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The Features of Structurization of the Dilute Aqueous Solution of Lithium Chloride at the Near-Critical and Supercritical Conditions

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Abstract—Method of integral equations in the RISM approximation was used for the study of the structural properties of the dilute aqueous solution of lithium chloride in the near-critical and supercritical state. The following general trends of structural changes in the solution at its transition from the standard conditions to the supercritical conditions were revealed: destruction of the solvent tetrahedral lattice, thermal dehydration of the cation and anion, and an increase in the contact association. We found that the effect of temperature on the decrease in the fraction of the hydrogen-bonded solvent molecules and the value of the thermal dehydration of the ions is comparable with the influence of the density on the same characteristics. The process of ion association is affected predominantly by temperature, the effect is maximal in the subcritical region.

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Among the supercritical fluids an important role in the geology and biochemistry processes belongs to water and aqueous solutions. In recent decades they were successfully implemented in the supercritical technologies in various sectors of industrial production. The understanding of the mechanisms of processes in supercritical fluids is crucial for the optimal choice of technological parameters and for the comprehension of a wide range of natural phenomena. However, despite intensive investigations of physical and chemical properties of supercritical aqueous fluids, still an unequivocal explanation is absent of their behavior at the microscopic and molecular level. This is due to the lack of physicochemical data, primarily the structural ones, owing to the problems arising at carrying out experiments under the extreme conditions. Moreover, there are difficulties and contradictions in the interpretation of existing structural information, largely due to the existence of several variable parameters (p, T, and ρ) and their interdependence, which can lead to opposite effects [1].

This paper continues a series of publications [2–6] on the study of structural state of supercritical aqueous solutions of 1:1 electrolytes and is devoted to the peculiar features of the structure of the 0.24 m aqueous solution of LiCl in the near-critical (T = 573 K, ρ_1 = 1 g cm^{-3} and ρ_2 = 0.74 g cm^{-3}) and supercritical (T = 1073 K, ρ = 0.74 g cm^{-3}) conditions. For comparison, we present the data for the same system under standard conditions (T = 298 K, p 0.1 MPa) with the model density ρ = 1 g cm^{-3}. Note that to date the structural studies for the system LiCl–H_2O in the pre- and supercritical conditions are rare. Basically, they concern the structural parameters of hydration of Li^+ and Cl^- in concentrated (≥ 3 m) solutions, and are obtained by neutron diffraction with isotopic substitution [7–10]. Features of the ion association in the system of interest have been discussed in [11] on the basis of analysis of interionic potentials of mean force and the association constants calculated by computer simulation (molecular dynamics). As an additional source of information on the structural state of supercritical LiCl solutions ion association constants obtained from the conductometric data can also be used [12–14]. The analysis of the results presented here allows us to assess the impact of various factors (the fluid temperature and density) on the structural changes occurring in the LiCl solution at its transition to the near-critical and supercritical states.

For the calculations of the structural characteristics of the studied system, we used a method of integral equations in the RISM (Reference Interaction Site

