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Structural Features of Ion Hydration in Sodium Nitrate and Thiosulfate

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Abstract—The features of formation of hydration spheres around electrolyte ions in aqueous solutions of sodium nitrate and thiosulfate in a wide concentration range (from 2 to 42 wt %) at temperatures from 278.15 to 318.15 K were determined from the isoentropy compressibility data. The structural characteristics of the solute hydration complexes were determined. The hydration numbers decrease with increasing concentration and are independent of temperature. $Na_2S_2O_3$ has the highest hydration number at infinite dilution (h^0) and is characterized by the lowest molar isoentropy compressibility of water in the hydration spheres of the ions ($\beta_{S,1h}V_{1h}$). Sodium thiosulfate, compared to sodium nitrate, interacts with water stronger, and its aqueous solutions show a greater degree of ordering.

One of the problems of physical chemistry is to study changes that occur in a solvent in the presence of an electrolyte and are reflected in the concentration and temperature dependences of macroscopic properties of solution. Despite the fact that the concentration dependences of solution properties were repeatedly discussed in the literature in terms of various models of ion hydration [1–5], the dependences of solvation on the temperature and concentration, the influence of the solution structure on solvation, and factors governing the solute hydration number and the electrostriction pressure are still poorly understood. These problems are discussed in our paper.

The solvent structure in solvation spheres of ions was simulated using the method of rational parameters [6] for isoentropy compression. This method furnishes quantitative structural characteristics of the solvation spheres from precisely measured speed of ultrasound and density of solutions [7–11]. This approach is based on the model taking into account the compressibility of the electrolyte hydration complexes ($\beta_{S,h}V_h$) and "free" solvent ($\beta_{S,1}V_1$):

$$\beta_S V_m = \beta_{S,1}V_1(X_1 - hX_2) + X_2\beta_{S,h}V_h, \qquad (1)$$

where $\beta_S V_m$ is the molar adiabatic compressibility of the solution under consideration; h, hydration number of the electrolyte; and X_1 and X_2, mole fractions of the solvent and solute. Substituting Eq. (1) in the known expressions for the apparent molar parameters of the compressibility and volume, we obtain

$$\phi_{k,S} = -h\beta_{S,1}V_1 + \beta_{S,h}V_h, \qquad (2)$$

$$\phi_V = V_h - hV_1. \qquad (3)$$

Here the molar volume of the hydration complex V_h can be expressed via the intrinsic molar volume of the stoichiometric mixture of electrolyte ions in solution (V_{2h}) and the molar volume of water in the hydration sphere (V_{1h}):

$$V_h = V_{2h} + hV_{1h}. \qquad (4)$$

Combining Eqs. (3) and (4), we obtain the following expression for the apparent molar volume of the electrolyte in water:

$$\phi_V = V_{2h} - h(V_1 - V_{1h}), \qquad (5)$$

where (V_1 – V_{1h}) is the volume compression of the solution. As the electrolyte concentration grows, the hydration spheres of ions overlap, which is accompanied by a decrease in the hydration number of the electrolyte and hydration volume. The effect of adiabatic pressure variation at constant entropy (S) on the volume of the hydration complex is given by

$$\beta_{S,h}V_h = h\beta_{S,1h}V_{1h} + \beta_{S,2h}V_{2h}, \qquad (6)$$

where $\beta_{S,2h}$ and $\beta_{S,1h}$ are the compressibilities of the ionic volume and hydration water, respectively.

Using this approach, we analyzed the concentration dependences of the compressibilities of aqueous $NaNO_3$ and $Na_2S_2O_3$ solutions in the temperature range from 278.15 to 318.15 K. It was interesting to study differences in the hydration of the ions of these

