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**VARIATION OF THE LOCAL STRUCTURE  
OF WATER DUE TO DISSOLUTION OF PROPANOL****N.O. ATAMAS', O.O. ATAMAS', L.A. BULAVIN**UDC 532.536  
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The work presents the results of Monte-Carlo calculations of radial distribution functions (RDF) for a "water-propyl alcohol" solution at  $T=300$  K in a wide range of concentrations, as well as analysis of the interaction of water molecules with one another. Hydrogen bond lengths and dimensions of the first and second hydration spheres were obtained at various mole concentrations of propanol. We also established the concentration ranges within which the local structure of the solution is reconstructed.

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**1. Introduction**

Water is a highly structured liquid characterized by a number of interesting physical properties insufficiently investigated on the molecular level. In ionic, polar, and hydrophobic water solutions, the structure of water changes depending on properties of a dissolved molecule, which results, in turn, in the existence of thermodynamic peculiarities of solutions that depend on the concentration of a foreign substance [1, 2]. It is worth noting that variations of the hydrogen-bond network in water due to the dissolution of a foreign substance are much less investigated as compared to the structure of pure water. A deep understanding of the microscopic behavior of liquids with hydrogen bonds represents an interdisciplinary problem for a lot of physical, chemical, and biological processes. In spite of the fact that water is a subject of many investigations [3, 4], statistical and dynamical properties of associated liquids are insufficiently studied for today, that is why "liquid water – hydrogen-bond liquid" systems represent a rather widespread subject of many experimental and theoretical researches [5], [6]. Computer modeling gives possibility for a rather efficient study of the statistical, energy, and dynamic properties of solutions.

A practically important class of nonelectrolytes used for such a kind of investigations is presented by organic molecules, namely amino-oxides and alcohols. These molecules contain both a hydrophilic polar group and a hydrophobic one, which forms a peculiar balance of contrast properties [7]. In practice, such a balance of hydrophilic and hydrophobic properties occurs in the case of long biopolymer molecules in water [8]. The presence of an alkyl chain and a pronounced polarity in a propanol molecule allows one to consider it as a suitable model system for the investigation of hydration processes of amphiphilic substances widely used in chemical industry and biology. That is why it is appropriate to study the interaction between water molecules in a water solution of propyl alcohol in a wide concentration range.

**2. Model**

For today, there exist several models for the description of liquid systems adequate both for pure liquids and for mixtures. The interaction in liquid can be described with the use of the Coulomb and Lennard–Jones interactions [9]:

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

where  $\sigma_{ij}$ ,  $\varepsilon_{ij}$  are the Lennard–Jones interaction constants,  $r_{ij}$  is the distance between the interacting particles, and  $q_i$  denotes the particle charge in the Coulomb interaction.

In our calculations, it was considered that water and propyl alcohol molecules represented Lennard–Jones particles, whose parameters  $\sigma$ (Å) and  $\varepsilon$  (kcal/mol) [10, 11] are given in Table 1. The calculations for these molecules were performed using the model of three force centers, i.e. the atoms of oxygen O, hydrogen H, and the C<sub>3</sub>H<sub>7</sub> group were presented by separate force centers. The interaction between the force centers in the case of interaction between propanol molecules was described with the help of the OPLS potential. The methyl and ethyl groups in the propanol molecule were considered as a single atom, whose characteristic parameters were determined according to the combination rule. The water molecule was described using the SPC/E model [11]. It was considered that interatomic bonds in molecules were rigid, while the intermolecular interaction was pairwise and additive.

### 3. Details of Computer Experiment

The solution was simulated with the help of the Monte-Carlo method in the NVT ensemble at the temperature  $T = 300$  K. The system consisted of 126 molecules located in a cubic cell with periodical boundary conditions. The initial system was formed as a cubic lattice with a length of the cube edge equal to 18.6 Å. The solution was simulated in the NVT ensemble at the density corresponding to the experimental densities of the solution at the specified content of propanol and the temperature  $T = 300$  K [12].

