Structure formation features of water and concentrated aqueous lithium halide solutions at low temperatures from the data of integral equation method

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The structure of water and the influence of halide ions on the structure formation of concentrated LiX : H_2O (1 : 5; X = Cl, Br, I) solutions at low temperatures were studied by the method of integral equations. Based on the results obtained, supercooling of pure water is expected to significantly enhance the tetrahedral ordering of its molecules, strengthen hydrogen bonding in the system, and decrease the number of the nearest-neighbor water molecules. The effects for the solutions on lowering the temperature include a partial restoration of the tetrahedral network of H-bonds of the solvent molecules, insignificant increase in the number of the nearest-neighbor water molecules, enhancement of the coordination ability of Li^+ cation, strengthening of hydrogen bonding between anions and water molecules in the first hydration shell, increase in the number of solvent-separated ion pairs, and weakening of the temperature effect on these structural parameters in the following order of solutions: LiCl > LiBr > LiI. The probability of contact ion pair formation in the systems studied should appreciably decrease. The temperature should to a greater extent influence the associative ability of larger anions.

Key words: method of integral equations, structural parameters, pair correlation functions, low-temperature effects.

Research into the physicochemical properties of supercooled water and low-temperature water—electrolyte systems is of considerable importance for medicine, biology, biochemistry, cryotechnology, electronics, and other fields of modern science. The key results obtained to the early 1980s were generalized in Refs. 1 and 2. However, the structural and dynamic properties of the above-mentioned objects have become the subject of atomic-level investigations due to wide use of modern methods (X-ray and neutron diffraction, as well as the IR, Raman, NMR spectroscopy, and EXAFS) only in the last decade. The data obtained by these methods give an insight into the mechanisms of changes in the structural and thermodynamic properties of the systems on lowering the temperature.

Water is known to exhibit anomalous properties under normal conditions. They become even more pronounced in the temperature range corresponding to metastable states, at temperatures below the freezing point. At atmospheric pressure, bulk water (>1 cm^3) can be rather easily supercooled down to 261 K, while small volumes of water (~1 cm^3) or water in capillaries ~0.5 mm in diameter can be supercooled down to 239 K. At temperatures below the freezing point, many physicochemical properties of water strongly depend on the temperature.[1]

Studies of the structure of aqueous electrolyte solutions under supercooling and glass transition conditions are of considerable scientific and practical interest. The results obtained allow one to explain peculiar features of crystallization and reactivity of these systems at ultralow temperatures, the mechanisms of hydrogen bond formation and ion association in solutions, and the phenomenon of ion hydration.

When studying processes occurring in supercooled water and low-temperature water—electrolyte systems, researchers face some problems. This is due to unpredictability of the beginning of crystallization of water and aqueous electrolyte solutions at temperatures below the freezing point on lowering the temperature. This phenomenon often depends on particular features of the sample under study (its purity and, hence, the presence of crystallization centers). In this connection the efforts made to elucidate the reasons for and temperature ranges of supercooling of the systems much exceeded those made to measure the physical properties of low-temperature objects.

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Aqueous lithium halide solutions are the most convenient objects for studying the influence of ultralow temperatures on the structure of concentrated water—electrolyte systems. Lithium halides are highly hygroscopic compounds and can form concentrated aqueous solutions (*e.g.*, the maximum [salt] : [water] ratio for the LiCl solution is 1 : 3 at room temperature), which can be readily supercooled and undergo a transition to the glassy state.

Recently, a number of studies on the structure of pure water and concentrated aqueous lithium halide solutions at low temperatures have been reported (see Refs. 3—12). The Raman spectra of aqueous LiCl, LiBr, and LiI solutions in the glassy state were measured.[6] A neutron diffraction study of LiCl : H_2O (1 : 4 and 1 : 6) solutions in the liquid, supercooled, and glassy states was reported.[7] The influence of low temperatures on the microscopic structure of LiX : H_2O (1 : 5; X = Cl, Br, I) solutions was studied by X-ray diffraction.[8,9] It was shown that lowering of temperature causes ordering in the first hydration shell of chloride ion as well as restoration and strengthening of hydrogen bonds. The results of this study are in good agreement with those obtained[10—12] in studying analogous solutions by neutron diffraction and inelastic neutron scattering.

At the same time, obtaining direct information on the structure of solutions by experimental methods presents some difficulties (see, *e.g.*, Ref. 3), especially when carrying out experiments under extreme conditions. Therefore, currently the structural parameters of solutions are determined and the structural properties of the water—electrolyte systems are predicted using theoretical methods, which involve calculations of the structural and thermodynamic properties of an object study from the known molecular interactions. Among these methods is the method of integral equations (IE), which provides a reasonable agreement between the results of calculations and the experimental data obtained under normal conditions (see, *e.g.*, Refs. 13—15). In addition, this method differs from other computer simulation techniques in that it is much less time-consuming and allows the description of diffusion-averaged structure of a real solution. Our studies[16—19] of the influence of extreme conditions on the structure formation of water and water—electrolyte systems showed that the IE method can also be successfully employed in this case.

This work was carried out in a continuation of our studies[17,20] on the structure of water and concentrated LiX : H_2O (1 : 5; X = Cl, Br, I) solutions under supercooling and glass transition conditions (LiCl solution) and presents some generalizations of the results obtained. The aim of this work was to study the solvent structure and the influence of halide ions on the structure formation of concentrated LiX : H_2O (1 : 5) solutions at low temperatures by the IE method.

Structural parameters were calculated using the site—site Ornstein—Zernike integral equation[21] with the hypernetted chain closure. Detailed analysis of this equation in the theory of ion-molecular systems and the procedure for numerical solution were reported earlier.[22] The modified SPC model[23] with the parameters taken from Ref. 24 was used for water. The short- and long-range ion—water interactions were described by the Lennard-Jones and Coulomb potentials, respectively. The ion—ion interactions were described by the Huggins—Mayer potential. Parameters of the ion—water and ion—ion pair potentials for the LiCl : $5H_2O$ solution were the same as those reported earlier.[25] For the LiX : H_2O (1: 5) systems with X = Br and I, parameters of the ion—water potentials were taken from Ref. 26, while parameters of the ion—ion potentials were calculated using the data reported in Ref. 27.