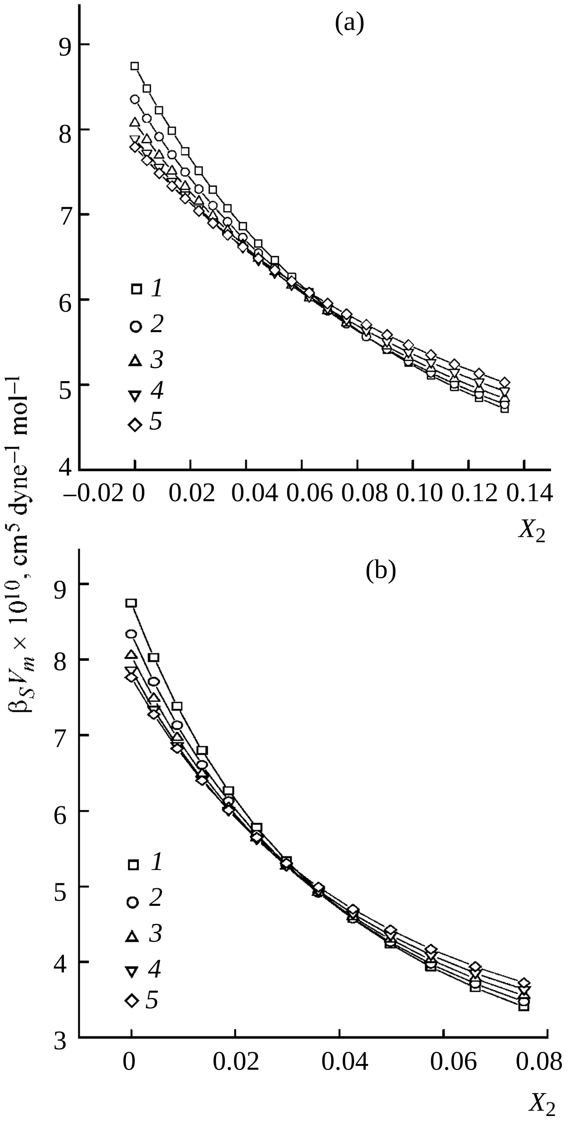

Fig. 1. Concentration dependence of the molar adiabatic compressibility of aqueous solutions of (a) $NaNO_3$ and (b) $Na_2S_2O_3$ at various temperatures: (*1*) 278, (*2*) 288, (*3*) 298, (*4*) 308, and (*5*) 318 K.

compounds in a wide concentration range (1.85–41.9 wt % $NaNO_3$, 3.4–41.9 wt % $Na_2S_2O_3$). The required data on the density of solutions were taken from [12], and data on the speed of ultrasound in solutions, from [13].

The coefficients of molar isoentropy compressibilities ($\beta_S V_m$) and the apparent molar values of the isoentropy compressibility ($\phi_{k,S}$) and volume (ϕ_V) of the electrolytes in water were estimated as follows:

$$\beta_S V_m = (\partial V_m/\partial P)_{S,T}, \quad (7)$$

$$\phi_{k,S} = (10^3/m\rho\rho_1)(\rho_1\beta_S - \rho\beta_{S,1}) + M_2\beta_S/\rho, \quad (8)$$

$$\phi_V = (10^3/m\rho\rho_1)(\rho_1 - \rho) + M_2/\rho, \quad (9)$$

where ρ and ρ_1 are the solution and solvent densities; β_S and $\beta_{S,1}$, the adiabatic compressibilities of the solution and water, respectively; and M_2, the molecular weight of the solute.

The molar compressibilities of the aqueous solutions of $NaNO_3$ and $Na_2S_2O_3$ monotonically decrease as the temperature and salt concentration grow. Dissolution of a substance in water is accompanied by compression due to solvent electrostriction. With increasing concentration, the molar compressibility undergoes inversion, and the temperature coefficient $\partial(\beta_S V_m)/\partial T$ changes sign at the $NaNO_3$ and $Na_2S_2O_3$ mole fractions of 0.062 and 0.029, respectively (Fig. 1). As the electrolyte concentration grows, the relative content of "free" water decreases, and in the inversion point $X_1 = hX_2$ and $\beta_S V_m = \beta_{S,\mathrm{h}} V_\mathrm{h}$, with these quantities being independent of temperature. Comparison of the $\beta_S V_m$ values in the inversion point for aqueous solutions of $NaNO_3$ and $Na_2S_2O_3$ (6.00×10^{-10} and 5.30×10^{-10} cm^5 dyne^{-1} mol^{-1}, respectively) shows that the ion–dipole interaction is stronger in $Na_2S_2O_3$ solutions. Such a state of solution corresponds to the boundary of full hydration of electrolytes [5].