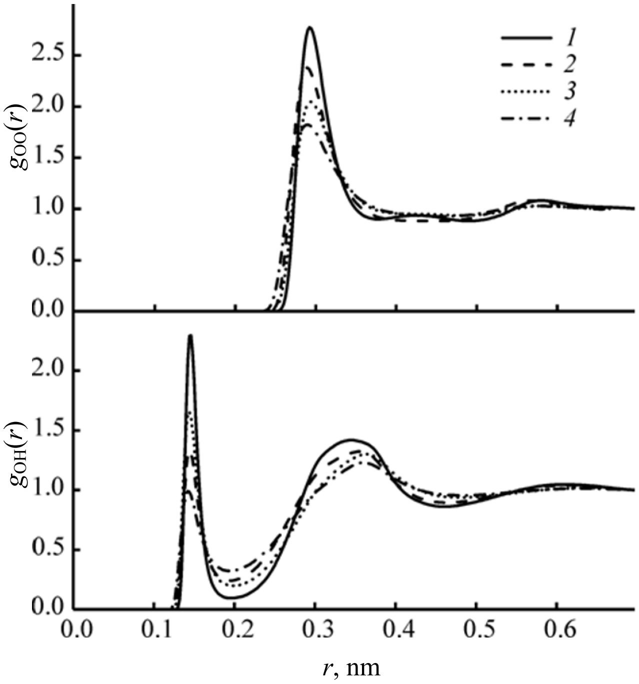

Fig. 1. Pair correlation functions $g_{OO}(r)$ and $g_{OH}(r)$ of the 0.24 m water solution of LiCl: (*1*) standard conditions (T = 298 K, p 0.1 MPa, ρ = 1 g cm^{-3}), (*2*) near-critical conditions (T = 573 K, ρ = 1 g cm^{-3}), (*3*) near-critical conditions (T = 573 K, ρ = 0.74 g cm^{-3}), and (*4*) supercritical conditions (T = 1073 K, ρ = 0.74 g cm^{-3}).

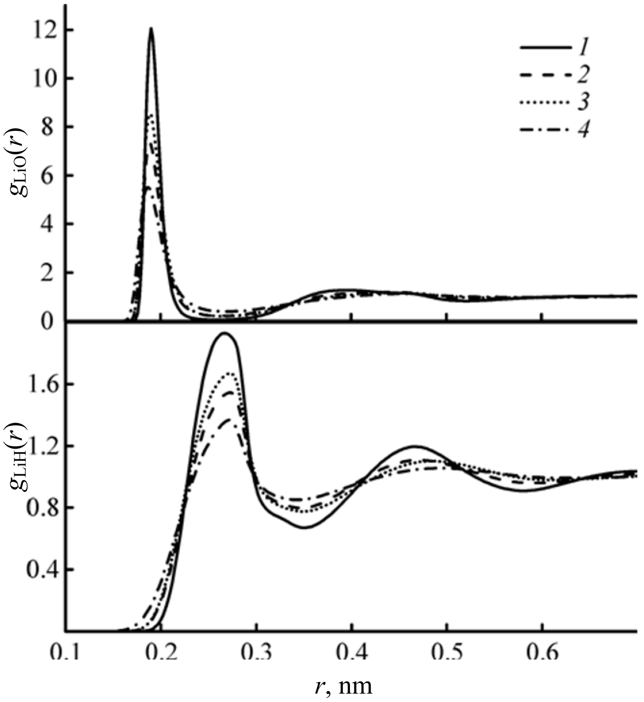

Fig. 2. Pair correlation functions $g_{LiO}(r)$ and $g_{LiH}(r)$ of the 0.24 m water solution of LiCl: (*1*) standard conditions (T = 298 K, p 0.1 MPa, ρ = 1 g cm^{-3}), (*2*) near-critical conditions (T = 573 K, ρ = 1 g cm^{-3}), (*3*) near-critical conditions (T = 573 K, ρ = 0.74 g cm^{-3}), and (*4*) supercritical conditions (T = 1073 K, ρ = 0.74 g cm^{-3}).

Model) approximation. In the framework of this method, the description of an ion-molecular system is performed in the terms of atom-atom distribution functions describing the probability density of distribution of the power centers belonging to different particles in the system. For the calculation of these functions the Ornstein–Zernike atom-atom equation is usually used [15] with the locking of the hyperchain type. The method of integral equations in the RISM-approach, the methodology of solving and the ways of the numerical realization of atom-atom Ornstein–Zernike equation is considered, for example, in [15–19].

