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## MONTE CARLO CALCULATIONS OF STRUCTURAL FEATURES OF AQUEOUS SOLUTIONS OF ETHYL ALCOHOL AT VARIOUS CONCENTRATIONS AND TEMPERATURES

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The Monte Carlo method has been used for studying the processes of hydrophobic hydration of ethyl alcohol in water within the temperature interval from 5 to 35 °C and at the mole fraction of ethyl alcohol from 0.005 to 0.5. Employing the method of computer simulation, the radial distribution functions for interactions between the molecules of different solution components have been obtained and used to analyze the influence of the temperature and the concentration of ethyl alcohol molecules on the local structure modifications in the solution.

detailed information about the character of the solvent—solute interaction at the molecular level to be obtained, which allows one, as well, to draw conclusions concerning the formation of intermolecular bonds.

In this work, the results of researches dealing with the influence of the hydrophobic properties of a solute, namely, ethyl alcohol (ethanol), which is dissolved in water, on the modification of the local water structure, occurring at the temperature variation, are presented.

### 1. Introduction

The interaction between molecules of a solvent and a solute is one of the dominating factors that govern various processes in liquids occurring at a molecular level and playing a significant role in chemistry, biochemistry, and modern technologies. The studying of hydration processes in solutions is in a close relation to the researches of the structure and macroscopic behavior of solutions, as well as the features of their thermodynamic properties. If a hydrophobic substance is dissolved in water, one may expect the modification of the local water structure around the solute molecules and the creation of hydrogen bonds between the solute and water molecules [1]. For today, the issue concerning the interrelation between hydrophobic properties of polar molecules, which are represented by a molecule of ethyl alcohol in our researches, and the changes in the network of hydrogen bonds between water molecules after introducing the substances of such a class into water still remains unresolved to the end. The use of the molecular dynamics and Monte Carlo methods enables a

### 2. Model

In the framework of the present consideration, the three-atom model or the model of three force centers has been used to simulate both the water and ethanol molecules (Fig. 1). The use of those models for molecules enables one to investigate the energy characteristics and structural properties of the solutions and pure liquids. For example, methyl-ethyl groups (CH<sub>3</sub>—CH<sub>2</sub>) as well as oxygen and hydrogen atoms were simulated by an isolated single force center. The interatomic bonds in molecules were supposed rigid, and the intermolecular interaction pairwise and additive.

It should be noted that the interaction between the molecule force centers was described in all calculations by an optimized potential for liquid systems (OPLS), which was the sum of the Lennard—Jones and Coulomb potentials, i.e. looked like [2]

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

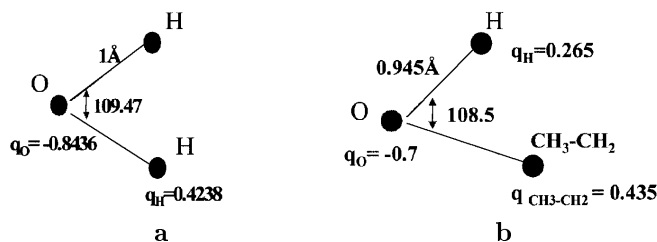


Fig. 1. Three-atom models for water (a) and ethanol (b) molecules

where  $\sigma_{ij}$  and  $\varepsilon_{ij}$  are the parameters of the Lennard–Jones potential,  $r_{ij}$  is the distance between interacting atoms, and  $q_i$  is the charge of the  $i$ -th atom. The values of the parameters  $\sigma$  and  $\varepsilon$  for the intermolecular interaction potential and the magnitudes of the atom charges in the water and ethanol molecules are listed in the Table.

The values of the geometrical parameters of molecules, used by us in calculations, as well as those of the charges and the parameters  $\sigma$  and  $\varepsilon$  for the OPLS at the force centers have been found by Jorgensen’s group [3]. The parameters  $\sigma$  and  $\varepsilon$  for the interaction between the solvent and solute atoms were calculated with the help of the Lorentz–Berthelot combination rule [2].

For water molecules, the TIP3P model was used [4]. The solution was simulated making use of the Monte Carlo method in an  $NVT$ -ensemble, the density of which corresponded to experimental densities of the solution provided the given ethanol content and temperature in it [5]. The initial system was selected as a cubic cell with the edge of 18.6 Å.

At every step of calculations, for a new configuration to be generated, a molecule was selected randomly, rotated randomly about an arbitrary axis within the limits of  $\pm 15^\circ$ , and translated randomly within the limits of  $\pm 0.15$  Å, which ensured an about 50%-yield of the successful variations of a configuration. All calculations were carried out according to the following routine: the first  $2 \times 10^6$  steps were done for the  $NVT$ -ensemble to come into balance, the next  $10^6$  steps for obtaining the configuration data, and  $5 \times 10^5$  more steps for obtaining the energy characteristics of the system.

