Investigation of the structure of concentrated aqueous solution of LiCl at low temperatures by the method of integral equations

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Peculiarities of the formation of the structure of aqueous LiCl solution (at a salt : water molar ratio of 1 : 5.3) in the temperature range 298—138 K were studied by the method of integral equations. Analysis of the results obtained suggests that transition of the system into the supercooled and glassy state is accompanied by an increase in the tetrahedral ordering of solvent molecules and a decrease in the number of interactions between the water molecules in unbound solvent. Lowering the temperature leads to an increase in the degree of structurization of water molecules surrounding the cation. Preferable formation of hydrogen bonds with the anion under extreme conditions was established. The glassy state of the solution is characterized by the absence of direct anion—cation correlations and increased (compared to standard conditions) probability of the formation of ion—water chains.

Key words: supercooled state, glassy state, method of integral equations, structural parameters, pair correlation functions, lithium chloride, its aqueous solution.

Currently, considerable attention is given to studying the structure of aqueous solutions of electrolytes on microscopic level in a wide range of pressures and temperatures. This subject is of great importance for elucidation of various physicochemical properties of solutions. Of particular interest is investigation of structural characteristics of aqueous solutions under extreme conditions (at ultralow temperatures and high pressures and temperatures).

Numerous data on structural properties of aqueous solutions of lithium chloride obtained by methods of X-ray[1—3] and neutron[4—9] diffraction under standard conditions and by computer simulation (the Monte Carlo[10,11] and molecular dynamics[12—14] methods) have been reported. At the same time, information on the results of structural studies of these systems under extreme conditions is scarce, though the structural properties of aqueous systems are most pronouncedly observed at such state parameters. Thus, aqueous solution LiCl : 6 H_2O in liquid, supercooled, and glassy states was studied by the neutron diffraction method.[9] Raman spectra of aqueous solutions of lithium chloride, bromide, and iodide in the glassy state have been recorded.[15] The effect of lowering temperature on the microscopic structure of LiCl : 5 H_2O aqueous solution has been studied using data of X-ray diffraction studies and computational experiments.[16]

Obtaining direct structural information on a solution by X-ray and neutron diffraction methods under extreme conditions is complicated by difficulties in performing corresponding experiments. Therefore, modern calculations of structural parameters of solutions are often carried out using theoretical methods of determination of their structural and thermodynamic properties from the known molecular interactions. In particular, the method of integral equations (IE) is used; the results obtained by this method are in fairly good agreement with the results of experiments carried out under standard conditions (see, *e.g.*, Refs. 17—19). The IE method can be successfully used for predicting the structural properties of water-electrolyte systems under extreme conditions.[17]

The aim of this work is to study the effect of lowering temperature on the structure of aqueous LiCl solution (at a salt : water molar ratio of 1 : 5.3) by the IE method.

Experimental

Calculations of structural parameters were performed using the Ornstein—Zernike atom-atom integral equation.[20] In the case of ion-molecular systems it is represented by a system of three equations describing solvent—solvent (W—W), solute—solvent (I—W), and solute—solute (I—I) correlations:

$$\rho_W \mathbf{h}_{WW}(k) = \mathbf{s}_W(k)\mathbf{c}_{WW}(k) + \rho_W \mathbf{s}_W(k)\mathbf{c}_{WW}(k)\mathbf{h}_{WW}(k),$$

$$\mathbf{h}_{IW}(k) = \mathbf{c}_{IW}(k)\mathbf{s}_W(k) + \rho_W \mathbf{c}_{IW}(k)\mathbf{h}_{WW}(k),$$

$$\mathbf{h}_{II}(k) = \mathbf{c}_{II}(k) + \rho_W \mathbf{c}_{IW}(k)\mathbf{h}_{IW}(k) + \rho_I \mathbf{c}_{II}(k)\mathbf{h}_{II}(k), \quad (1)$$

where ρ_W is the density of solvent molecules, ρ_I is the density of ions; and $\mathbf{h}_{\alpha\beta}(k)$, $\mathbf{c}_{\alpha\beta}(k)$, and $\mathbf{s}_{\alpha\beta}(k)$ are matrices with the elements