The fluid was modeled as a mixture of water molecules and ions with pair potentials of the following form. For the solvent a SPC (Simple Point Charge) model was used [20] with the modified parameters given in [21]. Note that this model does not account for the dissociation of water molecules, a process that near the critical point is known to be characterized by a constant more than threefold greater than the water dissociation constant in its normal state. However, testing individual models allowing this process [22–25] showed that dissociation does not affect significantly the results of the calculations, and hence the resulting data. The interactions between the water ions and molecules were described by Lennard–Jones (short range) and Coulomb (long range) potentials. For the interionic interactions the Huggins–Mayer potential was chosen Eq. (1):

$$U_{ij} = q_iq_j/r + B_{ij}\exp(-r/\rho_{ij}) - C_{ij}/r^6, \quad (1)$$

where q_i and q_j are the charges of the ith and jth ions located at a distance r, B_{ij}, C_{ij}, and ρ_{ij} are parameteric values. Parameters of the ion-water and ion-ion pair potentials for the LiCl solution are similar to those in [26].

By the numerical solution of the atom-atom Ornstein–Zernike equation pair correlation functions $g_{\alpha\beta}(r)$ were obtained allowing determination of the interparticle distances, the presence of ionic associates (contact and hydrate-separated ion pairs), and calculation of the partial coordination numbers of particles $n_{\alpha\beta}$:

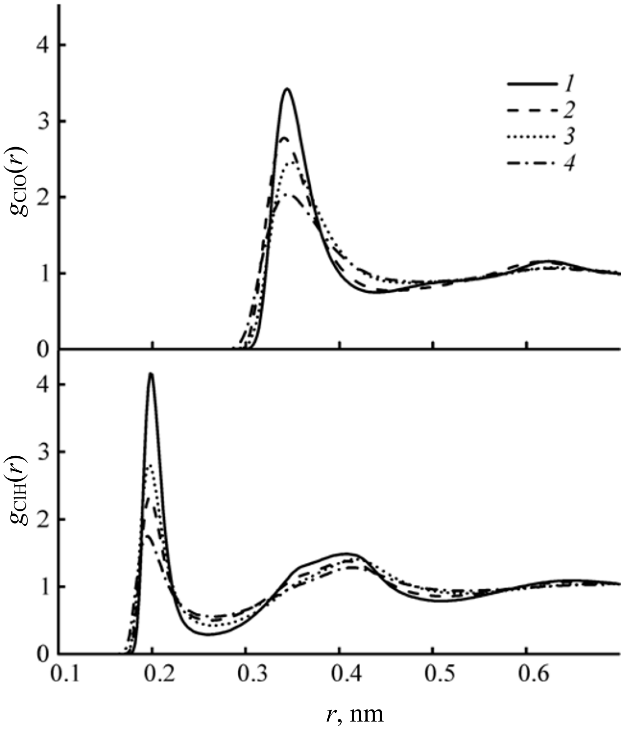

Fig. 3. Pair correlation functions $g_{ClO}(r)$ and $g_{ClH}(r)$ of the 0.24 m water solution of LiCl: (*1*) standard conditions (T = 298 K, p 0.1 MPa, ρ = 1 g cm^{-3}), (*2*) near-critical conditions (T = 573 K, ρ = 1 g cm^{-3}), (*3*) near-critical conditions (T = 573 K, ρ = 0.74 g cm^{-3}), and (*4*) supercritical conditions (T = 1073 K, ρ = 0.74 g cm^{-3}).

$$n_{\alpha\beta} = 4\pi\rho_\beta\int_0^{r_{mi}} g_{\alpha\beta}(r)\, r^2 dr. \qquad (2)$$