The intermolecular interaction was calculated according to (1). It was assumed that the interaction between molecules was pairwise and additive. In order to create a new configuration, we chose an arbitrary

**Table 1. Geometric parameters of water and propanol molecules [10, 12, 14]**

Molecule	Bond	Bond length, Å	Interbond angle	Angle, degr.
H–O–H	OH	1.00	$\angle(\text{H–O–H})$	109.47
H–O–C <sub>3</sub> H <sub>7</sub>	OH	0.945	$\angle(\text{H–O–C}_3\text{H}_7)$	108.5
	O–C <sub>3</sub> H <sub>7</sub>	3.30052		

**Table 2. Charges ( $q$ ) and OPLS parameters (Lennard–Jones parameter  $\sigma$ (Å) and  $\varepsilon$  (kcal/mol)) for water and propanol [10, 12, 14]**

Molecule	Atom	$q, e$	$\sigma, \text{Å}$	$\varepsilon, \text{kJ/mol}$
H–O–H	H	0.4238	0.0	0.0
	O	−0.8436	3.169	0.6502
H–O–C <sub>3</sub> H <sub>7</sub>	H	0.435	0.0	0.0
	O	−0.7	3.071	0.71162
	C <sub>3</sub> H <sub>7</sub>	0.265	3.905	0.86664

molecule at each step, rotated it about a random axis, and changed its three Cartesian coordinates, which provided the generation of approximately 50 % of successful changes of configurations. The interval for shifts amounted to  $\pm 0.15$  Å and for rotations –  $\pm 15^\circ$ . All calculations were performed according to the following scheme:  $2 \times 10^6$  steps for equilibration of the NVT ensemble, the next  $10^6$  steps for obtaining configuration data, and the following  $5 \times 10^5$  steps for obtaining the energy characteristics of the system.

### 4. Obtained Results and Their Analysis

We calculated the radial distribution functions (RDF) that carry information on the structural peculiarities of a liquid for all possible interactions in the “water – propanol” system at the temperature  $T = 300$  K. The RDFs determine the probability of the appearance of a particle as a function of the distance from some “test” particle relative to that expected for a single representation (for example, the ideal gas with the density  $\frac{N(r, \Delta r)}{V}$ ) [9]:

$$g(r, \Delta r) = \left( \frac{V}{N} \right) \frac{\langle \langle N(r, \Delta r) \rangle_M \rangle}{4\pi r^2 \Delta r}, \quad (2)$$

where  $N(r, \Delta r)$  denotes the number of particles in the area between  $r$  and  $r + \Delta r$  from another particle,  $4\pi r^2$  is the volume of the spherical shell with vanishing  $\Delta r$ . The peaks of the RDFs are identified with the local intermolecular structure of a liquid.

In the given work, we performed a detailed analysis of the RDFs (Figs. 1 and 2) that describe the interaction of atoms of water molecules with one another in a wide concentration range in the “water – propyl alcohol” system at  $T = 300$  K. A special attention was paid to the analysis of interatomic interactions that determine the structure of the hydrogen-bond network between water molecules in the system, namely the interactions between oxygen atoms of a water molecule,  $\text{O}^{\text{wat}} - \text{O}^{\text{wat}}$  (that determine the distance between the adjacent water molecules), and those between oxygen and hydrogen atoms of a water molecule,  $\text{O}^{\text{wat}} - \text{H}^{\text{wat}}$  (that determine the hydrogen-bond network). Analyzing the hydrogen-bond network between water molecules, we used the following criterion: the distance between the nearest neighboring oxygen atoms of a water molecule must be  $\leq 3.5$  Å. The hydrogen bond between the nearest neighbors was chosen so as to have the minimal length O...H (hydrogen bond length) among all possible intermolecular distances. The hydrogen bond angle was