The apparent molar isoentropy compressibilities of both electrolytes are negative in the entire temperature range. This parameter is very sensitive to the chemical structure of the electrolyte: on replacement of NO_3^- by $S_2O_3^{2-}$, $\phi_{k,S}$ of the electrolyte increases in the absolute value by a factor of more than 3. This fact also suggests stronger structural effects in aqueous solutions of sodium thiosulfate, primarily due to larger number of ions at their similar concentration in solution.

Under the conditions of adiabatic compression, the relationship of $\phi_{k,S}$ of the electrolyte in solution with the molar adiabatic compressibility of pure water ($\beta_{S,1}V_1$) follows Eq. (2) for both salts (Fig. 2). The values of $\beta_{S,\mathrm{h}}V_\mathrm{h}$ and h (Table 1) decrease with increasing salt concentration, indicating the contribution of the hydration complexes to variation of the volume properties of solutions. The linearity of Eq. (2) ($r_\mathrm{cor} > 0.996$) proves the independence of $\beta_{S,\mathrm{h}}V_\mathrm{h}$ and h from temperature under the examined conditions. As the electrolyte concentration increases, the ions start to interact with each other with overlap of the hydration spheres, which is accompanied by a decrease in the hydration number according to Eq. (10) [9]:

$$h = h^0 \exp(-kX_2). \quad (10)$$

Here h^0 is the hydration number of the electrolyte at infinite dilution, and k is a constant characterizing the concentration dependence of the hydration number and reflecting, according to [10], the electrolyte hydrophobicity. As the Na^+ ion is common for both salts under consideration, the fact that k for thiosulfate exceeds k for nitrate suggests that the interaction of the $S_2O_3^{2-}$ anion with water is somewhat more hydrophobic. Comparison of the h^0 values for $NaNO_3$ and $Na_2S_2O_3$ with those for NaCl [9] shows the following: $NaNO_3$ (22.0) < NaCl (26.2) < $Na_2S_2O_3$ (56.1). The quantity h^0 exceeds the coordination numbers obtained by other methods [14, 15]. Presumably, h^0 characterizes not only the water molecules entering into the first hydration sphere (h_k), but also more remote molecules changing their state (h_w): $h^0 = h_k + h_w$. It is important that the entropies of hydration of the ions ($\Delta S^0_{i,\mathrm{hydr}}$, J K^{-1} mol^{-1}) decrease with increasing h^0: NO_3^- (–77) > Na^+ (–117) > $S_2O_3^{2-}$ (–180) [14]. Along with the solvent electrostriction, certain hydrophobicity of the NO_3^- and $S_2O_3^{2-}$ ions decreases the translational and rotational mobility of the water molecules in the hydration spheres. The less compressible is the surrounding of the dissolved electrolyte compared to water in the bulk, the lower the entropy of hydration. All these facts indicate that aqueous solutions of $Na_2S_2O_3$ are more structured.

Formation of the hydration complexes by the ions of the electrolytes $NaNO_3$ and $Na_2S_2O_3$ is accompanied by a decrease in the solvent activity (a_w) [16]. An increase in the electrolyte concentration in solution causes the concentration of coordinated water to grow and the content of "free" water in the solution bulk to decrease. Using the rational activity coefficient of the solvent $\gamma_{R,1} = a_w/X_1^f$, where X_1^f is the mole fraction of water not incorporated into hydration shells, we analyzed the plots of $\gamma_{R,1} = f(h)$ for aqueous solutions of $NaNO_3$ and $Na_2S_2O_3$ at 298.15 K in a wide concentration range (Fig. 3). In the range of h from 13.7 to 11.1 for $NaNO_3$ and from 35.6 to 26.9 for $Na_2S_2O_3$, $\gamma_{R,1}$ undergoes dramatic changes. Analysis shows that the boundary of the full hydration (BFH) shifts toward higher concentrations in going from $Na_2S_2O_3$ to $NaNO_3$: $X_2^{\mathrm{BFH}}(Na_2S_2O_3) < X_2^{\mathrm{BFH}}(NaNO_3)$. It should be noted that the concentration interval in which $\gamma_{R,1}$ undergoes dramatic changes coincides with the interval of inversion of $\partial(\beta_S V_m)/\partial T$ in the plots $\beta_S V_m = f(X_2)$. Similar trends are seen in the dependence of the acoustic field density (ρu^2) on the electrolyte concentration (X_2). The quantity ρu^2 is essentially determined by the potential of repulsion forces [17], and these forces grow with increasing electrolyte concentration.