The partial coordination number is a statistically averaged number of particles of species β in the coordination sphere of a particle of species α. In Eq. (2): r_{mi} is the position of the ith minimum of the $g_{\alpha\beta}(r)$ function which corresponds to the radius of the ith coordination sphere, ρ_β is the density of particles of β species. The pair correlation functions $g_{WW}(r)$ and the n_{WW} values characterize the structural features of water; the pair correlation functions $g_{IW}(r)$ and the n_{IW} value (number of water molecules in the close environment of the ions) correspond to the hydration of ions; the pair correlation functions $g_{II}(r)$ and the ionic association n_{II} indicate the ion association. To assess the effect of the fluid temperature or density, we calculated also the relative change in the partial coordination numbers:

$$\Delta n_{\alpha\beta} = (n^2_{\alpha\beta} - n^1_{\alpha\beta})/n^1_{\alpha\beta}\times 100\%, \qquad (3)$$

where $n^1_{\alpha\beta}$ and $n^2_{\alpha\beta}$ are the partial coordination numbers at the initial Eq. (1) and final Eq. (2) temperatures or densities, respectively.

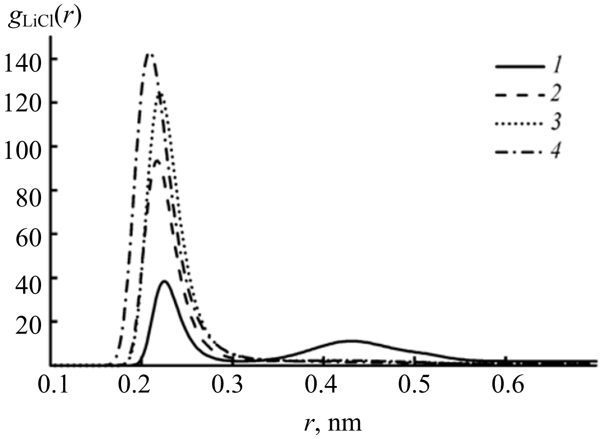

Fig. 4. Pair correlation functions $g_{LiCl}(r)$ of the 0.24 m water solution of LiCl: (*1*) standard conditions (T = 298 K, p 0.1 MPa, ρ = 1 g cm^{-3}), (*2*) near-critical conditions (T = 573 K, ρ = 1 g cm^{-3}), (*3*) near-critical conditions (T = 573 K, ρ = 0.74 g cm^{-3}), and (*4*) supercritical conditions (T = 1073 K, ρ = 0.74 g cm^{-3}).

Transfer of the LiCl solution to the near-critical and supercritical state proceeds with a significant structural rearrangements affecting the behavior of the $g_{\alpha\beta}(r)$ functions: the height and width of the main peaks are changed and the extrema are shifted (Figs. 1–4, Table 1).

The analysis of the results shows that upon increase in temperature a gradual destruction occurs of the tetrahedral water H-bond network with an increase in the number of the free water molecules. This is evidenced by "blurring" of the second peak in the $g_{OO}(r)$ function at r = 0.426 nm, which under standard conditions defines the tetrahedricity of the solvent structure, as well as an increase in height and broadening of the first peak at r = 0.292 nm, which reflects the interaction between the nearest water molecules. However, at high temperatures, the correct calculation of the fraction of free water molecules (nearest neighbors) in the solution is impossible due to the uncertainty of the first minimum in the $g_{OO}(r)$ function (Fig. 1, Table 1). Despite the absence of tetrahedral ordering, the near-critical and supercritical solutions still contain a certain number of hydrogen-bonded solvent molecules (Table 1, n_{OH}). Their proportion decreases by 37.4% when the temperature increases from standard to supercritical (T = 1073 K, ρ = 0.74 g cm^{-3}). These thermal changes in the structure of bulk water in solution are typical of water–salt systems at elevated temperatures [1–6, 27–31].

