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TEMPERATURE-INDUCED FEATURES IN THE LOCAL STRUCTURE OF AQUEOUS MONOVALENT ELECTROLYTE SOLUTIONS

The results of researches concerning the temperature influence on the formation of a local structure in infinitely dilute aqueous solutions of monovalent sodium electrolytes are reported. The analysis of experimental data shows that the dissolution of a salt leads to the formation of a local structure in water. The results obtained do not contradict, but significantly complement the results of other experimental studies of dielectric permittivity and those with the use of neutron and infrared spectroscopies.

Keywords: molecular dynamics, intermolecular interaction energy, local structure, hydrogen bond.

1. Introduction

The study of ionic mobilities and their dependences on the geometrical and physical parameters of ions and the properties of solvents is one of classical approaches, while researching the behavior of aqueous electrolyte solutions in molecular physics and physical chemistry. The present-day comprehension of the interaction between water molecules and ions at various concentrations, temperatures, and pressures makes it possible to solve problems that are of extreme interest for chemistry [1–3], physics [4, 5], and biophysics [6]. It is well known that the addition of salts into water results in a growth of the viscosity, because hydrogen bonds between water molecules are changed, which is confirmed by the neutron spectroscopy [7]. In addition, the IR researches showed [8] that ions do not affect the rotational dynamics of water molecules. Experimental data confirm the conclusion that the dissolution of ions in water does not result in modifications or breaks of hydrogen bonds between water molecules. At the same time, the data concerning the dielectric relaxation in aqueous salt solutions [9] also have to be taken into account: their analysis testifies that those solutions behave as supercooled liquid systems, in which the translational and rotational motions of separate water molecules can be distinguished and examined separately. The experimental data mentioned above testify to a discrepancy between the results concerning a variation of the viscosity in aqueous salt solutions and the data obtained, by using the nuclear magnetic resonance and infra-red spectroscopy methods. This contradiction can be resolved by applying a molecular simulation, which allows the processes of interaction between the molecules in a liquid system to be analyzed at the microscopic level.

This work was aimed at researching the temperature-induced features in the interaction between the solute and water in infinitely dilute solutions of sodium salts (NaCl and NaBr) in the temperature interval $T = 300{\div}355$ K, which should elucidate the difference between the interpretations of experimental data and make it possible to analyze the mechanisms of governing the processes of formation of a local structure in aqueous solutions by ionic parameters.

2. Model Representations for the Description of Properties of Aqueous Salt Solutions

In order to analyze how the parameters of anions of the sodium electrolytes NaCl and NaBr affect the processes of formation of a network of hydrogen bonds in the corresponding aqueous solutions, we study infinitely dilute water–electrolyte systems in the temperature interval $T = 300{\div}355$ K. The low concentrations of an electrolyte allowed us to exclude the interaction between anions and cations from consideration. It should be noted that, according to Samoilov's classification [10] and taking the results of work [11] into account, the Cl^- and Br^- ions are "chaotropic", i.e. they have rather a low charge density and rather a weak tendency to the ordering of a water structure. In turn, the Na^+ ion is "cosmotropic", i.e. it has a high charge density and should substantially affect the formation of a local structure in water at distances of about the radius of the first hydration shell. In Table 1, the values of crystal and Stokes radii for the used ions are listed.

The interaction between molecules in the examined systems was represented by a sum of the Lennard-Jones and Coulomb potentials [13],

$$U = U_{\mathrm{LJ}} + U_{\mathrm{C}} = \sum_{ij} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] + + \sum_{ij} \frac{q_i q_j}{r_{ij}}\,, \tag{1}$$

where the parameters σ_{ij} and ϵ_{ij}, which describe the interaction between the solute particles and the solvent, were calculated with the use of the Lorentz–Berthelot combination rule. The values of parameters σ_{ij} and ϵ_{ij} for waters and ions, which were used in calculations, are quoted in Table 2.

3. Details of a Computer Experiment

The molecular dynamics method was realized with the help of the modified software package DL POLY 4.05 [16]. The time step was selected to equal 2 fs. The long-range electrostatic interaction was taken into account, by using the Ewald summation method [17]. The energy parameters were determined from a series of independent calculations with time steps of 200, 160, and 80 fs. All radial distribution functions were obtained with a calculation step of 200 fs. In the calculations, the cations, anions, and atoms in solute molecules were simulated as hard charged model systems with a fixed configuration. The intermolecular parameters were found on the basis of the atom-to-atom representation for interactions between atoms of different kinds. All researches were carried out for systems consisting of 256 water molecules and one solute molecule at $T = 300 \div 355$ K.