After calculations we obtained the $g_{\alpha-\beta}(r)$ pair correlation functions (PCFs), which were used to determine the number of interparticle interactions

$$n_{\alpha-\beta}(r) = 4\pi\rho^*\int_0^r g_{\alpha-\beta}(r)r^2\mathrm{d}r, \qquad (1)$$

(ρ^* is the density of particles given in Å^{-3}) and the parameter A, which characterizes water—water association in the bulk of the system[28]:

$$A(r) = \frac{\gamma_p^4 h^2 a^2}{2\pi}\int_0^{r_{m1}} \frac{g_{\mathrm{H-H}}(r)}{r^4}\mathrm{d}r, \qquad (2)$$

where γ_p is the gyromagnetic ratio for proton, h is the Planck constant, r_{m1} is the first minimum position of the $g_{\mathrm{H-H}}(r)$ PCF, and a is the shortest interparticle (in this case, H—H) distance. To reveal the influence of lowering temperature on the structural parameters of the systems under study, changes in the number of interparticle interactions and in the association parameter were studied.

Investigations were carried out in the temperature ranges 298—239 K for liquid water, 298—138 K for the LiCl : H_2O (1 : 5) solution,[17] and 298—243 K for the LiX : H_2O (1 : 5; X = Br, I) solutions.[20]

The densities of the systems are plotted as functions of temperature in Fig. 1. Antiparallel changes of the densities of the pure solvent and LiX : H_2O (1 : 5) solutions can be rationalized as follows. A decrease in the density of water on cooling[29] causes a rapid increase in the molar volume of water, which is directly related to enhancement of tetrahedral ordering of water molecules on supercooling. In the case of solutions the effect of negative thermal expansion vanishes as the solute concentration increases, since the ion—ion and ion—water interactions become stronger than the solvent—solvent ones. There-

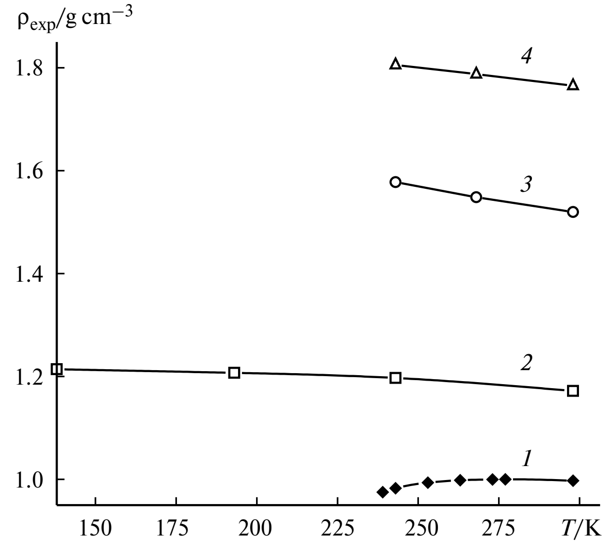

Fig. 1. Densities of water[29] (*1*) and LiX : H_2O (1 : 5) solutions with X = Cl (*2*), Br (*3*), and I (*4*) plotted as functions of temperature.

fore, in contrast to pure water, the aqueous lithium halide solutions are characterized by positive thermal expansion coefficients, *i.e.*, their densities increase as the temperature decreases.

Results and Discussion

Water—water (W—W) correlations. Table 1 lists the characteristic values of the $g_{W-W}(r)$ (W = O, H) PCFs obtained from our calculations. As can be seen, the $g_{O-O}(r)$ function for pure water obtained for a standard temperature (298 K) has three peaks at r = 0.292, 0.426, and 0.580 nm. The first maximum is determined by interactions between the nearest-neighbor water molecules, the second peak indicates the presence of tetrahedral network of hydrogen bonds in the system, while the third maximum is determined by interactions between the water molecules in the second hydration shell. The pair function $g_{O-H}(r)$ characterizing hydrogen bonding between solvent molecules in the systems has two intense peaks at r = 0.146 and 0.342 nm.

The $g_{W-W}(r)$ PCF of the concentrated lithium halide solutions calculated for standard conditions are significantly different from the corresponding functions obtained for pure water. A feature of the LiX : H_2O (1 : 5; X = Cl, Br) solutions is the absence of tetrahedral ordering of the solvent molecules, as indicated by the absence of the second peak of the $g_{O-O}(r)$ PCF (see Table 1). Destruction of the tetrahedral network of H-bonds in aqueous LiCl solutions with close concentrations at T = 298 K was also pointed out in a neutron diffraction study.[7] It should

Table 1. Influence of temperature on the most important characteristic values of the $g_{O-O}(r)$ and $g_{O-H}(r)$ PCFs of liquid water and LiX : H_2O (1 : 5) solutions with X = Cl, Br, I