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$$\mathbf{h}_{\alpha\beta}^{xy}(k) = \frac{4\pi}{k}\sqrt{\rho_x\rho_y}\int_0^\infty r\mathrm{d}r h_{\alpha\beta}^{xy}(r)\sin(kr),$$

$$\mathbf{c}_{\alpha\beta}^{xy}(k) = \frac{4\pi}{k}\sqrt{\rho_x\rho_y}\int_0^\infty r\mathrm{d}r c_{\alpha\beta}^{xy}(r)\sin(kr),$$

$$\mathbf{s}_{\alpha\beta}^{xy}(k) = \delta_{xy}\left[\delta_{\alpha\beta} + (1-\delta_{\alpha\beta})\frac{\sin(kl_{\alpha\beta}^{x})}{kl_{\alpha\beta}^{x}}\right],$$

where ρ_x is the density of the molecules of sort X; ρ_y is the density of the molecules of sort Y; $l_{\alpha\beta}^{x}$ is the intramolecular distance between the force centers α and β belonging to the molecule of sort X; $h_{\alpha\beta}^{xy}(r)$ and $c_{\alpha\beta}^{xy}(r)$ are respectively the total and direct atom-atom correlation function of the force centers α (for molecule X) and β (for molecule Y); $\mathbf{s}_{\alpha\beta}^{xy}(r)$ is the matrix of Fourier-transforms of the function describing intramolecular correlations; δ_{xy} is the Dirac delta function; and $\delta_{\alpha\beta}$ is the Kronecker delta.

The hyperchain closure was used for the system of equations (1):

$$h_{WW}(r) + 1 \equiv g_{WW}(r) = \exp[-BU_{WW}(r) + h_{WW}(r) - c_{WW}(r)], \quad (2)$$

$$h_{IW}(r) + 1 \equiv g_{IW}(r) = \exp[-BU_{IW}(r) + h_{IW}(r) - c_{IW}(r)],$$

$$h_{II}(r) + 1 \equiv g_{II}(r) = \exp[-BU_{II}(r) + h_{II}(r) - c_{II}(r)],$$

where $g(r) \equiv g_{\alpha\beta}^{xy}(r)$ is the pair atom-atom correlation function (PCF) of the force centers α and β respectively belonging to the molecules X and Y; $U(r) \equiv U_{\alpha\beta}^{xy}(r) = \varphi_{\alpha\beta}^{xy}(r) + \Phi_{\alpha\beta}^{xy}(r)$ is the initial potential of the atom-atom interaction (the functions $\varphi_{\alpha\beta}^{xy}(r)$ and $\Phi_{\alpha\beta}^{xy}(r)$ describe short-range and long-range interactions); $B = 1/kT$; and k is the Boltzmann constant.

In the course of simulation the solution under study was represented as a mixture of water molecules and ions. Ion—water and ion—ion interactions were described by pair potentials.[21] A modified TIPS model[22] with the known parameters[23] was used for water. The solution of the Ornstein—Zernike atom-atom IE for the system with long-range electrostatic interaction requires renormalization of the initial long-range potential in such a way that only the renormalized shielded potential describing the long-range interaction appeared in the equation. The scheme of this procedure as well as the method of numerical solution of the IE with the hyperchain closure are analogous to those reported previously.[24]

Our calculations by the IE method at different temperatures made it possible to obtain the $g_{\alpha\beta}(r)$ PCF for the LiCl : 5.3 H_2O aqueous solution and use it for determining interparticle distances and analyzing the associative and coordination ability of ions as functions of the number of interactions between corresponding particles depending on temperature. The number of ion—water interactions was calculated by the following formula:

$$g_{\alpha\beta}(r) = 4\pi\rho\int_0^r g_{\alpha\beta}(r)r^2\mathrm{d}r, \quad (3)$$

where ρ is the density of water molecules, the index α corresponds to the ion, and the index β corresponds to the oxygen atom of the water molecule. When determining the number of ion-ion interactions, ρ was considered as the density of ions and index β corresponded to the counterion.