According to Eq. (6), the dependence $\beta_{S,\mathrm{h}} = f(h)$ for aqueous solutions of sodium nitrate and thiosulfate is linear (r_{cor} = 0.999). These results allowed us to

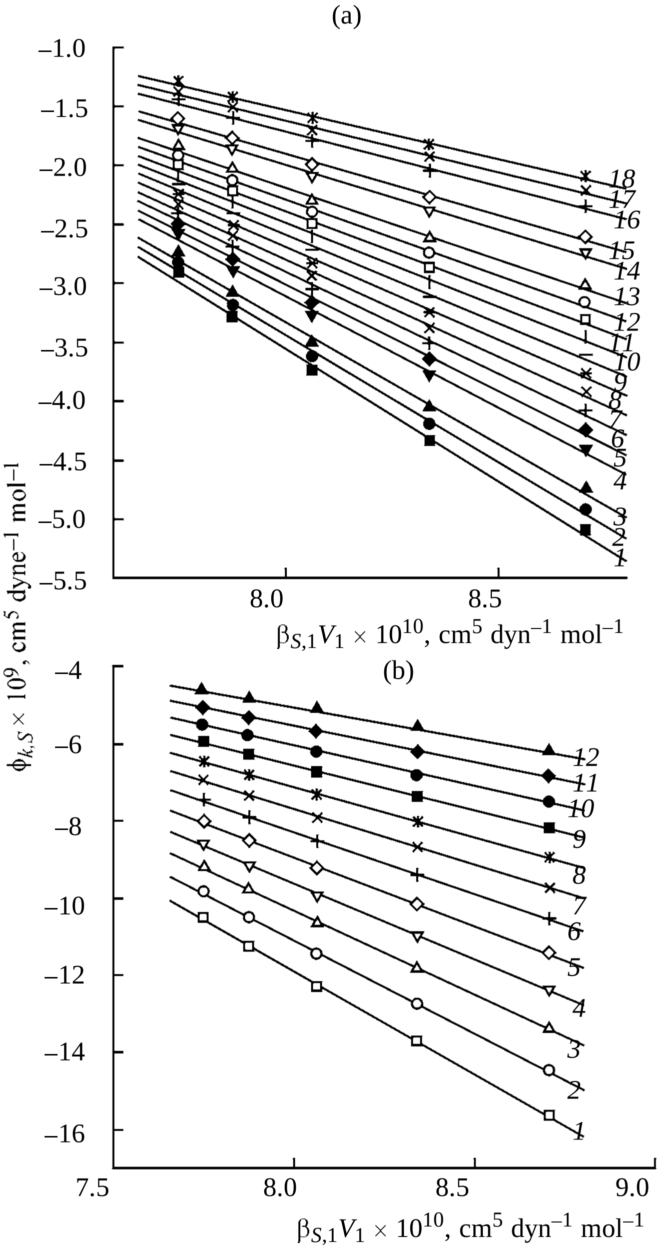

Fig. 2. Apparent molar compressibility $\varphi_{k,S}$ of the electrolyte in water as a function of the molar compressibility of pure water $\beta_1 V_1$. (a) $NaNO_3$ solutions, $NaNO_3$ mole fraction X_2: (*1*) 0.00431, (*2*) 0.00875, (*3*) 0.01335, (*4*) 0.02301, (*5*) 0.02809, (*6*) 0.03335, (*7*) 0.03881, (*8*) 0.04446, (*9*) 0.05032, (*10*) 0.05641, (*11*) 0.06273, (*12*) 0.06931, (*13*) 0.07615, (*14*) 0.0907, (*15*) 0.09844, (*16*) 0.11497, (*17*) 0.12381, and (*18*) 0.13306; (b) $Na_2S_2O_3$ solutions, $Na_2S_2O_3$ mole fraction X_2: (*1*) 0.00434, (*2*) 0.00888, (*3*) 0.01368, (*4*) 0.01874, (*5*) 0.02413, (*6*) 0.02987, (*7*) 0.03602, (*8*) 0.04264, (*9*) 0.04981, (*10*) 0.05760, (*11*) 0.06611, and (*12*) 0.07545.