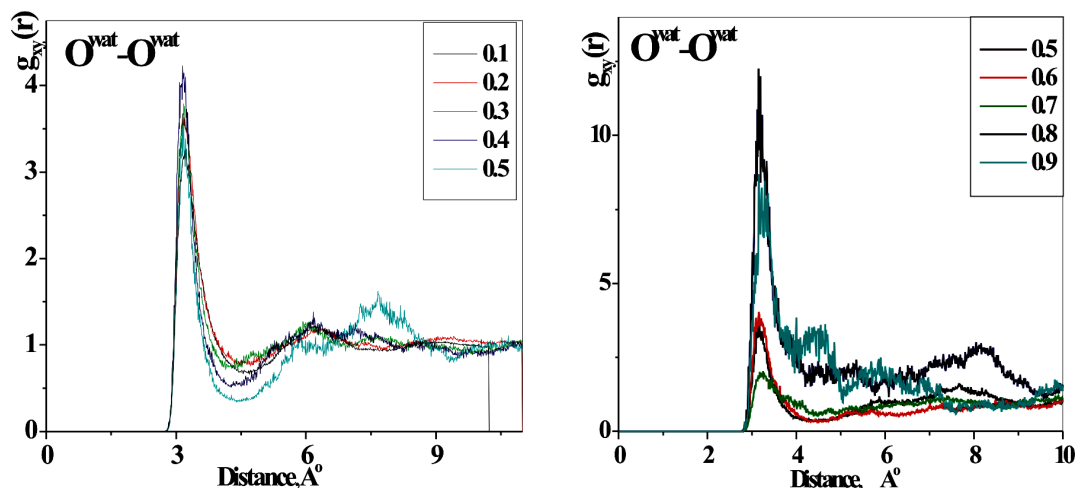


Fig. 1. RDFs for interactions between atoms of water molecules in the “water–propyl alcohol” system ( $O^{\text{wat}}-O^{\text{wat}}$ ) at  $T=300$  K

determined as the angle between the  $O\dots H$  bond of one water molecule and the  $O\dots H$  hydrogen bond vector of another water molecule and took values between 130 and 180 degrees. The hydrogen bond length for pure water was determined, by basing on results of the neutron experiment and was close to (2.5–2.8) Å [14].

The position of the first RDF maximum in Fig. 1, *a, b* that can be associated with the distance between the neighboring water molecules in the solution amounts to  $\sim 3.1$  Å and does not depend on the content of propanol in the system. It changes only the RDF value for the position of the first maximum for  $O^{\text{wat}}-O^{\text{wat}}$ . The determination error for the distance between adjacent atoms is equal to  $\pm 0.1$  Å. The RDFs also demonstrate a decrease of the position of the first minimum and a more pronounced second maximum at the propanol concentrations  $x_{\text{pr}} \geq 0.3$ , which testifies to the increase of the structuring of the system and the role of long-range interactions. An abrupt change of the RDF shape and values is observed at the concentrations  $x_{\text{pr}} \geq 0.7$  ppm. In this concentration region, one registers the following phenomena: first, an abnormal decrease of the RDF values for the first maximum at  $x_{\text{pr}}=0.7$  ppm, which testifies to the reconstruction of formations made of water molecules and, second, an abrupt increase of the RDF values, a decrease of the dimensions of the second hydration sphere, and the formation of the third one at  $x_{\text{pr}}=0.8$  ppm, which indicates, in total, the compaction of the formations generated from water molecules. At  $x_{\text{pr}}=0.9$  ppm, the RDFs demonstrate a further compaction of the structure of these formations. It is worth noting that, at the concentrations  $x_{\text{pr}} \geq 0.7$  ppm, the obtained RDFs are characterized by a rather high noise level. This noise is related to a relatively small

number of water molecules in the system and has no influence on the qualitative pattern of the obtained data.

The RDFs for the interaction between  $O^{\text{wat}}$  and  $H^{\text{wat}}$  are presented in Fig. 2. Similarly to the case of the  $O^{\text{wat}}-O^{\text{wat}}$  interaction, one does not observe any changes in the positions of the first and the second RDF maxima at  $x_{\text{pr}} \approx (0.1-0.3)$  ppm, which indicates that the hydrogen bond lengths between water molecules in the “water – propanol” system do not depend on the propanol content in water and amount to  $\sim 2.4$  Å. In addition, we did not register any variations of the dimensions of the first and second hydration layers in this concentration region: the first hydration sphere was determined as the area with the radius lower than 2.8 Å, while the second one – as the area with the radius  $R$  restricted by the inequality  $2.8 < R < 4.6$  Å. It is worth noting that an increase of the propanol content at the concentration  $x_{\text{pr}} \geq 0.4$  ppm results in a substantial (almost three-fold) increase of the RDF value, which testifies, in turn, to a change of the pattern of the interaction between water molecules with decrease in the content of water in the solution. An increase of the role of long-range  $O^{\text{wat}}-H^{\text{wat}}$  interactions in the “water – propanol” system with increase in the propanol concentration in the solution at  $x_{\text{pr}} \geq 0.4$  ppm is confirmed by the phenomena occurring in the third hydration layer: first, the RDF becomes more structured starting from the concentration  $x_{\text{pr}} \sim 0.4$  ppm; second, one observes a relatively stable RDF form in the concentration range  $x_{\text{pr}} \approx (0.5-0.7)$  ppm; and thirdly, the RDF forms change in a cardinal way starting from  $x_{\text{pr}} \approx 0.7$  ppm, namely the RDF values increase at  $x_{\text{pr}} \approx 0.8$  ppm. At  $x_{\text{pr}} \approx 0.9$  ppm, the dimensions of the