Table 1. Characteristic values of the $g_{\alpha\beta}(r)$ PCF and the numbers of interparticle interactions ($n_{\alpha\beta}$) depending on temperature

Parameter	298 K	243 K	193 K	138 K
R_1	0.290	0.290	0.292	0.294
$g_{OO}(R_1)$	3.086	3.342	3.639	4.122
$n^{(1)}{}_{O-O}$	7.36	7.40	7.42	7.25
R_2	Not defined	0.452	0.440	0.432
$g_{OO}(R_2)$	Not defined	0.815	0.825	0.873
$n^{(2)}{}_{O-O}$	Not defined	3.48	4.28	5.53
R_1	0.146	0.146	0.146	0.146
$g_{OH}(R_1)$	1.268	1.255	1.311	1.567
n_{O-H}	0.45	0.40	0.37	0.36
R_1	0.190	0.190	0.190	0.192
$g_{LiO}(R_1)$	12.317	15.040	17.900	21.624
n_{Li^+-O}	2.97	3.36	3.64	3.80
R_1	0.272	0.270	0.268	0.268
$g_{LiH}(R_1)$	2.131	2.365	2.568	2.797
n_{Li^+-H}	9.36	9.91	10.16	10.26
R_1	0.344	0.344	0.346	0.348
$g_{ClO}(R_1)$	3.577	3.752	3.867	3.949
n_{Cl^--O}	10.60	10.16	9.28	8.46
R_1	0.200	0.200	0.200	0.200
$g_{ClH}(R_1)$	4.361	5.766	7.322	9.208
n_{Cl^--H}	3.62	4.26	4.78	5.16
R_1	0.224	0.226	0.230	0.236
$g_{LiCl}(R_1)$	11.338	6.724	1.638	0.029
$n_{Li^+-Cl^-}$	1.54	0.89	0.22	~0
R_2	0.444	0.438	0.438	0.438
$g_{LiCl}(R_2)$	1.898	2.446	2.971	3.401
$n_{Li^+-H_2O-Cl^-}$	4.47	4.90	5.19	5.15

Note. R are the positions of maxima of the functions and $g_{\alpha\beta}(R)$ are the heights of corresponding peaks.

Results and Discussion

The characteristic values of the $g_{\alpha\beta}(r)$ PCF and the numbers of interactions between the ions and water molecules in the nearest hydration region and between anions and cations at all temperatures are listed in Table 1.

The effect of temperature lowering on peculiarities of the formation of the structure of the system under study was analyzed by comparing the results obtained with those of X-ray diffraction study of the same system under analogous conditions.[16]

Water—water (W—W) correlations

The plots of the $g_{W-W}(r)$ PCF at 298, 243, 193, and 138 K are shown in Fig. 1. The intensity of the main $g_{OO}(r)$ function peak determined by interactions between water molecules in the unbound solvent increases as temperature decreases. This is accompanied by narrowing of the peak and shift of the position of the first