The temperature change from the standard to the near-critical (T = 573 K) and further, to a supercritical

Table 1. The main structural characteristics of 0.24 m aqueous solution of LiCl in standard, near-critical, and supercritical conditions[a]

Parameter	298 K, 1 g cm^{-3}	573 K, 1 g cm^{-3}	573 K, 0.74 g cm^{-3}	1073 K, 0.74 g cm^{-3}
$g_{OO}(r_{M1})$	2.771 (0.292)	2.377 (0.288)	2.046 (0.294)	1.823 (0.290)
$g_{OO}(r_{m1})$	0.901 (0.378)	0.883 (0.446–0.448)	not defined	not defined
$g_{OO}(r_{M2})$	0.938 (0.426)	blurred	blurred	blurred
$g_{OO}(r_{m2})$	0.883 (0.490)	not defined	not defined	not defined
$g_{OH}(r_{M1})$	2.297 (0.146)	1.335 (0.144)	1.661 (0.144)	0.991 (0.142)
$g_{OH}(r_{m1})$	0.094 (0.196)	0.240 (0.194)	0.199 (0.198)	0.323 (0.194)
n_{OH}	0.91	0.80	0.68	0.57
$g_{LiO}(r_{M1})$	12.046 (0.190)	7.307 (0.188)	8.517 (0.190)	5.519 (0.186)
$g_{LiO}(r_{m1})$	0.055 (0.258)	0.210 (0.262)	0.207 (0.266)	0.393 (0.270)
n_{LiO}	3.61	3.14	2.70	2.40
$g_{LiH}(r_{M1})$	1.928 (0.266)	1.545 (0.272)	1.669 (0.272)	1.367 (0.272)
$g_{LiH}(r_{m1})$	0.671 (0.350)	0.799 (0.348)	0.776 (0.348)	0.852 (0.342)
$g_{ClO}(r_{M1})$	3.425 (0.344)	2.775 (0.342)	2.462 (0.348)	2.037 (0.344)
$g_{ClO}(r_{m1})$	0.747 (0.44)	0.770 (0.458)	0.871 (0.474)	0.886 (0.488)
$g_{ClH}(r_{M1})$	4.162 (0.198)	2.326 (0.198)	2.806 (0.198)	1.746 (0.196)
$g_{ClH}(r_{m1})$	0.288 (0.26)	0.499 (0.262)	0.424 (0.266)	0.554 (0.264)
n_{ClH}	4.09	3.45	2.87	2.44
$g_{LiCl}(r_{M1})$	38.480 (0.224)	93.403 (0.218)	124.359 (0.220)	143.078 (0.208)
$g_{LiCl}(r_{m1})$	1.905 (0.310)	1.975 (0.352)	2.235 (0.372)	not defined
n_{LiCl}	0.16	0.41	0.43	~0.5 (r_{m1} 0.372 at 573 K, 0.74 g cm^{-3})
$g_{LiCl}(r_{M2})$	11.143 (0.430)	2.255 (0.418)	2.311 (0.414)	not obtained
$g_{LiCl}(r_{m2})$	1.940 (0.616)	not defined	not defined	–
$n_{Li–H2O–Cl}$	0.63	–	–	–

[a] r_{Mi} and $g_{\alpha\beta}(r_{Mi})$ are position (nm) and height, respectively, of the function; r_{mi} and $g_{\alpha\beta}(r_{mi})$ are position and the function value of minima in the point of *i*th minimum; $n_{\alpha\beta}$ is partial coordination numbers of particles.

(T = 1073 K) leads to a decrease and broadening of the main peaks in the $g_{IW}(r)$ functions, as well as to a decrease in the depth of the first minimum (Figs. 2, 3, Table 1). Such functional changes, as well as reduction in the cation partial coordination number n_{LiO} and the number of H-bonds between the anions and the nearest water molecules n_{ClH} (Table 1) indicate the thermal dehydration of the cation and anion. Thus, in the range of T = 298–1073 K both n_{LiO} and n_{ClH} decrease by 33.5 and 40.3%, respectively. These our data confirm the conclusions of the majority of structural studies [1–10, 31–37] on the dehydration of ions in the solutions of the 1:1 electrolytes at elevated temperatures. In particular, the neutron diffraction studies of ion hydration in concentrated (≥ 3 m) solutions of lithium chloride in the pre- and supercritical conditions [10] showed that the number of water molecules in the close environment of Li^+ and Cl^- in the temperature