Table 1. Molar adiabatic compressibility of hydration complexes ($\beta_{S,\mathrm{h}}V_\mathrm{h}$, $\mathrm{cm^5\ dyne^{-1}\ mol^{-1}}$) of sodium nitrate and thiosulfate in water and their hydration numbers (h) at various mole fractions of the salts X_2

$NaNO_3$			$Na_2S_2O_3$		
$X_2 \times 10^2$	$\beta_{S,\mathrm{h}}V_\mathrm{h} \times 10^{11}$	h	$X_2 \times 10^2$	$\beta_{S,\mathrm{h}}V_\mathrm{h} \times 10^{11}$	h
0.431	1438.4	22.23	0.434	3085.2	53.48
0.875	1359.0	21.09	0.888	2756.7	48.31
1.335	1301.4	20.22	1.368	2459.6	43.64
1.810	1225.5	19.15	1.874	2173.8	39.43
2.301	1163.3	18.24	2.413	1955.6	35.60
2.809	1105.9	17.40	2.987	1741.9	32.13
3.335	1058.3	16.67	3.602	1549.9	28.97
3.881	998.7	15.81	4.264	1377.3	26.08
4.446	955.6	15.15	4.981	1222.1	23.45
5.032	900.4	14.35	5.760	1082.6	21.05
5.641	859.7	13.73	6.611	957.7	18.85
6.273	806.9	12.95	7.545	846.1	16.85
6.931	767.8	12.36			
7.615	723.7	11.69			
8.327	682.4	11.06			
9.070	644.8	10.48			
9.844	607.0	9.90			
10.65	571.2	9.35			
11.49	535.9	8.80			
12.38	501.8	8.27			
13.30	469.2	7.76			

separate out the compression of voids containing the stoichiometric mixture of the ions. For $NaNO_3$, $\beta_{S,2\mathrm{h}}V_{2\mathrm{h}}$ is lower than for $Na_2S_2O_3$ [$(6.24\pm0.76)\times10^{-10}$ against $(19.3\pm0.11)\times10^{-10}$ $\mathrm{cm^5\ dyne^{-1}\ mol^{-1}}$], which may be due to specific geometric features of the ions. The constancy of $\beta_{S,1\mathrm{h}}V_{1\mathrm{h}}$ at varied h allows the molar compressibility of water in the hydration spheres of ions to be considered as a concentration-independent quantity. Comparison of the $\beta_{S,1\mathrm{h}}V_{1\mathrm{h}}$ values ($\mathrm{cm^5\ dyne^{-1}\ mol^{-1}}$, 298.15 K) for solutions of $NaNO_3$ and $Na_2S_2O_3$ and for pure water revealed the following trend: $Na_2S_2O_3$ (6.07×10^{-10}) < $NaNO_3$ (6.72×10^{-10}) < H_2O (8.09×10^{-10}). The lower, compared to water, values of $\beta_{S,1\mathrm{h}}V_{1\mathrm{h}}$ in aqueous solutions of the electrolytes suggest occurrence of strong interactions in their hydration spheres. The $Na_2S_2O_3$ solutions appear to be less compressible and more closely packed than the $NaNO_3$ solutions. The results obtained are consistent with the above-given thermodynamic parameters of the ion hydration. Thus, the major contribution to the concentration dependence of the compressibility of electrolyte hydration complexes is made by variation of the hydration number.

Within the framework of our approach, the isotherms of the apparent molar volume of the solute (ϕ_V) are determined by variation of the electrolyte hydration number, and the concentration dependences of this quantity are satisfactorily fitted by straight lines according to Eq. (5) (Fig. 4). The volume compressions ($V_1 - V_{1\mathrm{h}}$) and volumes occupied by the stoichiometric mixture of ions ($V_{2\mathrm{h}}$) in aqueous solutions of $NaNO_3$ and $Na_2S_2O_3$ are concentration-independent (Table 2). The observed decrease in the volume compression with increasing temperature is typical for both systems studied. The derivative $\partial(V_1 - V_{1\mathrm{h}})/\partial T$ for aqueous $NaNO_3$ solutions (6.7×10^{-3}) is greater than for $Na_2S_2O_3$ solutions (4.7×10^{-3}). As expected, in aqueous solutions of both $NaNO_3$ and $Na_2S_2O_3$, $V_{2\mathrm{h}}$ remains virtually constant.