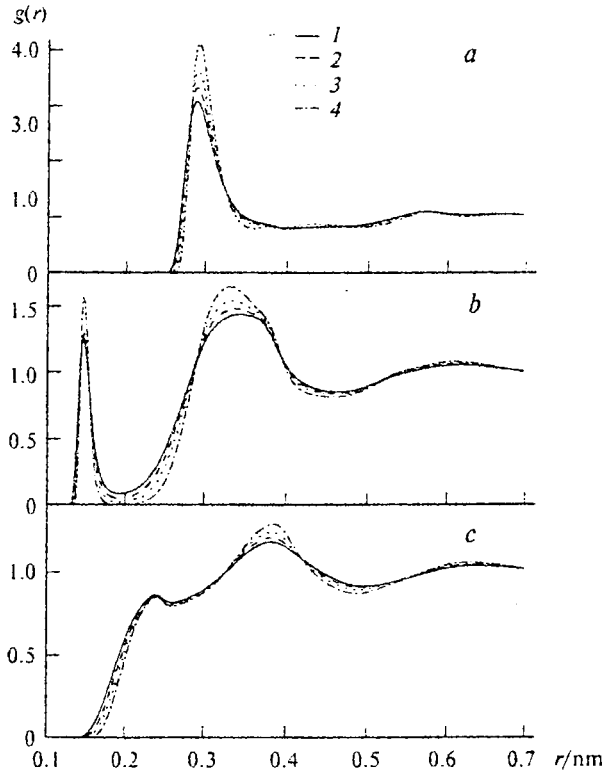

Fig. 1. The O—O (*a*), O—H (*b*), and H—H (*c*) PCF of the LiCl : 5.3 H_2O system at T/K = 298 (*1*), 243 (*2*), 193 (*3*), and 138 (*4*).

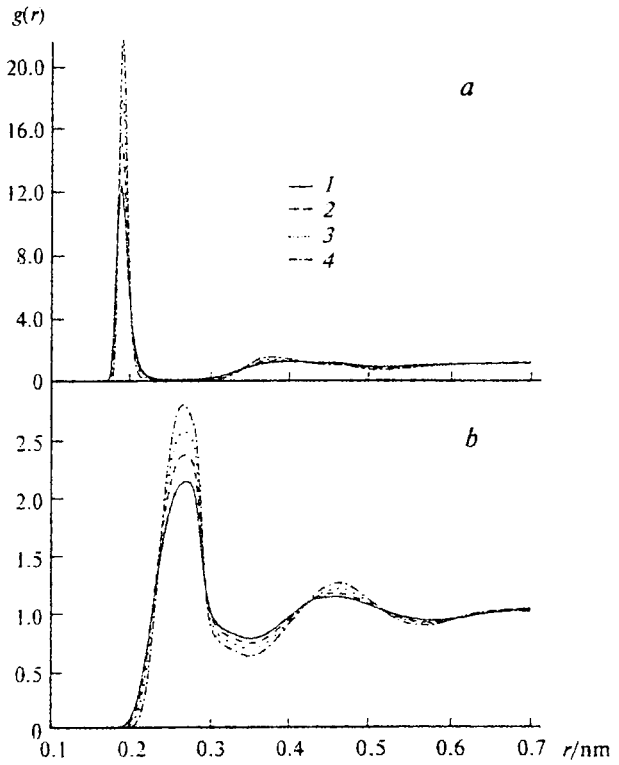

Fig. 2. The Li—O (*a*) and Li—H (*b*) PCF of the LiCl : 5.3 H_2O system at T/K = 298 (*1*), 243 (*2*), 193 (*3*), and 138 (*4*).

minimum of the $g_{OO}(r)$ function towards shorter distances and leads to a certain decrease in the number of interactions between water molecules in the unbound solvent ($n^{(1)}{}_{O-O}$ (298 K) = 7.36, $n^{(1)}{}_{O-O}$ (138 K) = 7.25 (see Table 1)).

On going to supercooled and further to glassy state (the system in question has a transition temperature $T_g \approx$ 141 K)[25] the shoulder in the region 0.41—0.46 nm on the plot of the $g_{OO}(r)$ function increases and is smoothly transformed into a peak whose height also increases (see Table 1). This peak is determined by interactions between water molecules in the tetrahedral structure. The increase in the height of the peak is accompanied by shift of the position of its maximum towards shorter distances. In this case the fraction of tetrahedrally ordered water molecules ($n^{(2)}{}_{O-O}$) increases from 3.48 to 5.53 (at T = 243 and 138 K, respectively). Noteworthy is that there is no tetrahedral ordering of solvent molecules at 298 K, which is in agreement with the reported results.[9]

Lowering the temperature also leads to increase in the intensity of the main $g_{OH}(r)$ function peak (see Fig. 1) accompanied by its considerable narrowing and shift of the position of the peak maximum towards shorter r. Simultaneously, the depth of the "valley" between the first and second peaks is increased. The n_{O-H} value at a distance corresponding to the position of the first minimum decreases from 0.45 (T = 298 K) to 0.36 (T = 138 K), or by 20.0% (see Table 1).

