta_S V_m = \beta_1 V_1 (X_1 - hX_2) + X_2 \beta_h V_h, \tag{4}$$

where $\beta_1 V_1$ and $\beta_h V_h$ are the molar compressibilities of the pure solvent and hydration complex. Substituting expression (4) for $\beta_S V_m$ into relationship (5) for the apparent molar compressibility, and expression (2) for V_m into relationship (6) for the apparent molar volume, we obtain Eqs. (7) and (8):

$$\varphi_k = (\beta_S V_m - \beta_1 V_1 X_1)/X_2, \tag{5}$$

$$\varphi_V = (V_m - V_1 X_1)/X_2, \tag{6}$$

$$\varphi_k = \beta_h V_h - h\beta_1 V_1, \tag{7}$$

$$\varphi_V = V_h - hV_1. \tag{8}$$

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Onori [5] studied aqueous solutions of some monochlorides and showed that at atmospheric pressure the temperature dependence of the compressibility of the hydration complex can be neglected as compared to the compressibility of pure water, and the temperature dependences of the apparent molar compressibilities of solutions can be considered at fixed solute concentrations.

According to Gurney [6], increase in the electrolyte concentration leads to overlap of the hydration cospheres of ions; as a result, h and V_h decrease. Using this approach, we analyzed the temperature and concentration dependences of the compressibilities of aqueous solutions of an acid (HCl), a base (NaOH), and a salt (NaCl). In our work we used data [7] on the density ρ of aqueous solutions of HCl and NaOH and on the ultrasound velocity u in them. These quantities were measured in the temperature range 278–318 K and the range of solute mole fractions from 0.002 to 0.018, with the errors $\pm 6 \times 10^{-6}$ g cm^{-3} and ± 0.2 m s^{-1}, respectively. Data on ρ and u for aqueous solutions of NaCl were taken from [8, 9]; they covered the range of solute mole fractions from 0.0045 to 0.098 and the temperature range from 298 to 318 K, and their error was $\pm 20 \times 10^{-6}$ g cm^{-3} and ± 0.3 m s^{-1}, respectively. Using these values of ρ and u, we calculated the adiabatic compressibility coefficients by the relationship $\beta_S = (\rho u^2)^{-1}$.

Before considering the features of hydration of HCl, NaOH, and NaCl, it should be emphasized that the heat of hydration of the H^+ ion is higher (in the absolute value) than the heats of hydration of the other ions, including OH^- (Table 1). This difference is ascribed to formation of a covalent bond in the hydroxonium ion H_3O^+ [10]. Therefore, the apparent molar quantities and characteristics of the hydration complexes of the electrolyte in the case of aqueous HCl solution were determined assuming the presence of H_3O^+ and Cl^- ions in the solution.

To compare the hydration of various electrolytes, we calculated the molar compressibility coefficients and the apparent molar volumes and compressibilities:

$$\beta_S V_m = (\partial V_m/\partial P)_{S,T}, \quad (9)$$

$$\varphi_V = (10^3/m\rho\rho_1)(\rho_1 - \rho) + M_2/\rho, \quad (10)$$

$$\varphi_k = (10^3/m\rho\rho_1)(\rho_1\beta_S - \rho\beta_{S,1}) + M_2\beta_S/\rho, \quad (11)$$

$$V_m = [M_1(1 - X_2) + M_2X_2]/\rho. \quad (12)$$

Here, ρ_1 and ρ are the densities of water and the solution; $\beta_{S,1}$ and β_S are the adiabatic compressibilities of water and the electrolyte solution, respectively; m is the solution molality; M_1 and M_2 are the molecular weights of water and the solute, respectively; and X_2 is the mole fraction of the electrolyte. The concentration and temperature dependences of $\beta_S V_m$ for aqueous solutions of HCl and NaOH (Fig. 1) appeared to be similar to those for NaCl [3]. The decrease in $\beta_S V_m$ with increasing temperature at low electrolyte concentrations is similar to the behavior of pure water; it means that in the examined concentartion and temperature range the intrinsic structure of water and its variation with temperature play a major role.