Parameter	System	298 K	268 K	243 K	193 K	138 K
$g_{O-O}(r_{max1})$	H_2O	2.796 (0.292)	2.844 (0.292)	2.895 (0.294)	—	—
	LiCl : H_2O (1 : 5)	3.086 (0.290)	—	3.345 (0.290)	3.639 (0.292)	4.122 (0.294)
	LiBr : H_2O (1 : 5)	3.389 (0.290)	3.576 (0.290)	3.770 (0.290)	—	—
	LiI : H_2O (1 : 5)	3.571 (0.290)	3.756 (0.290)	3.936 (0.290)	—	—
$g_{O-O}(r_{min1})$	H_2O	0.900 (0.376)	0.893 (0.374)	0.885 (0.370)	—	—
	LiCl : H_2O (1 : 5)	—	—	0.787 (0.400)	0.782 (0.398)	0.789 (0.392)
	LiBr : H_2O (1 : 5)	—	0.808 (0.402)	0.802 (0.402)	—	—
	LiI : H_2O (1 : 5)	0.817 (0.404)	0.811 (0.402)	0.810 (0.400)	—	—
$g_{O-O}(r_{max2})$	H_2O	0.942 (0.426)	0.955 (0.426)	0.976 (0.426)	—	—
	LiCl : H_2O (1 : 5)	—	—	0.815 (0.452)	0.825 (0.440)	0.873 (0.432)
	LiBr : H_2O (1 : 5)	—	0.827 (0.450)	0.825 (0.444)	—	—
	LiI : H_2O (1 : 5)	0.833 (0.448)	0.834 (0.444)	0.840 (0.442)	—	—
$g_{O-O}(r_{min2})$	H_2O	0.883 (0.490)	0.877 (0.494)	0.875 (0.500)	—	—
	LiCl : H_2O (1 : 5)	—	—	0.814 (0.458)	0.813 (0.476)	0.807 (0.488)
	LiBr : H_2O (1 : 5)	—	0.826 (0.456)	0.824 (0.462)	—	—
	LiI : H_2O (1 : 5)	0.832 (0.462)	0.832 (0.466)	0.834 (0.470)	—	—
$g_{O-H}(r_{max1})$	H_2O	2.328 (0.146)	2.523 (0.146)	2.752 (0.146)	—	—
	LiCl : H_2O (1 : 5)	1.268 (0.146)	—	1.255 (0.146)	1.311 (0.146)	1.567 (0.146)
	LiBr : H_2O (1 : 5)	1.152 (0.146)	1.151 (0.146)	1.151 (0.146)	—	—
	LiI : H_2O (1 : 5)	1.285 (0.146)	1.315 (0.146)	1.359 (0.146)	—	—
$g_{O-H}(r_{min1})$	H_2O	0.093 (0.196)	0.075 (0.196)	0.058 (0.196)	—	—
	LiCl : H_2O (1 : 5)	0.092 (0.192)	—	0.059 (0.192)	0.031 (0.192)	0.009 (0.192)
	LiBr : H_2O (1 : 5)	0.090 (0.192)	0.074 (0.190)	0.060 (0.190)	—	—
	LiI : H_2O (1 : 5)	0.092 (0.192)	0.074 (0.192)	0.059 (0.192)	—	—

be noted that the $n^{I}_{O-H}(r_{min1})$ parameters for the two solutions are nearly halved as compared to that of pure water, which also suggests that continuous network of H-bonds in these systems is destroyed. In contrast to the LiCl and LiBr solutions, a small fraction of the tetrahedrally ordered solvent molecules is present in the LiI : H_2O (1 : 5) system, which is indicated by the second peak of the corresponding $g_{O-O}(r)$ PCF (see Table 1). This peak is of much lower intensity as compared to the second peak for pure water; however, we can assume that the network of H-bonds of bulk water in the LiI solution is not completely destroyed by the ion field.

The plots shown in Fig. 2 also allow one to follow the changes in the structure of pure water and in the solvent structure in the solutions upon lowering the temperature. For instance, a decrease in the temperature of the pure solvent down to 239 K appreciably decreases the number of the nearest-neighbor water molecules, $n^{I}_{O-H}(r_{min1})$, insignificantly increases the intermolecular distance, increases the number of tetrahedrally ordered water molecules, and insignificantly strengthens hydrogen bonding in the system.

In contrast to pure solvent, whose density decreases under supercooling conditions (see Fig. 1), the number of nearest-neighbor water molecules in the aqueous solutions increases in the temperature range 298—243 K due to an increase in the solution densities. However, further lowering of the temperature of the LiCl : H_2O (1 : 5) solution causes an insignificant decrease in $n^{I}_{O-O}(r_{min1})$. Supercooling is also responsible for the appearance of tetrahedral ordering of water molecules in the LiCl and LiBr solutions (in the temperature ranges 268—243 and 298—268 K, respectively). Subsequent lowering of the temperature of the LiX : H_2O (1 : 5) systems additionally enhances the tetrahedral ordering of the solvent molecules. This is in agreement with the results of low-temperature neutron diffraction studies of aqueous LiCl solutions of close concentrations.[7] Analogous changes in the structural characteristics of the solvent were reported in a number of studies on the structure of aqueous electrolyte solutions at low temperatures (see, *e.g.*, Refs. 6, 30, 31). By and large, changes in the behavior of the $g_{O-H}(r)$ PCFs on supercooling of the LiX : H_2O (1 : 5) systems and those of the PCF of pure water follow an identical pattern (see Table 1). Nevertheless, the $n^{I}_{O-H}(r_{min1})$ values for the LiX solutions slightly decrease under these conditions in contrast to the pure water (see Fig. 2).