The height of the first peak of the $g_{HH}(r)$ function remains virtually unchanged as temperature decreases; however, the intensity of its second peak appreciably increases while the position of its maximum is shifted towards longer distances (see Fig. 1).

The aforesaid makes it possible to conclude that transition of the system to supercooled and then to glassy state will be accompanied by increase in the tetrahedral ordering of solvent molecules and decrease in the number of interactions between water molecules in unbound solvent, which is in agreement with the results of neutron diffraction studies.[9]

Cation—water (Li^+—W) correlations

The plots of the $g_{Li-W}(r)$ PCF at the same temperatures are shown in Fig. 2. The intensity of the main $g_{LiO}(r)$ PCF peak with a maximum at r = 0.190 nm, which is determined by the interactions between Li^+ cations and water molecules in the nearest environment, increases on cooling the system. The number of Li^+—O interactions also increases from 2.90 to 3.80 (at T = 298 and 138 K, respectively), or by 27.9% (see Table 1).

The function $g_{LiH}(r)$ behaves similarly to the $g_{LiO}(r)$ one: PCF, that is, the height of its main peak, increases as temperature decreases. The peak becomes appreciably

narrower and the position of its maximum is shifted towards shorter distances (see Table 1). As in the preceding case, the number of Li^+—H interactions (n_{Li^+-H}) increases from 9.36 to 10.26 (at T = 298 and 138 K, respectively), or by 9.6% (see Table 1). Hence, the degree of structurization of water molecules surrounding the cation at low temperatures will be higher compared to that under standard conditions.

Anion—water (Cl^-—W) correlation

As can be seen in Fig. 3 and Table 1, placing the system under extreme conditions leads to increase in the height of the main $g_{ClO}(r)$ PCF peak determined by the interactions between Cl^- anions and O atoms of water molecules in the nearest environment. These interactions are realized by means of hydrogen bonding. Simultaneously with the increase in the peak height, the position of its maximum is shifted towards longer r. However, it should be noted that, unlike Li^+—O interactions, in this case the increase in the intensity of the main peak is accompanied by its considerable narrowing. The depth of the "valley" between the first and second peaks is also increased and the position of the first minimum is shifted towards shorter distances. A consequence of these changes is the decrease in the $n_{Cl^-\cdots O}$ value from 10.60 to 8.46 (at T = 298 and 138 K, respectively), or by 20.2% (see Table 1). At the same time, the shoulder on the left slope of the second peak increases as temperature decreases, being transformed into an additional peak with a maximum near 0.500 nm.

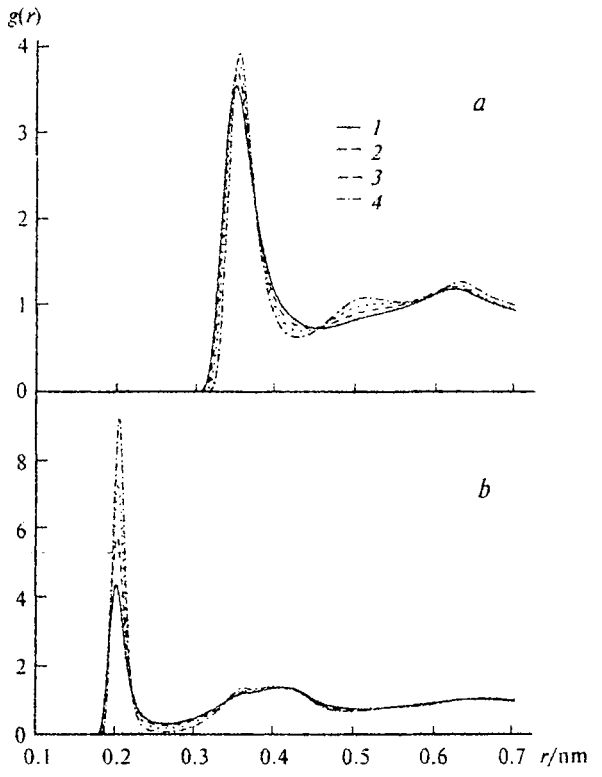

Fig. 3. The Cl—O (*a*) and Cl—H (*b*) PCF of the LiCl : 5.3 H_2O system at T/K = 298 (*1*), 243 (*2*), 193 (*3*), and 138 (*4*).