Table 1. Thermodynamic parameters of hydration of electrolyte ions at 298 K

Ion	B_η [10]	ΔH^0_{hydr} [11], kJ mol^{-1}	ΔS^0_{hydr} [11], J mol^{-1} K^{-1}
H^+	0.069	–1094	–22.2
OH^-	0.109	–529	11.4
Na^+	0.086	–407	36.8
Cl^-	–0.007	–376	78.7

Consideration of the dependences $\beta_S V_m = f(X_2)$ in a wide range of NaCl concentrations in water (Fig. 1a) shows that there is a certain inversion point of the molar compressibility, in which $\beta_S V_m$ is virtually independent of temperature: $[\partial(\beta_S V_m)/\partial T]_S \approx 0$. At lower concentrations $[\partial(\beta_S V_m)/\partial T]_S < 0$, and at higher concentrations $[\partial(\beta_S V_m)/\partial T]_S > 0$. As the electrolyte concentration is increased, the concentration of “free” water gradually decreases until all the water molecules become involved in the hydration spheres of the ions. Under these conditions, $X_1 = hX_2$ and $\beta_S V_m = \beta_h V_h$ at X_2 = const. Such a state of solution corresponds to the complete hydration boundary [12]. Presumably, for aqueous solutions of NaCl the complete hydration boundary is attained at X_2 ~0.065. In accordance with the accepted model, consideration of changes in the electrolyte solution compressibility is limited to the concentration range below the complete hydration boundary.

The correlations between the apparent molar compressibility φ_k of electrolyte solutions at constant concentration and the molar compressibility of pure water $\beta_1 V_1$ (Fig. 2) are linear, in accordance with Eq. (7). The $\beta_h V_j$ and h values obtained from these correlations are listed in Table 2. It is seen that in all cases $\beta_h V_h$ decreases with increasing electrolyte concentration.

The linearity of relation (7) ($r > 0.999$) shows that in the examined range $\beta_h V_h$ and h are independent of temperature. Our results show that, as the electrolyte concentration is increased, variation of the water com-