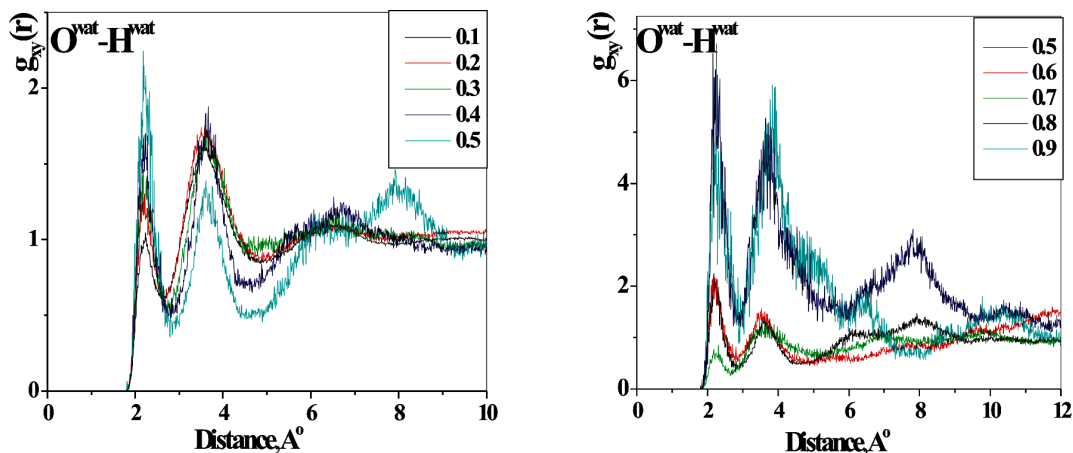


Fig. 2. RDFs for interactions between atoms of water molecules in the “water-propyl alcohol” system ( $O^{\text{wat}}-H^{\text{wat}}$ ) at  $T=300$  K

third hydration sphere reduce, which indicates both the compaction of the liquid local structure and the intensification of the intermolecular interaction between water molecules.

A quantitative characteristic of the structure of the investigated systems is the average number of the nearest neighbors which is numerically equal to the area under the first peak of the density distribution function  $4\pi r^2 \rho(r)$  calculated by the expression

$$\int_0^{Z_{\min}} 4\pi r^2 \rho(r) dr = \int_0^{Z_{\min}} 4\pi \rho_0 r^2 g_2(r) dr, \quad (3)$$

where  $\rho_0 = N/V$  is the number density of the system. In the case of the  $O^{\text{wat}}-H^{\text{wat}}$  interaction, this quantity can be associated with the number of hydrogen bonds formed by the molecule (Fig. 3). In the case of the interaction between oxygen atoms  $O^{\text{wat}}$  of different water molecules, the number of the nearest neighbors in the first hydration layer is always lower than  $0.5 \pm 0.1$ , which testifies to the fact that  $O^{\text{wat}}$  atoms of water do not completely realize the possibility of interaction with one another and interact with atoms of propanol molecules. In the case of the  $O^{\text{wat}}-H^{\text{wat}}$  interaction, the largest number of neighbors is registered in the neighborhood of the concentrations  $x_{\text{pr}} \approx 0.1$  ppm and  $x_{\text{pr}} \approx 0.8$  ppm, which can serve as an evidence of the fact that, in these regions, water molecules actively interact both with one another and with propanol molecules, and the liquid local structure is changed in a cardinal way due to this fact. The least number of neighbors is obtained at  $x_{\text{pr}} \approx 0.7$  ppm, which indicates that, at this concentration, almost all water molecules interact with propanol ones and do not participate in the interaction