4. Analysis of Results

In the course of computer experiments, we obtained and analyzed the energy, structural, and dynamic characteristics of the researched systems.

4.1. Energy properties of infinitely dilute aqueous solutions of sodium electrolytes at $T = 300 \div 355$ K

In our researches, the total interaction energy in the water – electrolyte system was described by expression (1). The analysis of the results obtained (Fig. 1) demonstrates that an increase in the temperature in the studied system gives rise to an increase in the E_Σ-values. In the whole temperature interval, the values of E_Σ for the water–NaCl system exceed the corresponding values obtained for the water–NaBr system. On the basis of this fact, we may assume that the local structure in the aqueous NaCl solution should have a higher density than that in an aqueous NaBr solution. As one can see from Fig. 1, the main contribution to the E_Σ-value is made by Coulomb interactions, the component E_{C}, and their role increases with the temperature.

The analysis of the temperature dependence of the van der Waals component E_{LJ}, which characterizes the short-range interaction in the examined aqueous systems, in the temperature interval $T = 300 \div 355$ K shows that an increase in the temperature results in a reduction of the E_{LJ}-contribution to E_Σ for the

Table 1. **Crystal and Stokes radii of ions at $T = 296$ K [12]**

Radius, Å	Na^+	Cl^-	Br^-
R_c	0.95	1.81	1.95
R_s	1.84	1.33	1.22

Table 2. **Charges $q(e)$, Lennard-Jones parameters σ_{ij} and ϵ_{ij}, and molecular masses M of atoms in water, NaCl, and molecules [14, 15]**

Atom	$q(e)$	σ, Å	ϵ, kJ/mol	M, g/mol
H	0.4238	0	0	1
O	–0.8436	3.169	0.6502	15.99
Na^+	+1	2.35	0.1	22.9898
Cl^-	–1	4.4	0.1	35.453
Br^-	–1	3.85	0.1	79.904

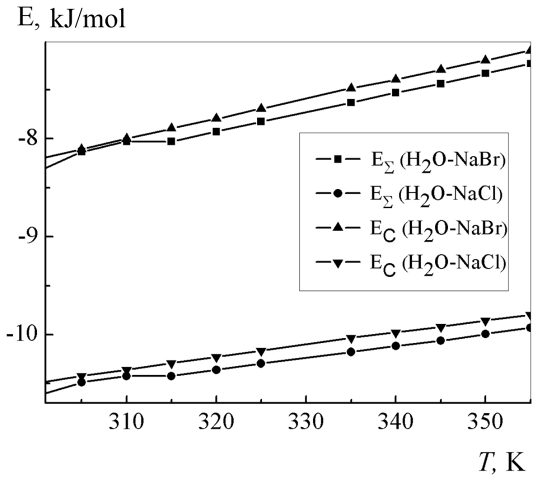

Fig. 1. Temperature dependences of the total interaction energy between molecules E_Σ and its Coulomb component $E_{\rm C}$ in infinitely dilute aqueous solutions of sodium electrolytes

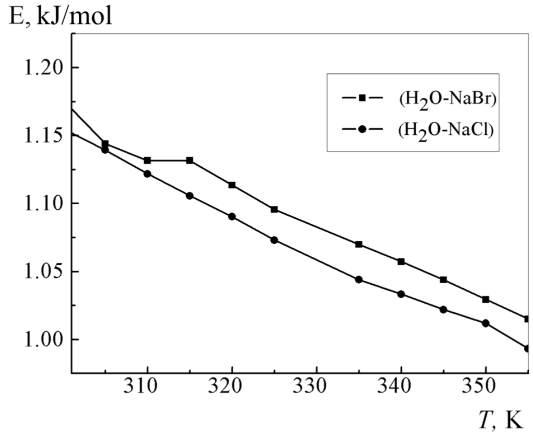

Fig. 2. Temperature dependence of the van der Waals component $E_{\rm LJ}$ in infinitely dilute aqueous solutions of sodium electrolytes

solution. The obtained result correlates with a scenario, in which the role of concentration fluctuations increases with the temperature and confirms that the temperature-induced increase in the mobility and the diffusion of particles should result in a reduction of the interaction role at short distances.