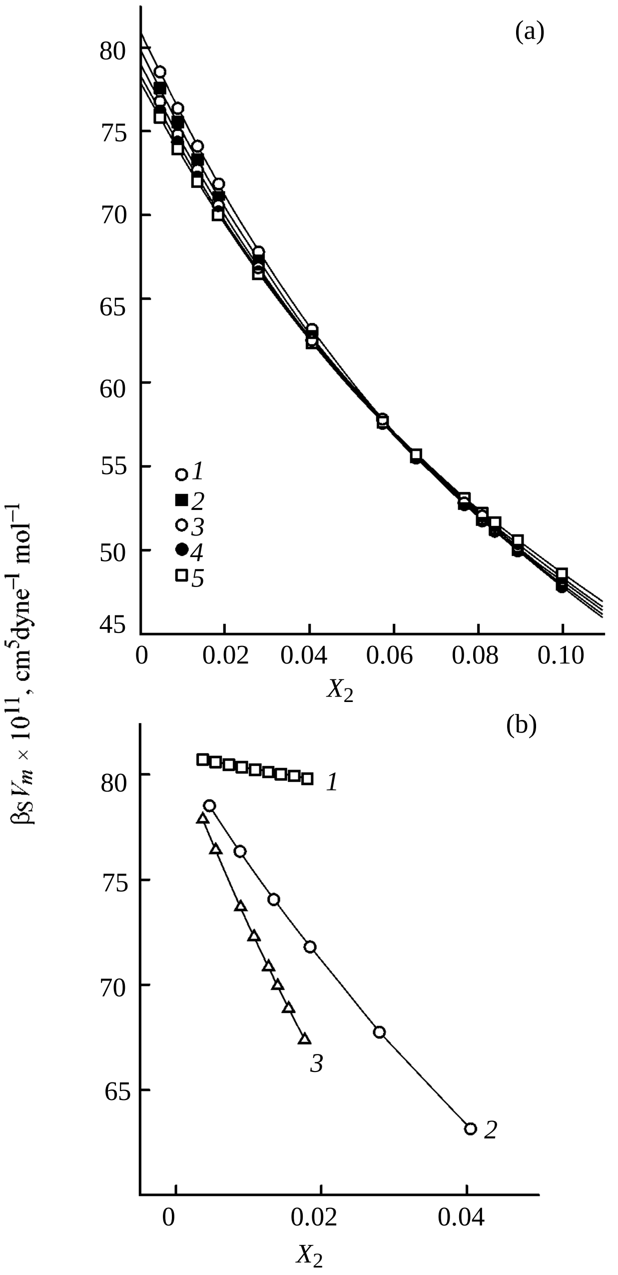

Fig. 1. Concentration dependence of the molar adiabatic compressibility of aqueous solutions: (a) NaCl at (*1*) 298, (*2*) 303, (*3*) 308, (*4*) 313, and (*5*) 318 K; (b) (*1*) HCl, (*2*) NaCl, and (*3*) NaOH at 298 K.

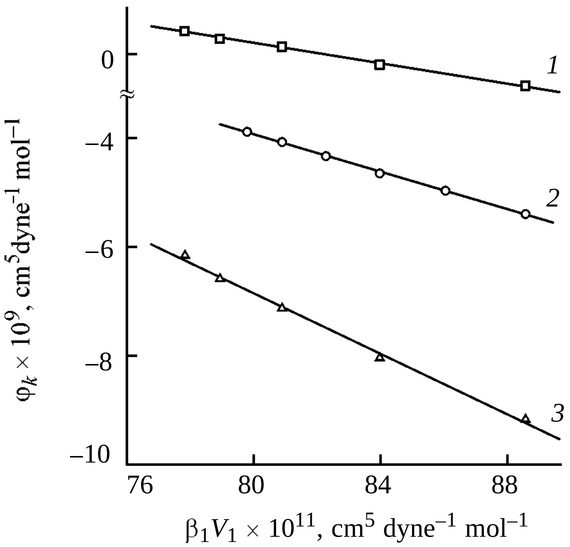

Fig. 2. Correlation between the apparent molar compressibility φ_k of electrolyte in water and the molar compressibility of pure water $\beta_1 V_1$: (*1*) HCl (at X_2 0.0137), (*2*) NaCl (at X_2 0.0134), and (*3*) NaOH (at X_2 0.0139).

pressibility in the hydration spheres of ions, along with variation of the water compressibility in the bulk solution, starts to make a certain contribution to variation of the solution compressibility. The hydration numbers of the electrolytes, listed in Table 2, decrease with increasing solute concentration because of the overlap of ion cospheres. Thorough analysis of the dependences $h = f(X_2)$ shows (Fig. 3) that they are exponential [13] rather than linear [3]:

$$h = h^0 \exp(-kX_2), \qquad (13)$$

where k is a constant characterizing the concentration dependence of the hydration number of the electrolyte. It should be noted that the obtained hydration numbers h exceed the coordination numbers (in the usual sence) of a stoichiometric mixture of ions, determined by other methods, e.g., by NMR [14]. This is due to the fact that the hydration number evaluated from the compressibility data corresponds to the number of water molecules that are subject to the electrostriction effect of the ion, altering the molar compressibility of hydration water as compared to "free" water in solution. Apparently, this number differs from the hydration number defined in terms of coordination chemistry.