In contrast to the behavior of the $g_{ClO}(r)$ function, cooling of the system leads to appreciable increase in the height of the main $g_{ClH}(r)$ PCF peak and its considerable narrowing. In this case the position of the maximum of the $g_{ClH}(r)$ function remains unchanged. As for Li^+—H interactions, the number of Cl^-—H interactions increases from 3.62 to 5.16 (at T = 298 and 138 K, respectively), or by 42.5% (see Table 1). Analogously to the $g_{ClO}(r)$ function, a shoulder in the region 0.360—0.365 nm appears on the left slope of the second $g_{ClH}(r)$ function peak at 243 K. It is transformed into a small peak whose height increases on further cooling of the system.

Noteworthy is that the decrease in the $n_{Cl^-\cdots O}$ value is mainly due to decrease in the number of hydrogen bonds between solvent molecules (n_{O-H}), since at low temperatures they are preferably formed with Cl^- ions, which is confirmed by the increase in the $n_{Cl^-\cdots H}$ value.

Anion—cation (Cl^-—Li^+) correlations

Cooling of the system leads to appreciable decrease in the intensity of the first $g_{LiCl}(r)$ PCF peak (Fig. 4), determined by Li^+—Cl^- interaction. The peak becomes considerably narrower and the position of its maximum is shifted towards longer r. The depth of the "valley" between the first and second peaks appreciably increases. It should be noted that the first peak of this function is

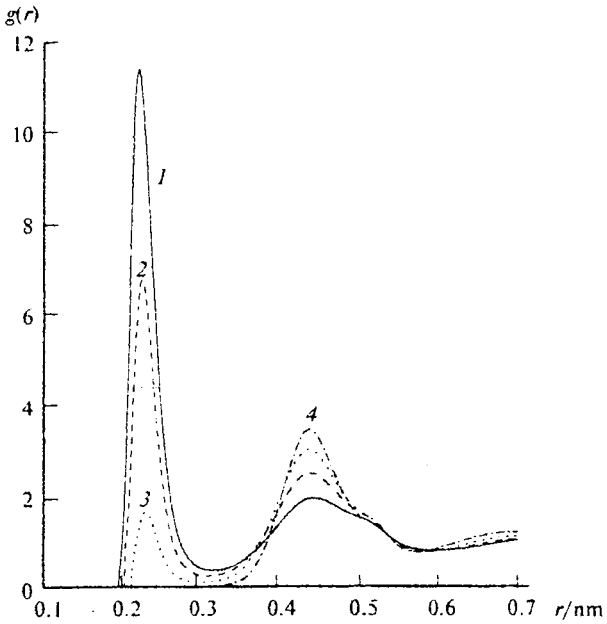

Fig. 4. The Li—Cl PCF of the LiCl : 5.3 H_2O system at T/K = 298 (*1*), 243 (*2*), 193 (*3*), and 138 (*4*).