The temperature interval $T = 305 \div 315$ K attracts a special attention, while analyzing the temperature dependences of the energy parameters E_Σ, $E_{\rm C}$, and $E_{\rm LJ}$. In this interval, the indicated dependences demonstrate a deviation from the linear behavior (see Fig. 2). This means that, at those temperatures, one should expect some features in the formation of a local structure in the studied solutions.

Hence, the analysis of the energy parameters for infinitely dilute solutions of sodium electrolytes testifies that the processes of formation of a local structure in the solutions can have specific features in the temperature interval $T = 305 \div 315$ K.

4.2. Local structure in aqueous solutions of sodium electrolytes at $T = 300 \div 355$ K

One of the leading places in researches that apply numerical methods is occupied by the calculation and the analysis of radial distribution functions (RDFs), which characterize the probabilities of atomic arrangements [18]. Experimentally, RDFs are obtained from the data of x-ray or neutron spectroscopy. The integration of a RDF up to the first maximum allows the number of the nearest neighbors to be precisely determined. Note that the position of the first RDF maximum is identified with the average distance between atoms in the fluid system. The analysis of the network of hydrogen bonds, which exists between water molecules, was carried out, by using the following criteria of the existence of a hydrogen bond. A hydrogen bond can be formed if the distance between the nearest neighbor oxygen atoms in water molecules does not exceed 3.5 Å. The hydrogen bond between the nearest neighbors was selected as that, which had the minimum distance between the O and H atoms among all possible intermolecular distances. The hydrogen bond angle was determined as the angle between two OH bond vectors in two water molecules; its value varied from 130° to 180° [19].

To verify the assumptions made in the previous section, we calculated and analyzed RDFs for various interactions between atoms. While analyzing the processes of formation of a local structure in the examined ionic solutions [20], the special attention was focused on the atom-to-atom interactions that can considerably affect changes in a local structure of aqueous solutions and result in stable molecular formations; namely, these are $\rm Na^+...O^W$, $\rm Cl^-...H^W$, $\rm Br^-...H^W$ interactions.

The analysis of RDF (see Fig. 3) shows that the abnormal growth of RDF values is observed at $T =$ $= 305$ K, which testifies to a higher probability for the considered class of interactions to take place.

At $T = 305$ K, the RDF values at the first and second maxima increase, which points to the existence of a more ordered local structure in the studied ionic solution at this temperature, which, in turn, gives rise to the growth of a local density in the fluid system. The corresponding position of the first RDF maximum indicates that the $\mathrm{Br}^{-}...\mathrm{H}^{\mathrm{W}}$ interaction leads to the formation of stable hydrogen-coupled systems with a length of 2.1 Å. It is worth noting that the temperature variation does not affect the sizes of the first (2.7 Å) and second (4.1 Å) hydration shells. Hence, the analysis of the RDF that characterizes the $\mathrm{Br}^{-}...\mathrm{H}^{\mathrm{W}}$ interaction allows us to assert that the interaction between a Br^{-} ion and the hydrogen atom in a water molecule gives rise to the formation of hydrogen-coupled complexes, the dimensions of which do not depend on the temperature.

In the case of infinitely dilute aqueous NaCl solutions in the temperature range $T = 300 \div 355$ K, the first RDF maximum for the $\mathrm{Cl}^{-}...\mathrm{H}^{\mathrm{W}}$ interaction is located at a distance of 2.3 Å. Therefore, according to the criterion of hydrogen bond formation, the interaction between Cl^{-} and the hydrogen atom in the water molecule gives rise to the formation of hydrogen-coupled complexes between Cl^{-} and water molecules, the length of which does not depend on the temperature. The dimensions of the first and second hydration spheres do not depend on the temperature, being equal to 3.1 and 4.3 Å, respectively.

It should be noted that an increase in the $G^{\mathrm{Cl}^{-}...\mathrm{H}^{\mathrm{W}}}(R)$-values for the first and second RDF maxima is observed at $T = 315$ K, which testifies to the existence of a more ordered local structure in the system at this temperature in comparison with other ones.