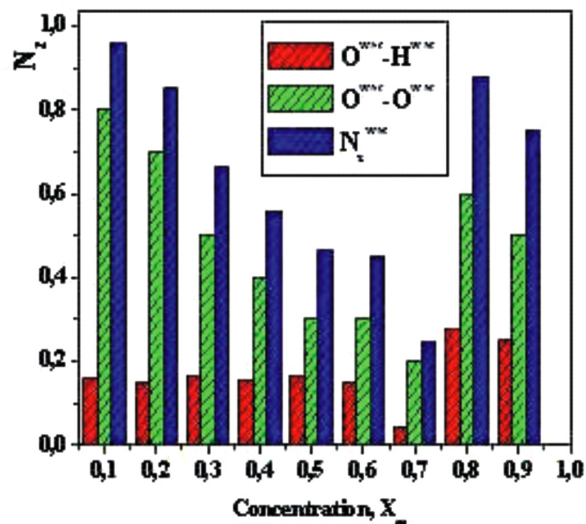


Fig. 3. Dependence of the number of the nearest neighbors on the propanol concentration in the “water-propanol” solution at  $T=300$  K

with one another. The variation of the solution structure takes place at  $x_{\text{pr}} \approx 0.8$  ppm, where one observes not only a compaction of the second hydration layer but also an abrupt increase of the number of the nearest neighbors. The obtained result correlates with data of dielectric investigations [12]. Based on the analysis of the concentration dependence of the shape parameter that characterizes an asymmetric representation of the relaxation time, the authors established that the neighborhood of the concentrations  $x_{\text{pr}} \approx (0.7-0.8)$  ppm is critical for all monatomic alcohols. The obtained result is confirmed by the fact that, at the concentration  $x_{\text{sp}} \approx 8$  ppm, water alcoholic solutions are inhomogeneous on the microscopic level. They also

established that, in the case of the “propyl alcohol – water” system, the structure of the clusters forming the solution is changed at  $x_{pr} \approx 0.83$  ppm. Thus, based on the obtained data, we can state that, in the concentration regions  $x_{pr} \approx (0.1-0.3)$  ppm and  $x_{pr} \approx (0.7-0.8)$  ppm, the pattern of the interaction between water molecules is changed, which results in the reconstruction of the local structure of the solution. The obtained data correlate with those presented in [7, 8]. Thus, we have established the presence of the concentration regions, within which there exist relatively stable formations made of both water molecules, propanol ones, and water and propanol molecules: the region of diluted solutions at  $x_{pr} \leq 0.1$  ppm, where the structure of formations made of water molecules does not differ from the structure typical of pure water, the region of solutions with  $x_{pr} = (0.1-0.3)$  ppm, where there takes place a reconstruction of the local structure of the solution and the abnormal behavior of the thermodynamic characteristics of the solution, the region  $x_{pr} = (0.3-0.7)$  ppm characterized by a relatively stable structure of the solution, and the region  $x_{pr} \approx (0.7-0.1)$  ppm, where one observes a cardinal reconstruction of the liquid local structure. Moreover, the highest intensity of these processes is registered at the propanol content  $x_{pr} \approx 0.8$  ppm.

Thus, the obtained results testify to the existence of four concentration regions in the “water – propanol” solution at  $T=300$  K, within which there takes place a reconstruction of the structure of formations made of water molecules, which will influence, in turn, the structure of the “water – propanol” solution. It is established that, in the neighborhood of the concentrations  $x_{pr} \approx 0.1, 0.2, 0.7,$  and  $0.8$  ppm, one registers peculiarities of the structural behavior of formations made of water molecules, which correlates with the data of experimental investigations presented in [15, 16]. The obtained results confirm the fact that, with increasing content of the solvent in water, the lengths of hydrogen bonds between water molecules are not changed, whereas the reconstruction of the liquid local structure takes place due to the interaction between water molecules and solvent ones (in our case, propanol molecules). It is established that, at the propanol concentrations lower than  $\approx 0.3$  ppm and higher than

$\approx 0.7$  ppm, the main contribution to the formation of the hydrogen bond network is made by interactions between water molecules at relatively small distances, whereas, in the concentration range  $(0.4-0.7)$  ppm, the dominant role is played by interactions between water and propanol molecules.

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Received 21.12.07.

Translated from Ukrainian by H.G. Kalyuzhna

#### ЗМІНА ЛОКАЛЬНОЇ СТРУКТУРИ ВОДИ ПРИ РОЗЧИНЕННІ ПРОПАНОЛУ

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#### Резюме

У роботі подано результати розрахунків методом Монте-Карло радіальних функцій розподілу (РФР) для розчину вода-пропиловий спирт при  $T=300$  К в широкому діапазоні концентрацій та проаналізовано взаємодію молекул води між собою. Одержано довжини водневих зв'язків, розміри перших та других гідратних оболонок для різних мольних концентрацій пропанолу. Встановлено області концентрацій, в межах яких відбувається перебудова локальної структури розчину.