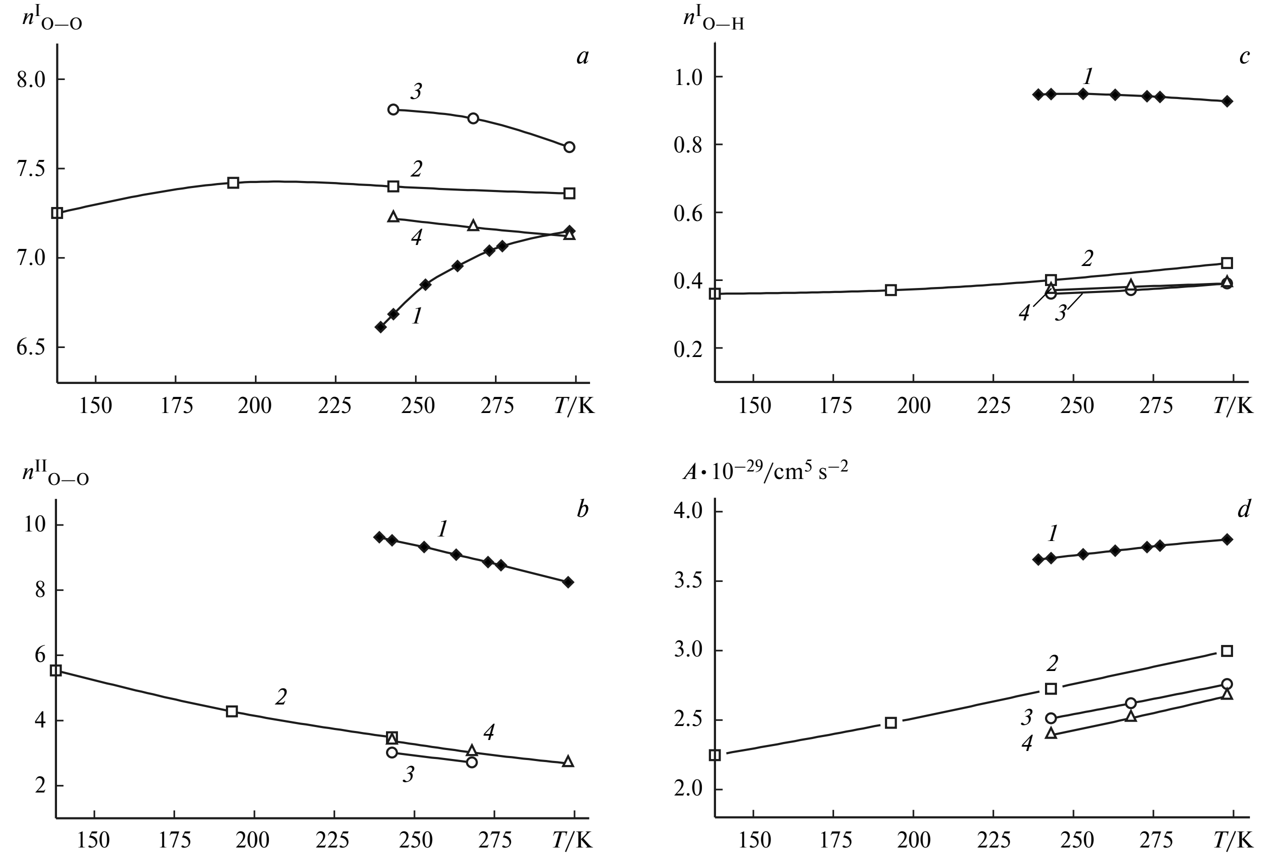

Fig. 2. Temperature dependences of parameters $n^{I}_{O-O}(r_{min1})$ (*a*), $n^{II}_{O-O}(r_{min2})$ (*b*), $n^{I}_{O-H}(r_{min1})$ (*c*), and association parameter *A* (*d*) for pure water (*1*) and LiX : H_2O (1 : 5) solutions with X = Cl (*2*), Br (*3*), and I (*4*).

Figure 2 also presents the temperature dependences of the association parameter *A* (criterion for the structural state of solvent). As mentioned earlier,[28,32] an increase in the solute concentration in solutions containing positively hydrated (structure-forming) ions is accompanied by a decrease in the *A* parameter. The reverse situation is observed for solutions containing negatively hydrated (structure-breaking) ions. Conventionally, the influence of ions on the structure of water in solutions is similar to the action of an increase or a decrease in temperature.[33] For instance, the so-called structural temperature of water decreases in the presence of structure-forming ions and increases in the presence of structure-breaking ions. One can assume that lowering the temperature will cause a structural strengthening of water molecules and, hence, a decrease in the *A* parameter. The $A(T)$ dependences shown in Fig. 2 confirm this assumption.

In particular, the LiCl, LiBr, and LiI solutions contain positively hydrated lithium cations and negatively hydrated halide anions. The association parameters for these solutions calculated for $T = 298$ K are much smaller than that obtained for pure water, since the structure-forming influence of the cation on the structure of water is much stronger than the structure-breaking influence of anions. This is in good agreement with the molecular-kinetic concepts of ion hydration[34] and with the results of an experimental study[28] which allowed experimental determination of the dependences of the *A* parameter on the solute concentration for 1 : 1 and 1 : 2 aqueous electrolyte solutions under standard conditions.

As temperature decreases, the association parameters for all the systems under study appreciably decrease, which agrees well with the assumption of structural strengthening of water (see above). Analysis of the $A(T)$ dependences for the LiX : H_2O (1 : 5) systems with X = Br, I suggests that lowering the temperature of these systems below 243 K will be followed by further structural strengthening of the solvent similarly to the LiCl : H_2O (1 : 5) solution. Analysis of the temperature dependence of the molar volume of water[29] and an increase in the viscosity of water[3,35] also pointed out enhanced structuring of pure water on supercooling. A neutron diffraction study[4] of supercooled water and analysis of changes in the self-diffusion coefficient of water under supercooling conditions[36] led to analogous conclusions. Enhancement of bulk water structuring in electrolyte (in particular, lithium halide) solutions on lowering the temperature was also reported (see, *e.g.*, Refs. 3, 6, 30, and 31).

Cation—water (Li^+—W) correlations. Since the shape of the $g_{Li-W}(r)$ PCFs and their changes with variation of external conditions for all the LiX : H_2O (1 : 5) solutions studied in this work follow identical patterns, the effect of low temperatures on hydration of Li^+ cation was considered taking the LiCl : H_2O (1 : 5) system as an example (Fig. 3). The $g_{Li-O}(r)$ PCF calculated for $T = 298$ K has an intense peak at $r = 0.190$ nm, which is determined by interactions between the lithium cation and nearest-neighbor water molecules.