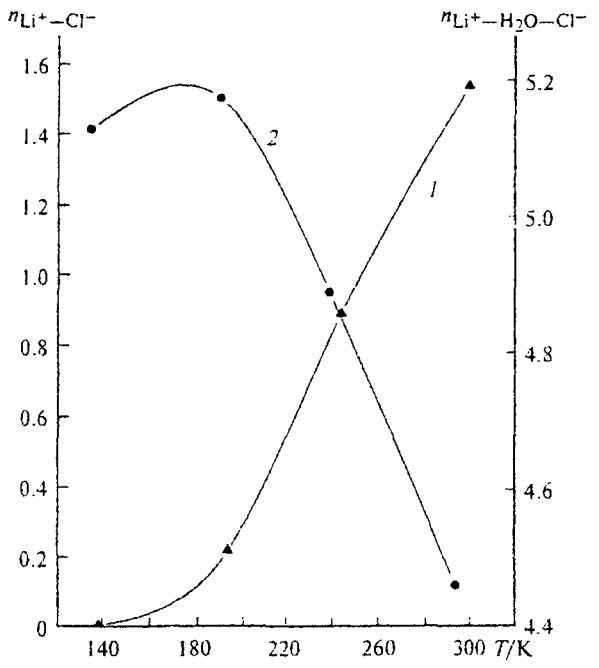

Fig. 5. Dependence of the number of $Li^+—Cl^-$ and $Li^+—H_2O—Cl^-$ interactions in the LiCl : 5.3 H_2O system on temperature: *1*, $n_{Li^+-Cl^-}(T)$; *2*, $n_{Li^+-H_2O-Cl^-}(T)$.

virtually absent at 138 K (see Table 1). Thus, the number of $Li^+—Cl^-$ interactions substantially decreases as temperature decreases ($n_{Li^+-Cl^-}$ = 1.54 and ≈ 0 at T = 298 and 138 K, respectively) (see Table 1).

The intensity of the peak in the region 0.438—0.440 nm, determined by interaction between Li^+ and Cl^- ions in $Li^+—H_2O—Cl^-$ chains, appreciably increases as temperature decreases. The peak becomes narrower and the position of its maximum is shifted towards shorter distances. The $n_{Li^+-Cl^-}$ value (*i.e.*, the sum of the number of $Li^+—Cl^-$ interactions and that of $Li^+—H_2O—Cl^-$ interactions) at a distance corresponding to the position of the second minimum of the $g_{LiCl}(r)$ function increases on cooling the system. In this case the fraction of ion-water $Li^+—H_2O—Cl^-$ chains increases (only a slight decrease is observed at 138 K). This is in agreement with the results obtained in studies of the LiCl : 6 H_2O system,[26] in which the ions in glassy state are surrounded by a complete hydration sphere and no direct ion-ion correlations are observed.

An interesting peculiarity of the $n_{Li^+-H_2O-Cl^-}(T)$ dependence for the system under study (Fig. 5) should be mentioned. At T ≈ 177.15 K (crystallization temperature), it passes through a maximum at which $n_{Li^+-H_2O-Cl^-}$ = 5.21. It is known[9,27] that a compound formed at a LiCl : water molar ratio of 1 : 5 (pentahydrate) is stable in supercooled and glassy state and is crystallized at −173 K. It is also known[9,27] that the compound LiCl : 5.3 H_2O is crystallized at somewhat higher temperature (T ≈ 178 K), which is in agreement with our results (T = 177.2 K).

Hence, the number of direct anion—cation correlations decreases on cooling the LiCl : 5.3 H_2O system and counterions virtually do not interact at 138 K. At the same time, the net probability of the formation of $Li^+—H_2O—Cl^-$ chains increases. The $n_{Li^+-Cl^-}$ (T) and $n_{Li^+-H_2O-Cl^-}$ (T) dependences (see Fig. 5) were obtained by spline approximation.

To test the adequacy of the results obtained against the data of direct structural studies,[16] we performed the following test. Using the PCF determined by the IE method, we calculated the radial distribution functions (RDF) in the form $D(r) - 4\pi r^2\rho_0$,[16] where $D(r) = G(r) \cdot 4\pi r^2\rho_0$, $G(r)$ is the normalized total correlation function, which is defined as

$$G(r) = 1 + \frac{1}{2\pi^2\rho r} \cdot \int_0^{k_{max}} k \cdot i(k) \cdot M(k) \cdot \sin(kr) \cdot dk, \quad (4)$$

where ρ is the number of molecules (LiCl + H_2O) in 1 Å^3, k is the wave vector, $M(k)$ is the modifying function, and $k \cdot i(k)$ is the structural function calculated by the formula

$$k \cdot i(k) = \frac{\sum_i \sum_j x_i x_j \zeta_i \zeta_j}{(\sum_i x_i \zeta_i)^2} \cdot \int_0^{r_{max}} 4\pi\rho \cdot r \cdot (g_{ij}(r) - 1) \cdot \sin(kr) \cdot dr. \quad (5)$$

where x is the mole fraction of the ion, ζ is the atomic scattering factor, and $g(r)$ is the PCF.