In going from pure water to water in the hydration sphere, its structure and hence its properties change. We have determined the molar volume ($V_{1\mathrm{h}}$) and compressibility ($\beta_{1\mathrm{h}}$) of water in the hydration spheres of the ions. These quantities differ from those characteristic of pure water (V_1, β_1): $V_{1\mathrm{h}} < V_1$ and $\beta_{1\mathrm{h}} < \beta_1$, suggesting volume compression of the water molecules in the electrostatic field of the ions. It should be noted that, in both systems, the temperature dependences of $V_{1\mathrm{h}}$ are ascending, and those of $\beta_{1\mathrm{h}}$, descending. Table 2 shows that, at T = const, the com-

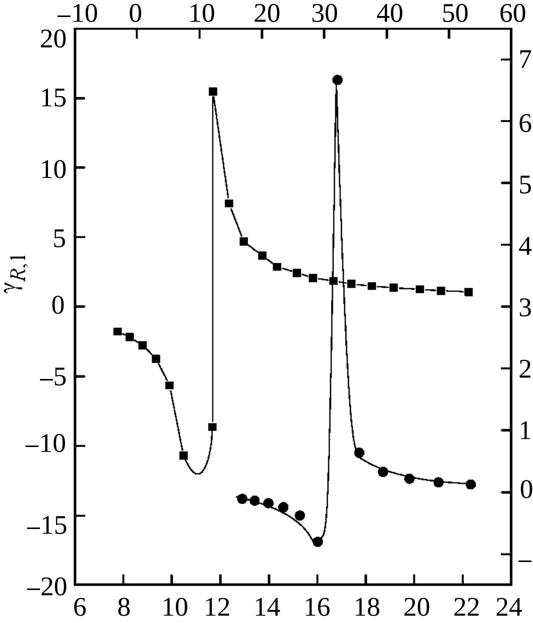

Fig. 3. $\gamma_{R,1}$ vs. hydration number of (*1*) $NaNO_3$ and (*2*) $Na_2S_2O_3$ in aqueous solutions.

Table 2. Characteristics of hydration spheres of sodium nitrate and thiosulfate at various temperatures

T, K	NaNaO$_3$				$Na_2S_2O_3$			
	$V_1 - V_{1h}$, cm^3 mol^{-1}	V_{1h}, cm^3 mol^{-1}	$\beta_{1h} \times 10^{11}$ cm^2 dyne^{-1}	V_{2h}, cm^3 mol^{-1}	$V_1 - V_{1h}$, cm^3 mol^{-1}	V_{1h}, cm^3 mol^{-1}	$\beta_{1h} \times 10^{11}$ cm^2 dyne^{-1}	V_{2h}, cm^3 mol^{-1}
278	0.550	17.46	3.848	37.5	0.530	17.48	3.472	56.3
288	0.451	17.57	3.825	37.2	0.489	17.54	3.461	56.2
298	0.380	17.68	3.801	37.2	0.456	17.61	3.447	56.2
308	0.320	17.79	3.777	37.2	0.430	17.69	3.432	56.3
318	0.282	17.91	3.752	37.2	0.409	17.78	3.414	56.3

pressibility of hydration water β_{1h} is higher for $NaNO_3$ than for $Na_2S_2O_3$, suggesting stronger ion–water interactions in the hydration sphere of sodium thiosulfate. Interesting results follow from comparison of the temperature dependences of V_{1h} of electrolytes and V_1 of pure water at various pressures. In the region of normal temperatures, the mean pressure in the hydration spheres of electrolyte ions is 600 atm for $Na_2S_2O_3$ and 500 atm for $NaNO_3$. As seen from Fig. 5, the temperature affects the molar volume of hydration water V_{1h} in $NaNO_3$ solutions more strongly compared to $Na_2S_2O_3$ solutions.