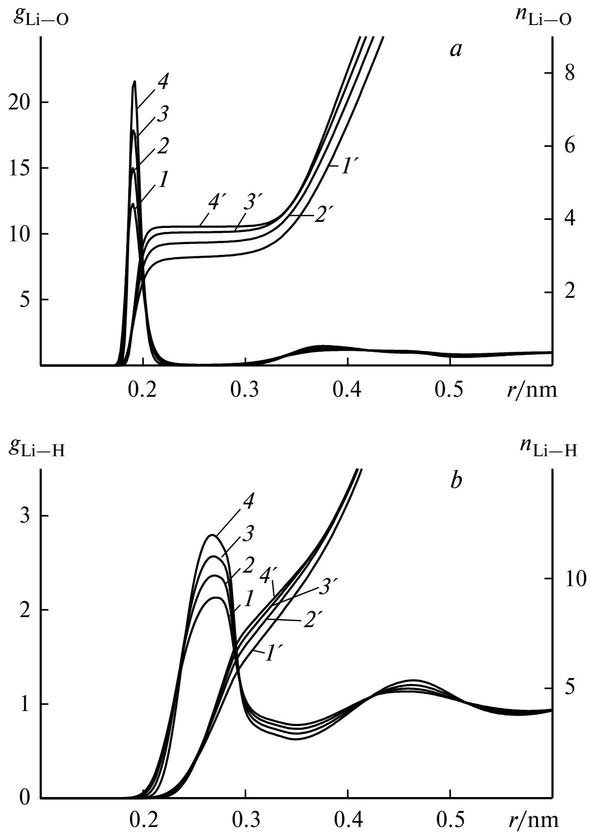

Fig. 3. Plots of the $g_{Li-O}(r)$ (*a*) and $g_{Li-H}(r)$ (*b*) PCFs and the $n_{Li-O}(r)$ (*a*) and $n_{Li-H}(r)$ (*b*) functions for the LiCl : H_2O (1 : 5) system under supercooling and glass transition conditions calculated for 298 (*1, 1′*), 243 (*2, 2′*), 193 (*3, 3′*), and 138 K (*4, 4′*): $g_{Li-O}(r)$ (*a*) and $g_{Li-H}(r)$ (*b*) (*1—4*) and $n_{Li-O}(r)$ (*a*) and $n_{Li-H}(r)$ (*b*) (*1′—4′*).

The temperature dependences of the coordination number (CN) of lithium cation, $n^{I}_{Li-O}(T)$, presented in Fig. 4 demonstrate a slight increase in the $n^{I}_{Li-O}(r_{min1})$ parameter under standard conditions in the following order of solutions: LiCl < LiBr < LiI. Analysis of the published data[37—39] on lithium halide solutions also reveals an increase in the CN of the cation with an increase in the radius of the counterion.

A decrease in temperature causes an appreciable increase in the intensity and a marked narrowing of the main peak of the $g_{Li-O}(r)$ PCF, the peak position being unchanged (see Fig. 3). As a consequence, the number of solvent molecules in the nearest environment of the cation, $n^{I}_{Li-O}(r_{min1})$, substantially increases (see Fig. 4). This is in good agreement with the results of a neutron diffraction study.[7]

Similarly to the $g_{Li-O}(r)$ PCF, the height of the main peak of the $g_{Li-H}(r)$ function increases as the temperature

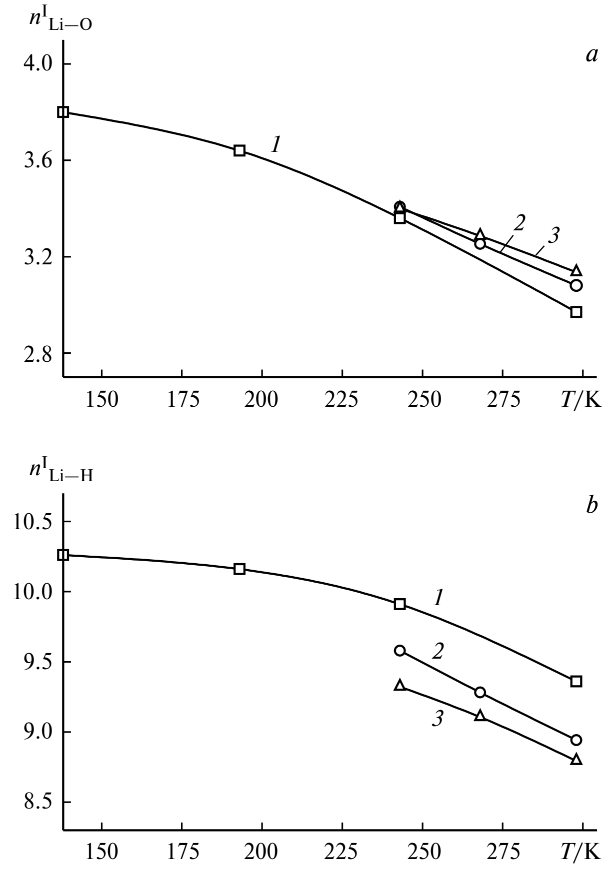

Fig. 4. Parameters $n^{I}_{Li-O}(r_{min1})$ (*a*) and $n^{I}_{Li-H}(r_{min1})$ (*b*) of the LiX : H_2O (1 : 5) solutions with X = Cl (*1*), Br (*2*), and I (*3*) plotted as functions of temperature.

decreases. The peak also becomes much narrower and shifts toward shorter distances. As a result, the interaction number, $n^{I}_{Li-H}(r_{min1})$, increases.

Analysis of the $n^{I}_{Li-W}(T)$ dependences revealed that the effect of temperature on the coordination ability of Li^+ cation weakens in the following order of solutions: LiCl > LiBr > LiI. One can expect that supercooling of the solutions down to 243 K will cause an increase in the $n^{I}_{Li-O}(r_{min1})$ value by 13 (LiCl), 10 (LiBr), and 8% (LiI). On further decrease in temperature of the LiCl solution down to 138 K one should expect enhancement of the coordination ability of Li^+ cation. The plots shown in Fig. 4 also allow one to assume that replacement of anion at $T < 243$ K will have no effect on the coordination ability of cation, *i.e.*, the hydration properties of cation in the supercooled state will be nearly identical in all the solutions considered.

Anion—water (X—W) correlations. When the $g_{X-O}(r)$ PCFs are calculated for the standard temperature, the intensities of the main peaks determined by hydrogen bonding between the halide ion and water molecules in the first hydration shell, considerably decrease with an increase in the anion radii (Fig. 5). As a consequence, the CN of chloride ion in the LiCl : H_2O (1 : 5) solution is much higher than the CNs of Br^- and I^- anions in the corresponding solutions (Fig. 6). This is in agreement with a concept,[40] according to which the CNs of anions in concentrated aqueous electrolyte solutions decrease as their radii increase due to keen competition between cations and anions for the solvent molecules.

Figure 5 also presents the plots of the $g_{X-H}(r)$ PCFs. Similarly to the $g_{X-O}(r)$ functions, the intensities of the main peaks of these functions substantially decrease in the following order of solutions: LiCl > LiBr > LiI, thus indicating weakening of H-bonds between halide ions and water molecules with an increase in the anion radii. Weakening of electrostatic interactions (H-bonds) between anions and water molecules in the first hydration shells in the order $Cl^- > Br^- > I^-$ was reported earlier.[8] This is also supported by an increase in the solvation enthalpies of anions in the order $Cl^- < Br^- < I^-$ (according to Ref. 8, $\Delta H° = -362.8$, -331.8, and -291.5 kJ mol^{-1}, respectively).