Table 2. Comparative analysis of the effect of the fluid temperature and density on the relative change in the partial coordination numbers

Relative change in the partial coordination number	Effect of temperature		Effect of the fluid density
	ΔT 298–573 K (ρ 1 g cm^{-3})	ΔT 573–1073 K (ρ 0.74 g cm^{-3})	Δρ 1.0–0.74 g cm^{-3} (T 573 K)
Δn_{OH}	–12.1%	–16.2%	–15%
Δn_{LiO}	–13%	–11.1%	–14%
Δn_{ClH}	–15.6%	–15%	–16.8%
Δn_{LiCl}	in 2.6 times	16.3%	5%

range 298–647 (648) K decreased by 31.7% and 55.4% respectively, which is comparable with our data. However, we cannot compare our numerical data with the data [10] correctly due to significant difference in the investigated ranges of the state parameters and the solution concentrations.

Now we consider the features of ion association at the transfer the system from the standard to the supercritical conditions. As follows from the calculations (Table 1), under standard conditions the ability of ions to the association in 0.24 m aqueous solution of LiCl is low, but the proportion of hydrate-separated ion pairs is almost 4 times higher than that of the contact ion pairs. According to the data obtained for the near-critical and supercritical conditions, in this system the hydrate separated ion pairs are formed. This is evidenced by the lack of a second peak in the $g_{LiCl}(r)$ function (Fig. 4, Table 1). At heating from 298 to 1073 K an increase occurs in the first peak in the $g_{LiCl}(r)$ function (Fig. 4, Table 1), indicating the existence in the system of contact ion pairs. Simultaneously, the broadening and shifting of position of this peak occurs to smaller r. A special feature of the $g_{LiCl}(r)$ function in supercritical conditions is the absence of the first minimum, and the correct calculation of the proportion of contact ion pairs for this case is impossible. However, this value at 1073 K can be estimated roughly using for the calculation of the number of contact associates the position of the first minimum r_{m1} 0.372 nm, determined at the near-critical temperature 573 K at the same fluid density (ρ 0.74 g cm^{-3}). This approach shows that the temperature change from the standard (T = 298 K) to supercritical (T = 1073 K) causes a more than 3-fold increase in the proportion of the contact ion pairs (Table 1), but, as in the standard conditions, it remains rather low. The increase in the ion association is explained by the fracture of the water H-bond network that decreases dielectric constant to the value several times lower than that observed under standard conditions. As a result, the loss of electrostatic shielding reduces the salt solubility, which leads to an increase in the proportion of contact pairs in solution. As was shown in [38], in dilute aqueous solutions at high temperatures and low pressures the singly charged ions have a common tendency of binding to form neutral (contact) ion pairs. Evaluation of the experimental values of association constants defined in [12–14] from the conductometric data also indicates an increase in the contact association in dilute solutions of LiCl with increasing temperature and decreasing density.

The observed features of ion association at the transition of the system from the standard to the supercritical conditions was confirmed by computer simulation [11] of the mean force ion–ion potentials and the corresponding constants of ion association for the same solution. According to [11], in 0.24 m LiCl solution under standard conditions the proportion of hyrate separated pairs is higher than that of the contact pairs, as evidenced by a deeper second minimum of interionic potential of mean force characterizing the presence of the hydrate separated pairs, compared to the first minimum characterizing the presence of contact associates. Under the supercritical conditions (T = 1073 K) the situation is reversed: the second minimum is blurred, and the depth of the first increases significantly. Such changes in the mean force interionic potential reflects the increase in the number of contact pairs and a gradual disappearance of the hydrate separated pairs in the transition of the solution to the supercritical state. The same direction of the ion association process indicates the change of calculated ion association constants [11], which, like the experimental constants, as mentioned above, tend to increase with increasing temperature and decreasing density of the fluid. This is consistent with the fact that in the supercritical conditions the solubility of ionic compounds in water decreases and the probability of the salt precipitation increases [39, 40].