The characteristic values of the $D(r) - 4\pi r^2\rho_0$ RDF are listed in Table 2. The plots of temperature dependences of these functions are shown in Fig. 6. The intensity of a small RDF peak at 0176 nm (298 K) increases and the position of its maximum is simultaneously shifted towards longer distances (to 0.180 nm at 138 K) as temperature decreases (see Table 2).

The intensity of the main RDF peak in the region 0.350 nm increases as temperature decreases. A shoul-

Table 2. Characteristic values of the RDF depending on temperature

Peak	298 K		243 K		193 K		138 K	
	r/nm	*D*(*r*)	*r*/nm	*D*(*r*)	*r*/nm	*D*(*r*)	*r*/nm	*D*(*r*)
1	0.176	−−0.94	0.176	−−0.92	0.178	−0.889	0.180	−0.869
2	0.350	3.570	0.350	3.876	0.352	4.137	0.352	4.515
3	0.634	1.271	0.632	1.276	0.634	1.222	0.644	1.282

Note. *D*(*r*) is the height of the peak of the function and *r* is the position of its maximum.

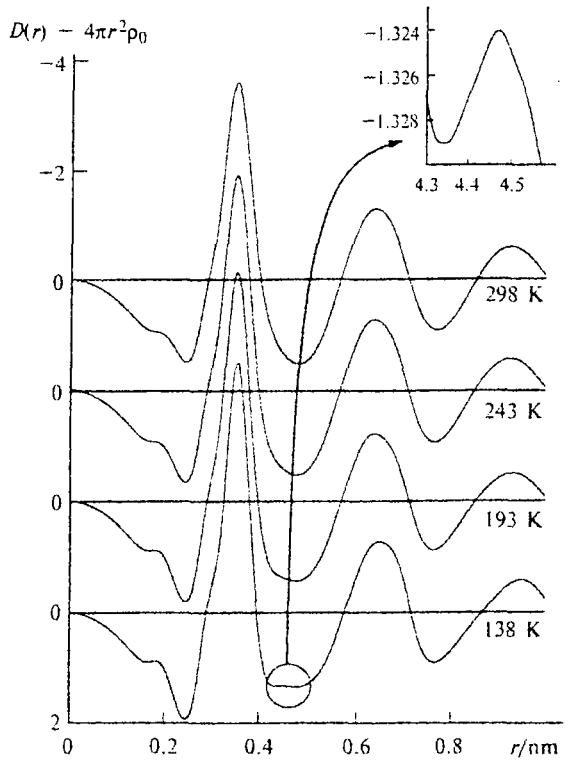

Fig. 6. Radial distribution functions of the LiCl : 5.3 H_2O system calculated as $D(r) - 4\pi r^2\rho_0$. The inset shows a peak in the 0.446—0.448 nm region at 138 K.

der in the region 0.290—0.295 nm that appears on the left slope of the peak on cooling the system behaves analogously. A tendency toward the formation of a peak at 0.446—0.448 nm on the RDF plot is observed on going to extreme conditions. The height of the peak in the region 0.634 nm (298 K) increases as temperature decreases and the position of its maximum is shifted towards longer r. By and large, changes in the intensities and positions of RDF peaks (see Fig. 6) are in good agreement with the results obtained for the same system under analogous conditions.[16]

Thus, analysis of the results obtained for a concentrated aqueous solution of lithium chloride at a salt : water molar ratio of 1 : 5.3 makes it possible to suggest that transition of the system to supercooled and glassy state will be accompanied by increase in tetrahedral ordering of solvent molecules and decrease in the number of interactions between water molecules in unbound solvent. It should be expected that the degree of structurization of water molecules surrounding the cation will increase with lowering temperature. Preferable formation of hydrogen bonds with anion under extreme conditions was established. The glassy state of the solution is characterized by the absence of direct correlations between Li^+ and Cl^- ions and an increased (compared to standard conditions) probability of the formation of ion-hydrogen chains.

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