Lowering the temperature down to 243 K causes an increase in the intensity of the main peak of the $g_{Cl-O}(r)$ function but has virtually no effect on the heights of the corresponding peaks of the $g_{Br-O}(r)$ and $g_{I-O}(r)$ PCFs. In all cases the positions of the first minima also shift toward shorter distances. As a result, the CNs of the anions decrease despite the increase in the solution densities (see Fig. 6). As the temperature of the LiCl solution decreases down to 138 K, the first peak becomes more intense, and the position of the first minimum shifts toward shorter distances.

For all the systems the intensities of the main peaks of the $g_{X-H}(r)$ PCFs markedly increase, the peaks become narrower, while the positions of their maxima remain unchanged on lowering the temperature down to 243 K. As a result, the number of interactions, $n^{I}_{X-H}(r_{min1})$, in the LiCl, LiBr, and LiI solutions increases by 17.6, 15.7, and 13.7%, respectively (see Fig. 6). Subsequent glass transition of the LiCl solution is accompanied by further increase in the $n^{I}_{Cl-H}(r_{min1})$ value. The $n^{I}_{X-H}(T)$ dependences shown in Fig. 6 allow one to assume that the number of H-bonds between the anion and water molecules in the LiBr and LiI solutions will also increase on further cooling, though the changes will be less pronounced compared to those occurring in the LiCl solution. Strengthening of the hydrogen bonding between anions and water molecules in related systems on cooling was also confirmed by the earlier studies.[8,9] Besides, a decrease in $n^{I}_{O-H}(r_{min1})$ and an increase in $n^{I}_{X-H}(r_{min1})$ indicate preferred formation of H-bonds between water molecules and anions under supercooling conditions, which was also confirmed earlier.[8,9]

A peculiar feature of the behavior of the $g_{Cl-O}(r)$ PCF is transformation of a shoulder on the left side of the second peak. As temperature decreases, the shoulder

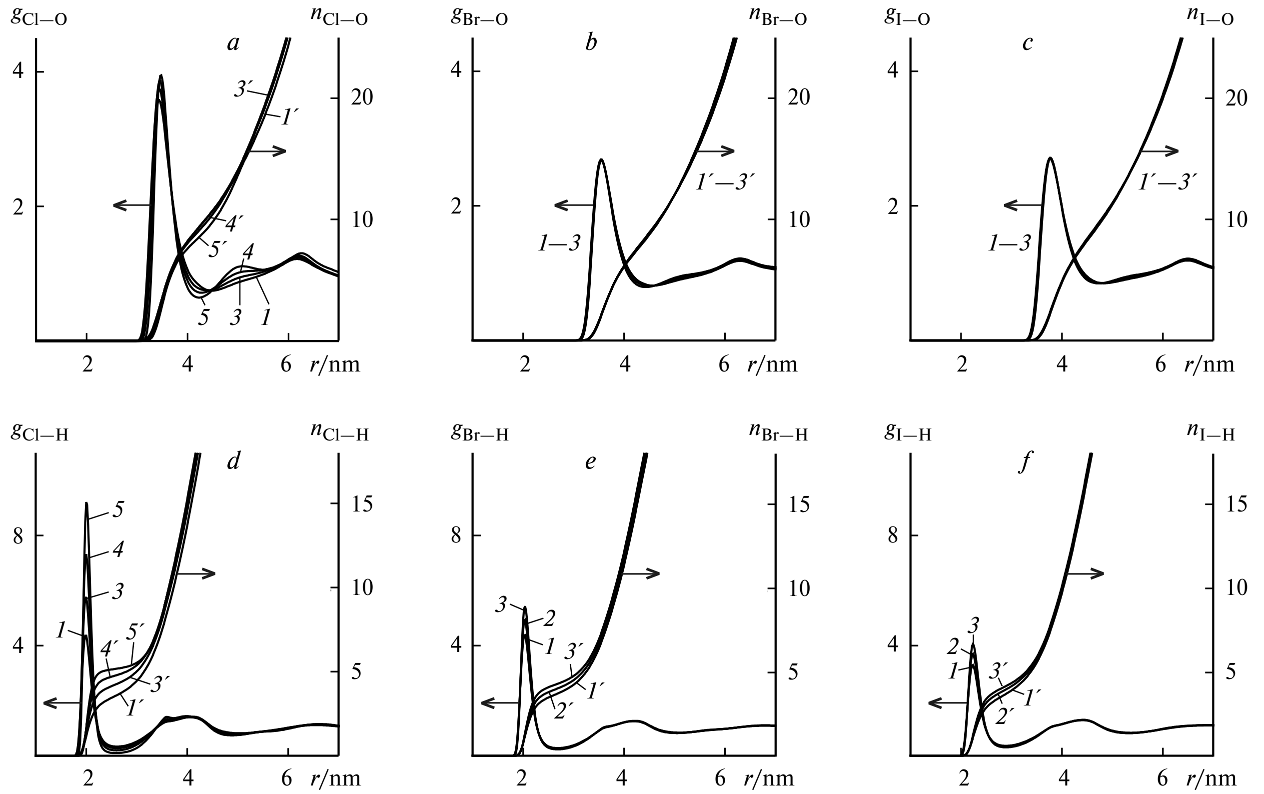

Fig. 5. Plots of the $g_{X—O}(r)$ (*a—c*) and $g_{X—H}(r)$ (*d—f*) PCFs and the $n_{X—O}(r)$ (*a—c*) and $n_{X—H}(r)$ (*d—f*) functions for the LiX : H_2O (1 : 5) systems with X = Cl (*a*, *d*), Br (*b*, *e*), and I (*c*, *f*) calculated for 298 (*1*, *1´*), 268 (*2*, *2´*), 243 (*3*, *3´*), 193 (*4*, *4´*), and 138 K (*5*, *5´*).