Thus, using an approach based on the molar compressibility parameters of solutions, we revealed structural features of the hydration complexes formed by the ions of the electrolytes $NaNO_3$ and $Na_2S_2O_3$ in a wide range of temperatures and concentrations. As the electrolyte concentration is increased, the hydration numbers of ions decrease, being temperature-independent in the examined range of the parameters of state. Under these conditions, our results allow the hydration number h to be considered as the major factor in the concentration dependence of solvation, and the temperature, as the

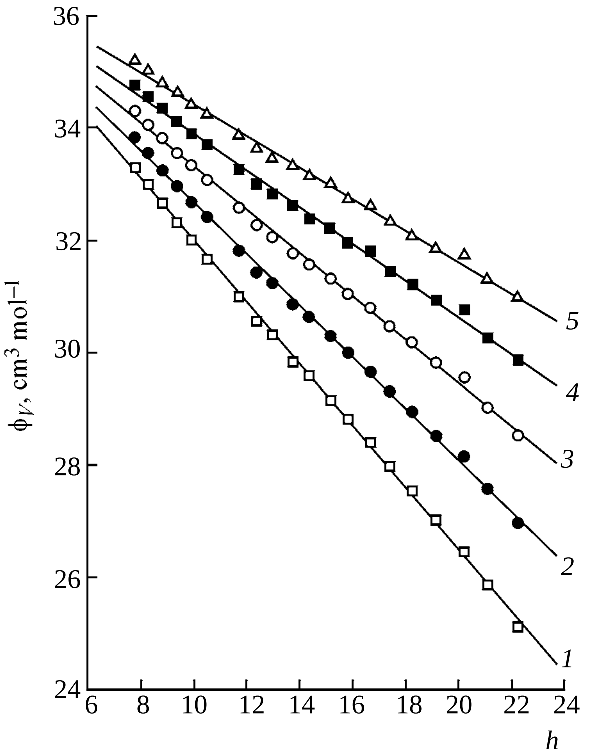

Fig. 4. Apparent molar volume ϕ_V of sodium nitrate in water as a function of its hydration number h at (*1*) 278, (*2*) 288, (*3*) 298, (*4*) 308, and (*5*) 318 K.

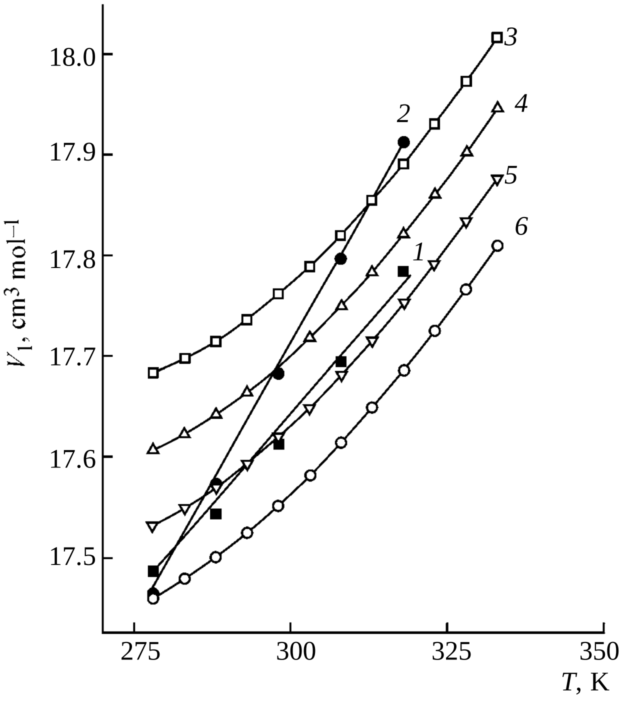

Fig. 5. Temperature dependence of the molar volume of water (V_{1h}) in the hydration spheres of (*1*) $Na_2S_2O_3$ and (*2*) $NaNO_3$ and the molar volume of pure water (V_1) at pressures of (*3*) 400, (*4*) 500, (*5*) 600, and (*6*) 700 atm.

factor affecting solvation through variations in the solvent structure.

Comparison of the state of water in the hydration spheres of ions differing in chemical properties showed that $Na_2S_2O_3$, compared to $NaNO_3$, has a higher hydration number h^0 and a lower molar isoentropy compressibility of hydration water $\beta_{S,1h}V_{1h}$, which unambiguously indicates that the interactions of sodium thiosulfate with water are stronger and its aqueous solutions are more ordered. In the hydration spheres of ions of $Na_2S_2O_3$, water occurs under higher pressure compared to $NaNO_3$. Our results confirm the previous conclusion [7, 10, 11] that the solid-sphere model of solvated ion [4] considering the complex of an ion with solvent molecules as an incompressible species is inadequate.

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