Hence, it was established that the hydrogen-coupled complexes are formed between anions and water molecules in infinitely dilute aqueous solutions of sodium electrolytes. Their length increases as the mass and the polarization of an ion decrease, i.e. in the direction from Br^{-} to Cl^{-}, and does not depend on the temperature. In the infinitely dilute aqueous NaBr solution at $T = 305$ K and in the infinitely dilute aqueous NaCl solution at $T = 315$ K, the both analyzed fluid systems have some structural features, which lead to a growth of the local density in them.

Another class of interactions that considerably influence the processes of formation of a local structure in aqueous solutions includes interactions between an ion and the oxygen atom in a water molecule (see Fig. 5). The analysis of the RDF for the $\mathrm{Na}^{+}...\mathrm{O}^{\mathrm{W}}$ interaction (Fig. 5) shows that stable groups 2.4 Å in dimensions are formed between interacting particles. At this kind of interactions, as well as in the case of $\mathrm{Cl}^{-}...\mathrm{H}^{\mathrm{W}}$ and $\mathrm{Br}^{-}...\mathrm{H}^{\mathrm{W}}$ interactions, a pronounced growth of the RDF values $G^{\mathrm{Na}^{+}...\mathrm{O}^{\mathrm{W}}}(R)$ is observed at the temperature $T = 305$ K. The temperature elevation does not affect the sizes of the first (3.3 Å) and second (5.9 Å) hydration spheres.

The analysis of the results of computer experiments demonstrates that, in the infinitely dilute solutions, when the solute ions do not interact with one another, the sizes of the first and second hydration shells

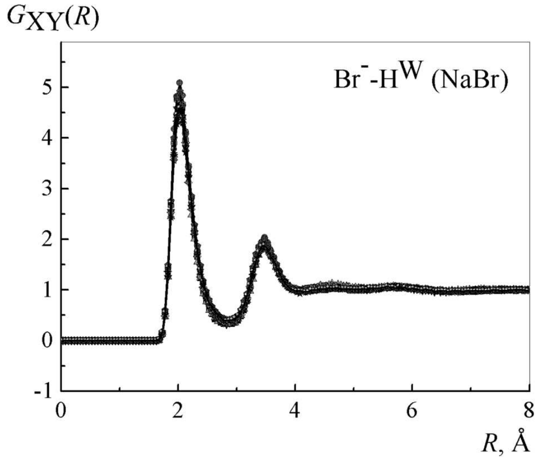

Fig. 3. RDF for Br^{-} anions with respect to the H^{W} atom in the infinitely dilute NaBr aqueous solution at $T = 300 \div 355$ K

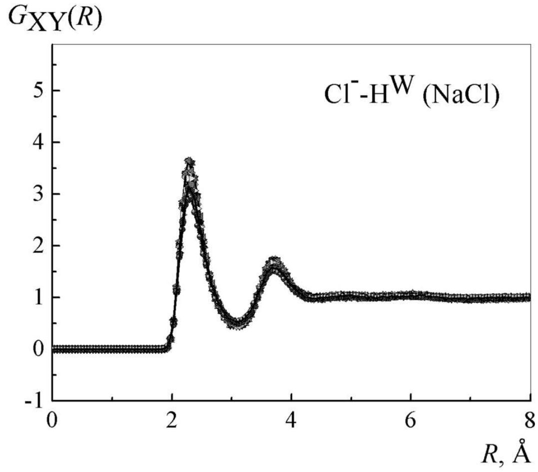

Fig. 4. The same as in Fig. 3, but for Cl^{-} anions in the infinitely dilute NaCl aqueous solution

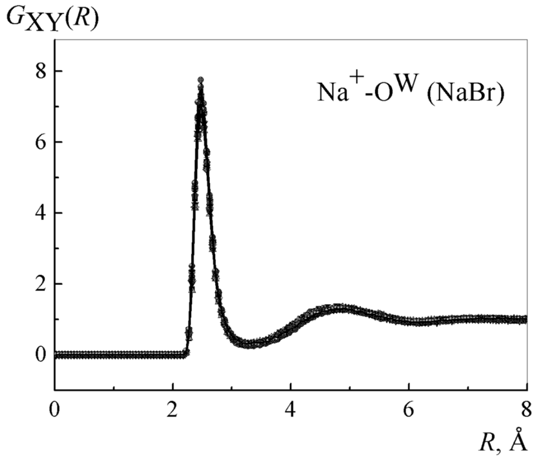

Fig. 5. The same as in Fig. 3, but for Na$^+$ cations with respect to an O^W atom in the infinitely dilute NaBr aqueous solution