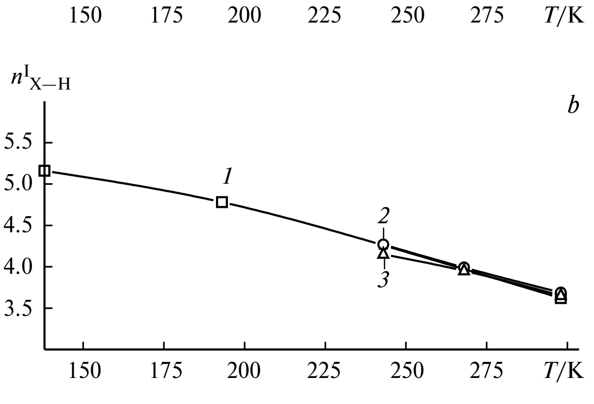

Fig. 6. Parameters $n^{I}_{X—O}(r_{min1})$ (*a*) and $n^{I}_{X—H}(r_{min1})$ (*b*) of the LiX : H_2O (1 : 5) solutions with X = Cl (*1*), Br (*2*), and I (*3*) plotted as functions of temperature.

gradually transforms into a peak with progressively increasing height and a maximum at $r \approx 0.500$ nm. Similar trends, namely, the appearance of a small peak at $r = 0.358$ nm, were also observed for the $g_{Cl—H}(r)$ function. The $g_{Br—W}(r)$ and $g_{I—W}(r)$ functions behave analogously, their changes being somewhat less pronounced.

The behavior of the $g_{X—W}(r)$ PCFs (see above) indicates a significant structural rearrangement in the first hydration shell of the anion on supercooling and glass transition. The results obtained suggest that a fraction of water molecules leaves the nearest environment of the anion. The process is accompanied by reorientation of the remaining water molecules, which are thought to rotate in such a manner that both protons are oriented toward the halide ion, thus causing strengthening of the hydrogen bonding.

Cation—anion (Li—X) correlations. Figure 7 presents the plots of the $g_{Li—X}(r)$ (X = Cl, Br, I) PCFs. The temperature dependences of the numbers of contact and solvent-separated ion pairs ($n^{I}_{Li—X}(r_{min1})$ and $n^{II}_{Li—X}(r_{min2})$, respectively) are shown in Fig. 8. The $n^{I}_{Li—X}(T)$ and $n^{II}_{Li—Cl}(T)$ dependences were spline approximated. The $g_{Li—X}(r)$ PCFs calculated for $T = 298$ K exhibit two well-resolved peaks. The first peak is determined by the cation—anion contact interaction, while the second peak

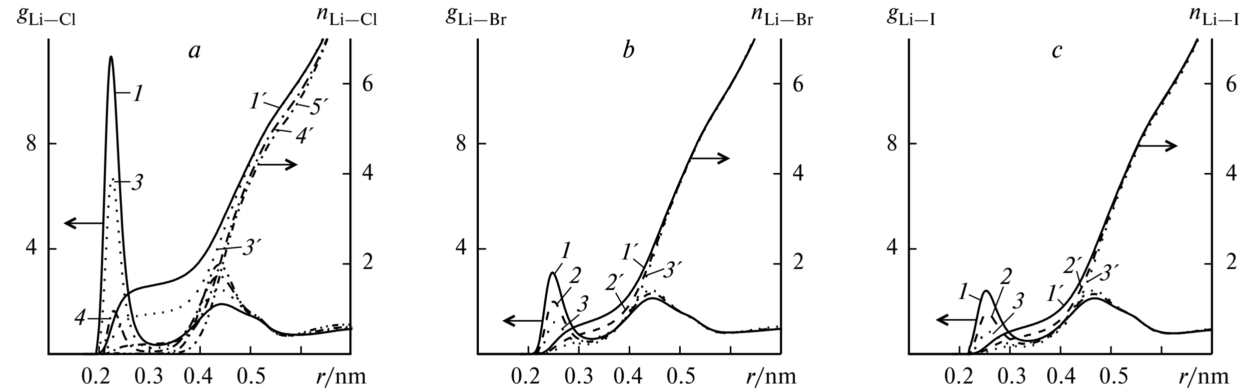

Fig. 7. Plots of the $g_{Li-X}(r)$ PCFs (*1—5*) and $n_{Li-X}(r)$ functions (*1′—5′*) for the LiX : H_2O (1 : 5) systems with X = Cl (*a*), Br (*b*), and I (*c*) calculated for 298 (*1*, *1′*), 268 (*2*, *2′*), 243 (*3*, *3′*), 193 (*4*, *4′*), and 138 K (*5*, *5′*).

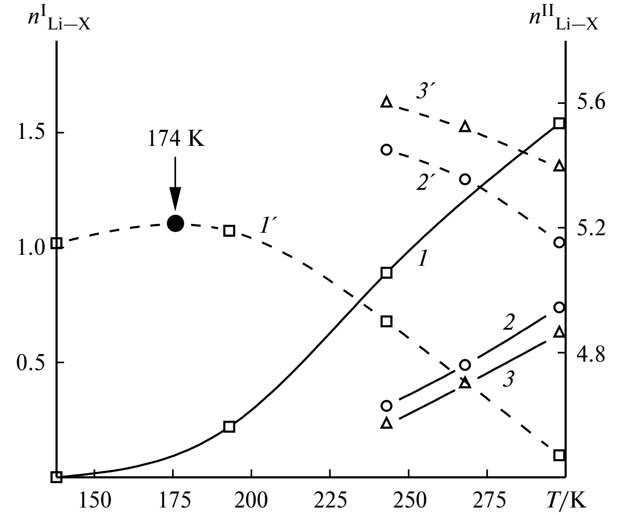

Fig. 8. Temperature dependences of the $n^{I}_{Li-X}(r_{min1})$ (*1—3*) and $n^{II}_{Li-X}(r_{min2})$ (*1′—3′*) parameters obtained for the LiX : H_2O (1 : 5) solutions with X = Cl (*1*, *1′*), Br (*2*, *2′*), and I (*3*, *3′*).

indicates the presence of solvent-separated ion pairs in the system. According to calculations for T = 298 K, the first peak for the LiCl solution is more than three times higher than those for the LiBr and LiI solutions and the number of contact ion pairs in the LiCl : H_2O (1 : 5) system is twice as large as those in the LiX : H_2O (1 : 5) solutions with X = Br and I. All the systems are characterized by nearly the same heights of the second peaks of the $g_{Li-X}(r)$ PCFs obtained for 298 K and different numbers of solvent-separated ion pairs, which increase in the following order of solutions: LiCl < LiBr < LiI. A comparison of the $n^{I}_{Li-X}(r_{min1})$ and $n^{II}_{Li-X}(r_{min2})$ values for the three systems suggests reduction of the associative ability of ions with an increase in the anion radius (see Ref. 41).