Our results allow us to compare the effect of various factors (temperature at a constant density of the fluid and/or density of the fluid at a constant temperature) on structural changes in the solution (Table 2). The comparison shows that the effect of temperature (Table 2) on reducing the proportion of hydrogen-bonded solvent molecules and the magnitude of thermal dehydration of the ions is comparable with the effect of density and falls to the range of 11 to 17%. The situation differs from the impact of these factors on the process of ion association. As seen from Table 2, the effect of temperature at its change from standard to near-critical value (ρ_{const} = 1 g cm^{-3}) on the Δn_{LiCl} magnitude is many times greater than its effect at the transition from the near-critical to the supercritical state (ρ_{const} = 0.74 g cm^{-3}). At the same time, the effect of density on the ionic association in the near-critical conditions (T_{const} = 573 K) is negligible. Thus, the temperature produces the main influence on the process of ion association, the effect is maximal in the subcritical region. However, the maximum effect on the structural changes in the solution has a cumulative effect of the T and ρ factors, namely: in the temperature range 298–1073 K and density 1.0–0.74 g cm^{-3}, as shown above, there is a decrease in n_{OH} by 37.4%, n_{LiO} by 33.5%, and n_{ClH} by 40.3%, and 3.13 times increase in n_{LiCl}.

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REFERENCES

1. Chialvo, A.A. and Cummings, P.T., *Advances in Chemical Physics*, Prigogine, I. and Rice, S.A., Eds., 1999, vol. 109, p. 115.
2. Fedotova, M.V., *Zh. Obshch. Khim*., 2006, vol. 76, no. 12, p. 1979.
3. Fedotova, M.V., *J. Mol. Liq*., 2008, vol. 143, no. 1, p. 35.
4. Fedotova, M.V., *Zh. Fiz. Khim*., 2008, vol. 82, no. 11, p. 2181.
5. Fedotova, M.V., *Zh. Obshch. Khim*., 2009, vol. 79, no. 9, p. 1429.
6. Fedotova, M.V., *Zh. Fiz. Khim*., 2009, vol. 83, no. 12, p. 2391.
7. Yamaguchi, T., Yamagami, M., Ohzono, H., Wakita, H., and Yamanaka, K., *Chem. Phys. Lett.,* 1996, vol. 252, nos. 5–6, p. 317.
8. Yamaguchi, T., *J. Mol. Liq.,* 1998, vol. 78, nos. 1–2, p. 43.
9. Yamaguchi, T. and Soper, A.K., *J. Chem. Phys*., 1999, vol. 110, no. 7, p. 3529.
10. Yamaguchi, T., Ohzono, H., Yamagami, M., Yamanaka, K., Yoshida, K., and Wakita, H., *J. Mol. Liq*., 2010, vol. 153, no. 1, p. 2.
11. Zhang, Z. and Duan, Z., *Chemical Physics*, 2004, vol. 297, no. 1, p. 221.
12. Zimmerman, G.H., Gruszkiewicz, M.S, and Wood, R.H., *J. Phys. Chem*., 1995, vol. 99, no. 29, p. 11612.
13. Ho, C. and Palmer, D.A., *J. Chem. Eng. Data*., 1998, vol. 43, no. 2, p. 162.
14. Mangold, K. and Franck, E.U., *Ber. Bunsenges., Phys. Chem*., 1969, vol. 73, p. 21.
15. Chandler, D. and Andersen, H.C., *J. Chem. Phys*., 1972, vol. 57, no. 5, p., 1930.
16. Hirata, F., *Molecular Theory of Solvation*, Dordrecht: Kluwer Academic, 2003.
17. Holovko, M.F. and Kalyuzhnyi, Yu.V., *Mol. Phys.,* 1989, vol. 68, no. 6, p. 1239.
18. Hansen, J.P. and McDonald, I.R., *Theory of Simple Liquids,* 3nd ed., New York: Academic Press, 2006.
19. Labic, S., Malijevsky, A., and Vonka, P., *Mol. Phys*., 1985, vol. 56, no. 3, p. 709.
20. Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., and Hermans, W.F., *Jerusalem Symp. on Quantum Chem. and Biochem*., Pullman, B., Ed., Dordrecht: Reidel, 1981, p. 331.
21. Pettitt, B.M. and Rossky, P.J., *J. Chem. Phys*., 1982, vol. 77, no. 3, p. 1451.
22. Pettitt, B.M. and Rossky, P.J., *J. Chem. Phys*., 1986, vol. 84, no. 10, p. 5836.
23. Bondarenko, G.V., Gorbaty, Yu.E., Okhulkov, A.V., and Kalinichev, A.G., *J. Phys. Chem., A*., 2006, vol. 100, no. 11, p. 4042.
24. Balbuena, P.B., Johnston, K.P., and Rossky, P.J., *J. Phys. Chem*., 1996, vol. 100, no. 7, p. 2706.
25. Cui, S.T. and Harris, J.G., *Chem. Eng. Sci*., 1994, vol. 49, no. 17, p. 2749.
26. Fedotova, M.V. and Gavrilova, E.L., *Zh. Obshch. Khim*., 2009, vol. 79, no. 1, p. 9.
27. Fedotova, M.V., *J. Mol. Liq*., 2010, vol. 153, no. 1, p. 9.
28. de Jong, P.H.K., Neilson, G.W., and Bellisent-Funel, M.C., *J. Phys. Chem*., 1996, vol. 105, no. 12, p. 5155.
29. Fulton, J.L., Pfund, D.M., Wallen, S.L, Newville, M., and Stern, E.A., *J. Chem. Phys*., 1996, vol. 105, no. 6, p. 2161.
30. Wallen, S.L., Palmer, B.J., Pfund, D., M., Fulton, J.L., Newville, M., Ma, Y., and Stern, E.A., *J. Phys. Chem., A,* 1997, vol. 101, no. 50, p. 9632.