that are formed around Cl$^-$ ions exceed the sizes of hydration shells formed around Br$^-$ ions. The distances between the Cl$^-$ ions and the atoms in water molecules are also larger than the distances between the Br$^-$ ions and the corresponding atoms of water molecules. Hence, we may assume that the increase in the Stokes ionic radius, the value of which is related to the ionic mobility, enhances the influence of the ion on the processes of formation of a local structure in the liquid, which manifests itself in the growth of the first RDF maximum position and the dimensions of hydration shells. The length of the specific hydrogen bond Cl$^-$...H^W between Cl$^-$ ions and water molecules amounts to 2.3 Å. A hydrogen bond Br$^-$...H^W 2.1 Å in length is formed between Br$^-$ ions and water molecules. It was also found that the increase in the Stokes ionic radius results in the growth of temperatures, at which the "anomalous" RDF behavior is observed. This testifies to the existence of a more ordered local structure in the examined system at this temperature in comparison with other ones. This special temperature equals 315 and 305 K in the case of infinitely dilute salts NaCl and NaBr, respectively, in water.

The obtained result can be explained in the framework of the following speculations. The hydrogen bond length is known to equal 2.8–3.2 Å on the average [21]. The ionic crystallographic radii of Cl$^-$ and Br$^-$ ions are almost half as large as the hydrogen bond length (Table 1), and the distance between the neighbor water molecules is shorter than or equal to 2.8 Å. Taking those facts into account, we may consider that Cl$^-$ and Br$^-$ ions can easily move between water molecules during the time of the free motion of an ion before creating stable complexes with water molecules. Since Cl$^-$ ions are much lighter and smaller than Br$^-$ ones, they have a higher charge density, which results in a stronger interaction with atoms in water molecules, so that the bonds emerging between Cl$^-$ ions and atoms in water molecules are shorter. In the case of the chlorine ion dissolution in water, the dimensions of the first and second hydration spheres are smaller than in the case of water interaction with Br$^-$ ions.

The growth of the special temperature at changing from Br$^-$ to Cl$^-$ is explained, first of all, by the fact that, when the temperature increases, the processes of local reconstruction in water near the Br$^-$ ion, owing to its relatively heavy mass and low mobility, should run faster than in the water–Cl$^-$ system. The mobility of a Na$^+$ cation with a Stokes radius of 1.95 Å (Table 1) is identical in the studied aqueous systems and can result in the break of hydrogen bonds between water molecules followed by the formation of stable groups Na$^+$–water.

To summarize, our researches of ionic solutions of sodium electrolytes carried out within the molecular dynamics method allow us to assert that experimental data on the physical properties of indicated solutions obtained by neutron scattering, IR spectroscopy, and dielectric permittivity studies do not contradict, but supplement one another. The analysis of the results obtained in the framework of the MD method shows that the processes of salt dissolution in water give rise to the formation of local structures either accompanied by the break of hydrogen bonds between water molecules (the motion of Na$^+$ cation in water and their interaction) or not (the motion of Cl$^-$ and Br$^-$ ions between water molecules without breaking the hydrogen bonds between them and followed by the formation of Cl$^-$–water or Br$^-$–water complexes).

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ТЕМПЕРАТУРНІ ОСОБЛИВОСТІ ЛОКАЛЬНОЇ СТРУКТУРИ ВОДНИХ РОЗЧИНІВ ОДНОЗАРЯДНИХ ЕЛЕКТРОЛІТІВ

Резюме

В роботі викладені результати дослідження впливу температури на процеси формування локальної структури нескінченно розбавлених водних розчинів однозарядних натрієвих електролітів. Аналіз експериментальних даних показує, що при розчиненні солей однозарядних електролітів у воді відбуваються процеси формування локальних структур. Результати виконаної роботи дозволяють зробити висновок, що дані інших експериментальних досліджень (нейтронна і ІК спектроскопія, експериментальні дослідження діелектричної проникності) не перебувають у протиріччі, а суттєво доповнюють одне одного.