When the temperatures of all solutions are lowered down to 243 K, the intensities of the first peaks of the $g_{Li-X}(r)$ PCFs substantially decrease, the peak positions shift toward larger r values, while the first minima of these PCFs become deeper and shift toward shorter distances. As a result, the number of contact ion pairs drastically decreases by 42, 58, and 64% in the LiX : H_2O (1 : 5) systems with X = Cl, Br, and I, respectively. The glass transition of the LiCl : H_2O (1 : 5) system at T = 143 K [42] is accompanied by disappearance of the first peak. As a consequence, no direct Li^+—Cl^- correlations were found for the glassy state (see Fig. 8). Analysis of the $n^{I}_{Li-X}(T)$ dependences for the LiBr and LiI solutions allows one to assume that further lowering of the temperature of these systems also should cause disappearance of contact ion pairs and that the larger the anion radius, the higher the temperature corresponding to disappearance of direct correlations between the counterions.

For all three systems the intensities of the second peaks of the $g_{Li-X}(r)$ PCFs considerably increase, the peaks become narrower, and their maxima shift toward shorter distances (see Fig. 7). As a result, the number of solvent-separated ion pairs in the solutions, $n^{II}_{Li-X}(r_{min2})$, considerably increases (see Fig. 8). The greatest increase (9.6%) in the temperature range 298—243 K was found for the LiCl : H_2O (1 : 5) system (for the LiBr and LiI solutions these values are 5.8 and 3.9%, respectively). The results obtained agree well with the data of neutron diffraction[7] and X-ray diffraction[8] studies.

A feature of the $n^{II}_{Li-Cl}(T)$ dependence is a maximum at $T \approx 174$ K, which is associated with the beginning of crystallization of the LiCl : H_2O (1 : 5) system. This is consistent with the experimental data,[7] according to which a pentahydrate is formed in the system (this compound is stable in the supercooled and glassy states and undergoes crystallization at $T \approx 173$ K).

Based on the results obtained, one can expect that supercooling of pure water will significantly enhance tetrahedral ordering of the water molecules, strengthen the hydrogen bonding in the system, considerably decrease the number of the nearest-neighbor water molecules, and insignificantly increase the intermolecular distance.

In concentrated aqueous lithium halide solutions (T = 298 K) the ion field causes destruction of tetrahedral network of H-bonds of the solvent molecules. A decrease in temperature is expected to cause the followinf changes: (i) partial restoration of tetrahedral ordering of water molecules (the larger the anion radius, the higher the temperature at which tetrahedral ordering appears); (ii) slight increase, irrespective of the type of anion, in the number of water molecules in the nearest environment; and (iii) preferred formation of H-bonds between anions and the nearest-neighbor water molecules.

The generalized temperature dependences of some structural properties of ions in the systems are diagrammed in Fig. 9. The effects expected for the solutions on lowering the temperature down to 243 K include enhancement of the coordination ability of Li^+ cation, strengthening of the hydrogen bonding between anions and water molecules in the first hydration shell, an increase in the number of solvent-separated ion pairs, and weakening of the effect of temperature on these structural parameters in the following order of solutions: LiCl > LiBr > LiI. In addition, the probability of the contact ion pair formation in these systems will appreciably decrease. Temperature changes will to a greater extent influence the associative ability of larger anions.

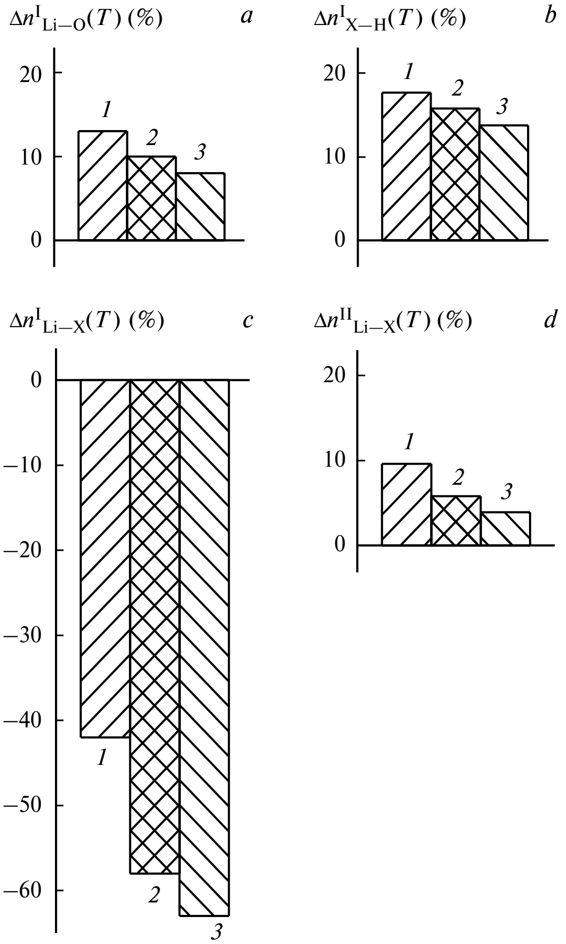

Fig. 9. Parameters Δn^{I}_{Li-O} (*a*), Δn^{I}_{X-H} (*b*), Δn^{I}_{Li-X} (*c*), and Δn^{II}_{Li-X} (*d*) of the LiX : H_2O (1 : 5) systems with X = Cl (*1*), Br (*2*), and I (*3*) plotted as functions of temperature.

Based on the results obtained, we also established that all changes in the LiCl : H_2O (1 : 5) system caused by a decrease in the solution temperature down to and below the glass transition temperature are similar to those observed in the temperature range 298—243 K and characteristic of strongly supercooled solutions. Besides, these results make it possible to assume that structural changes in the LiX : H_2O (1 : 5) solutions with X = Br, I on lowering the temperature down to the corresponding glass transition temperatures will be analogous to the changes found for the lithium chloride solution.

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