The parameter k increases in the order HCl < NaOH < NaCl (Table 3). Such a trend may be due to competition of the contributions to hydration of more (H^+, OH^-, Na^+) and less (Cl^-) hydrophilic ions. As a measure of the hydrophilicity as the capability of ions to interact with water molecules, it is appropriate to use the viscosity coefficient B_η from the Jones–Dall equation [10]. Its positive values for the H^+, OH^-, and Na^+ ions and negative values for the Cl^- ions (Table 1) suggests that the Cl^- ion, as compared to the other ions, is hydrophobic. This conclusion can be confirmed by the enthalpies ($\Delta H^0_{\mathrm{hydr}}$) and entropies ($\Delta S^0_{\mathrm{hydr}}$) of ion hydration, given in Table 1; these

Table 2. Coefficients of Eq. (7) for aqueous solutions of 1–1 electrolytes

HCl			NaOH			NaCl		
$X_2 \times 10^3$	$\beta_h V_h \times 10^{11}$, cm^5 dyn^{-1} mol^{-1}	h	$X_2 \times 10^3$	$\beta_h V_h \times 10^{11}$, cm^5 dyn^{-1} mol^{-1}	h	$X_2 \times 10^3$	$\beta_h V_h \times 10^{11}$, cm^5 dyn^{-1} mol^{-1}	h
3.60	760.7	9.6	1.8	1655.8	30.3	4.52	1658.2	26.3
5.40	777.6	9.5	3.61	1653.3	30.0	8.76	1491.1	24.0
7.21	776.3	9.5	5.38	1634.1	29.6	13.4	1450.8	23.3
9.01	774.8	9.5	8.83	1596.4	28.9	18.39	1343.2	21.7
10.81	773.7	9.4	10.69	1577.5	28.5	27.91	1248.1	20.3
12.61	771.0	9.4	13.92	1547.7	27.9	40.48	1094.2	17.9
14.41	770.01	9.4	15.45	1534.2	27.6	57.27	972.9	16.0
16.21	769.0	9.3	17.64	1516.0	27.3	65.2	936.3	15.4
18.02	768.2	9.3						

Table 3. Comparative characteristics of hydrated electrolyte ions at 298 K

Substance	h^0	k [Eq. (13)]	V_{2h}, cm^3 mol^{-1}	V_{1h}, cm^3 mol^{-1}	$\beta_{1h} V_{1h} \times 10^{11}$, cm^5 dyn^{-1} mol^{-1}
HCl	9.6	1.98	45.6	17.1	45.2 ± 0.7
NaCl	26.3	8.83	24.4	17.8	64.14 ± 0.03
NaOH	30.4	6.57	13.3	17.4	54.1 ± 0.2

quantities decrease (become more negative) as the ordering of water molecule around the given ion increases [11]. Hence, the capability of ions for hydration decreases in the order $H^+ > OH^- > Na^+ > Cl^-$. Thus, variation in h with concentration is more pronounced for less hydrophilic ions. For the compounds NaCl and HCl, containing the same Cl^- anion, $k_{NaCl} > k_{HCl}$, which suggests that the H^+ ion is more hydrophilic than Na^+ $[(\Delta S^0_{hydr})_{H^+} < (\Delta S^0_{hydr})_{Na^+}]$. For the compounds NaCl and NaOH containing the same Na^+ cation, $k_{NaCl} > k_{NaOH}$, which reflects the different interaction of the hydrophilic OH^- and hydrophobic Cl^- ions with water. The hydrophobic character of Cl^- was also noted in a paper [2] devoted to molecular-dynamic simulation of aqueous solution of NaCl.

As the electrolyte concentration is increased, the properties of the hydration complexes change. The overlap of the hydration spheres of ions decreases the volume of the hydration complex and its molar compressibility. The observed dependences of $\beta_h V_h$ on the hydration numbers h can be described by the equation [3]

$$\beta_h V_h = \beta_{2h} V_{2h} + h \beta_{1h} V_{1h}, \qquad (14)$$

where β_{2h} and β_{1h} are the compressibilities of the ions and ion hydration volume, respectively. Analysis of Eq. (14) for HCl, NaOH, and NaCl solutions shows that the dependence $\beta_h V_h = f(h)$ is linear (Fig. 4). For aqueous solutions of NaCl and NaOH in the examined concentration range, the term $\beta_{2h} V_{2h}$ is close to zero within determination error, whereas for the aqueous HCl solution this term cannot be neglected:

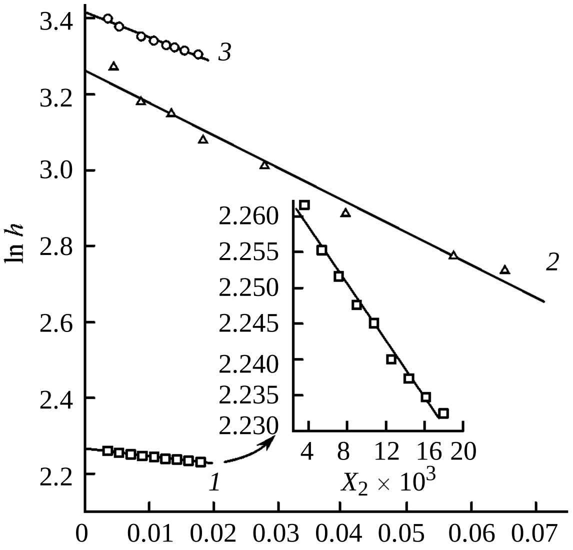

Fig. 3. Concentration dependence of the hydration numbers of (*1*) HCl, (*2*) NaCl, and (*3*) NaOH.

Table 4. Volume compressions $V_1 - V_{1h}$ and molar volumes of electrolytes V_{2h} and hydration water V_{1h} for aqueous solutions of 1–1 electrolytes at various temperatures

HCl				NaOH				NaCl			
T, K	V_{2h}, $cm^3 mol^{-1}$	$(V_1 - V_{1h})$, $cm^3 mol^{-1}$	V_{1h}, $cm^3 mol^{-1}$	T, K	V_{2h}, $cm^3 mol^{-1}$	$(V_1 - V_{1h})$, $cm^3 mol^{-1}$	V_{1h}, $cm^3 mol^{-1}$	T, K	V_{2h}, $cm^3 mol^{-1}$	$(V_1 - V_{1h})$, $cm^3 mol^{-1}$	V_{1h}, $cm^3 mol^{-1}$
278	44.3	0.94	17.1	278	13.4	0.70	17.3	298	24.4	0.26	17.8
288	44.1	0.87	17.2	288	8.27	0.43	17.6	303	24.5	0.25	17.8
298	45.6	0.95	17.1	298	13.3	0.58	17.4	308	24.6	0.24	17.9
308	45.7	0.93	17.2	308	14.5	0.59	17.5	313	24.6	0.23	17.9
318	45.9	0.93	17.3	318	16.3	0.65	17.5	318	24.7	0.23	17.9

$\beta_{2h}V_{2h}(\text{HCl}) = (34.64 \pm 0.75) \times 10^{-10}$ cm^5 dyne^{-1} mol^{-1}. The factor $\beta_{1h}V_{1h}$ determined from the slope of function (14) is constant, which suggests that the molar volume and compressibility of water in the hydration sphere of an ion are virtually independent of the electrolyte concentration. The parameter $\beta_{1h}V_{1h}$ characterizes the strength of interaction in the ion hydration spheres. It is known [15] that strong acids and alkalis interact with water considerably more strongly than salts. This is also confirmed by the molar compressibilities of hydration water in the complexes ($\beta_{1h}V_{1h}$), which decrease in the order NaCl > NaOH > HCl. The greater structural ordering of aqueous solutions of HCl and NaOH, compared to NaCl, may be due to the possibility of hydrogen bonding of the H_3O^+ and OH^- ions with water dipoles [10].