31. Pfund, M., Darab, J.C., Fulton, J.L., and Ma, Y., *J. Phys. Chem*., 1994, vol. 98, no. 50, p. 13102.
32. Flanagin, L.W., Balbuena, P.B., Johnston, K.P., and Rossky, P.J., *J. Phys. Chem*., 1995, vol. 99, no. 14, p. 5196.
33. Reagan, M.T., Harris, J.G., and Tester, W.J., *J. Phys. Chem., B*, 1999, vol. 103, no. 37, p. 7935.
34. Oelkers, E.H. and Helgeson, H.C., *Geochim. Cosmochim. Acta,* 1991, vol. 55, no. 5, p. 1235.
35. Marshall, W.L. and Franck, E.U., *J. Phys. Chem. Ref. Data*, 1981, vol. 10, no. 2, p. 295.
36. Franck, E.U., Rosenzweig, S., and Christoforakos, M., *Ber. Bunsenges., Phys. Chem*., 1990, vol. 94, p. 199.
37. Reagan, M.T., Harris, J.G., and Tester, W.J., *J. Phys. Chem., B*, 1999, vol. 103, no. 37, p. 7935.
38. Oelkers E.H. and Helgeson, H.C., *Geochim. Cosmochim. Acta*, 1991, vol. 55, no. 5, p. 1235.
39. Marshall, W.L. and Franck, E.U., *J. Phys. Chem. Ref. Data*, 1981, vol. 10, no. 2, p. 295.
40. Franck, E.U., Rosenzweig, S., and Christoforakos, M., *Ber. Bunsenges.: Phys. Chem*., 1990, vol. 94, p. 199.