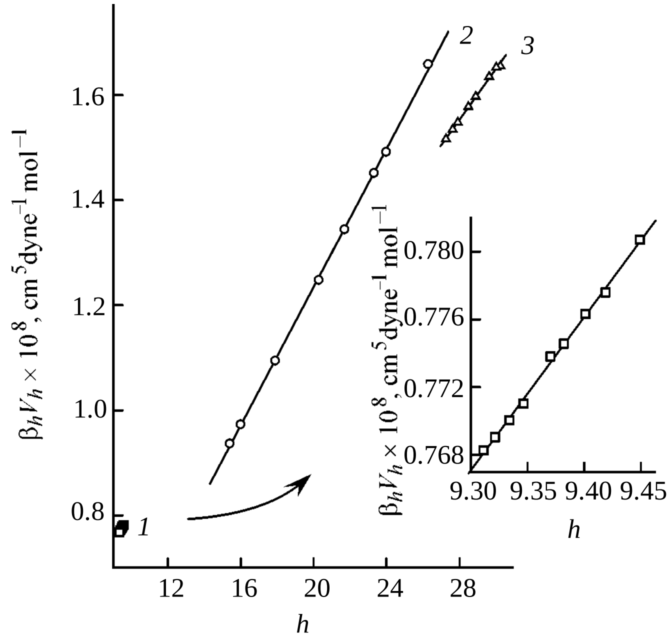

Fig. 4. Molar adiabatic compressibility of the hydration complex $\beta_h V_h$ as a function of the hydration number h of the electrolyte: (*1*) HCl, (*2*) NaCl, and (*3*) NaOH.

In terms of the model used in this work, the apparent molar volume should linearly correlate with the hydration number at T = const:

$$\varphi_V = V_{2h} - h(V_1 - V_{1h}), \qquad (15)$$

where $V_1 - V_{1h}$ is the volume compression, and V_{2h} is the volume of voids containing a stoichiometric mixture of ions. For the solutions under consideration, in the examined concentration range, relationship (15) is fulfilled with a fairly high accuracy ($r > 0.99$), confirming independence of V_{2h} and $V_1 - V_{1h}$ from concentration [5]. At the same time, despite the fact that the data on density of aqueous HCl and NaOH solutions, used in this work, are quite reliable, at low concentrations the accuracy of ρ is insufficient. As shown in [16, 17], adequate description of the concentration dependence of φ_V is possible in the concentration range $m < 0.2$ mol kg^{-1}, provided that the absolute error of density determination does not exceed $\pm 2 \times 10^{-6}$ g cm^{-3}.

As seen from Table 4, certain increase of V_{2h} with temperature is typical of all the systems studied. The molar volume of water in the ion hydration sphere depends on the particular electrolyte and decreases in the order NaCl > NaOH > HCl, in contrast to solutions of alkali metal chlorides in which it is virtually constant [5, 13]. These values indicate that in the hydration sphere water is in the compressed state ($V_{1h} < V_1 = 18.068$ cm^3 mol^{-1} for pure water at 298 K).

Thus, the approach based on the Onori method appeared to be advantageous in studying the structural aspects of ion hydration in electrolyte solutions on the basis of the molar characteristics of compressibility. We found that, as the electrolyte concentration is increased, the compressibility of hydration water in the cospheres of ions, along with the compressibility of water in the bulk solution, contributes to variation in the volume properties of acid (HCl), base (NaOH), and salt (NaCl) solutions. The decrease in the molar compressibility of solutions $\beta_S V_m$ with increasing temperature is similar to the behavior of pure water. Apparently, in the examined temperature range the variation of the state of bulk water (beyond the hydration spheres of ions) plays the major role. As the electrolyte concentration is increased, the hydration numbers of the ions decrease owing to overlap of the hydration spheres; the dependence $h = f(X_2)$ can be approximated by an exponential function. NaOH has the highest hydration number h^0 at infinite dilution. We found that variation in h with the concentration is less pronounced for hydrophilic (H_3O^+, OH^-, Na^+) and more pronounced for hydrophobic (Cl^-) ions. The lower molar compressibility of hydration water ($\beta_{1h} V_{1h}$) for HCl and NaOH, compared to NaCl, unambiguously indicates that, as compared to the salt, the acid and base interact with water more strongly and form more ordered aqueous solutions. This is also confirmed by the thermodynamic parameters of hydration of the electrolyte ions (ΔH^0_{hydr}, ΔS^0_{hydr}), which become more negative in the series Cl^-, Na^+, OH^-, H^+, as the ordering of water molecules around the ion increases. The molar volume of water in the hydration sphere of ions decreases in the order NaCl > NaOH > HCl ($V_{1h} < V_1$).

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