**The atomic charges  $q$  and the atomic potential parameters  $\sigma$  and  $\varepsilon$  for water and ethanol molecules [3]**

Molecule	Atom	$q, e$	$\sigma, \text{Å}$	$\varepsilon, \text{kcal/mol}$
H–O–H	H	0.4238	0.0	0.0
	O	-0.8436	3.169	065020
H–O–CH <sub>2</sub> –CH <sub>3</sub>	H	0.4350	0.0	0.0
	O	-0.7000	3.071	0.71162
	CH <sub>2</sub> –CH <sub>3</sub>	0.2650	3.840	0.65420

### 3. Analysis of the Obtained Results

From the computer experiment, we obtained the radial distribution functions (RDFs)  $g_{xy}(r)$ , which characterize the probability density for the availability of  $y$ -atoms around  $x$ -ones and were the functions of the distance [2]:

$$g_{xy} = \frac{\langle N_y(R, R + dR) \rangle}{\rho_y 4\pi R^2 dR}. \quad (2)$$

Here, the numerator is equal to the average number of  $y$ -atoms in a spherical layer between the radii  $R$  and  $R + dR$  and the denominator normalizes the distribution in such a way that  $g_{xy} = 1$  for the spatially uniform density  $\rho_y = N/V$ . It is necessary to point out that the position of the first maximum of the RDF is identified with the length of the interatomic bond, while the positions of the first and second minima of the RDF determine the dimensions of the first and second hydration shells. The first hydration shell is defined as a sphere with the radius numerically equal to the position of the first RDF minimum. The second hydration shell is defined as a spherical layer with the radius between the first and the second RDF minima.

We have calculated the RDFs for all possible interatomic solvent-solute interactions in the aqueous solution of ethanol within the range of its mole fraction  $x_{et} = 0.005 \div 0.5$  and at the temperatures  $T = 10, 20,$  and  $30^\circ \text{C}$ . We point out that a special attention has been given to the following types of interactions: (i) the interactions which can result in the formation of hydrogen bonds between molecules of different kinds, i.e. molecules of water and ethanol, and (ii) the interactions between ethanol molecules.

The following interactions may lead to the formation of hydrogen bonds between water and ethanol molecules: between the oxygen of the water molecule and the hydrogen of the ethanol molecule,  $O_w\text{--}H_{et}$ , between the oxygen of the water molecule and the methyl-ethyl group of the ethanol molecule,  $O_w\text{--}C_{et}$ , and between the oxygen of the ethanol molecule and the hydrogen of the water molecule,  $O_{et}\text{--}H_w$ . When analyzing the network of hydrogen bonds between interacting molecules, we used the following criterion: for the hydrogen bond to exist between water molecules, it is necessary that the distance between the nearest oxygen atoms of the neighbor water molecules be smaller than 3.5 Å and the angle between the vectors of the OH bonds to the neighbor molecules be within the limits of 120–180° [6]. The hydrogen bond between the nearest neighbors was selected as if it had the minimal O...H length among all the possible interatomic distances.

Using the Monte Carlo method, it is possible to carry out the detailed analysis of the modification of the local structure of water at various temperatures provided that only one ethanol molecule should be introduced into water, i.e. at the mole fraction of ethanol  $x_{\text{et}} = 0.005$ . The number of the nearest neighbors, i.e. the number of water molecules around the ethanol one, is proportional to the area of the first maximum of the RDF curve [2]. This parameter was established to be equal to  $n = 2 \pm 0.2$  at the temperatures within the interval  $T = 5 \div 20$  °C, which allows us to assume that every oxygen atom of water molecules does not use opportunities to establish hydrogen bonds with ethanol in full. In the specified range of temperatures, hydrophobic properties of water molecules play a dominating role in the interaction between water and ethanol molecules. At the temperatures about 20 °C, hydrophobic properties of ethanol molecules play a leading role in the modifications of the network of hydrogen bonds between water molecules. At  $T > 30$  °C, the number of the nearest neighbors exceeds the neighbor number at  $T = 30$  °C,  $n = 3.8 \pm 0.2$ . This points out that the arrangement of water molecules around the ethanol one can be described making use of the model of hard spheres [6, 7], which confirms a growing role of fluctuations in the system, when the temperature increases. It was also found that the hydrogen bond, which arises due to the interaction between the oxygen of the water molecule and the methyl-ethyl group of the ethanol molecule, is more sensitive to the temperature variations than that emerging due to the interaction between the oxygen of the water molecule and the hydrogen of the ethanol molecule. The analysis of the RDF (Fig. 2) shows that, as the temperature increases, the greatest modifications occur in the second hydration shell, which testifies to the enhancement of the role of long-range interactions without formation of hydrogen bonds in the solution [9].

The analysis of the RDF for the ethanol-ethanol interactions at various temperatures (Fig. 3) points out that, as the solution temperature increases, there is a reduction of the first RDF maximum value for the interaction  $\text{O}_{\text{et}}-\text{H}_{\text{et}}$ . That is, the solution becomes less structured with the temperature growth. We also note that no significant changes of the first and second hydration shells' dimensions were observed.

A special attention is attracted by the  $\text{O}_{\text{et}}-\text{C}_{\text{et}}$  interaction which is characterized by the following features of concentration and temperature behavior:

— At the ethanol concentrations within the range of  $0.005 < x_{\text{et}} < 0.2$ , the RDF behavior for the  $\text{O}_{\text{et}}-\text{C}_{\text{et}}$

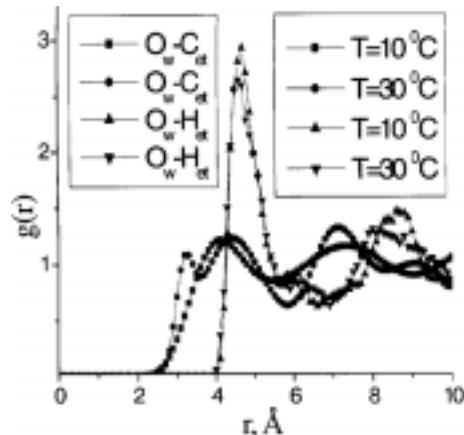


Fig. 2. RDFs for the  $\text{O}_{\text{w}}-\text{H}_{\text{et}}$  interaction between the oxygen of a water molecule and the hydrogen of an ethanol molecule and for the  $\text{O}_{\text{w}}-(\text{CH}_2-\text{CH}_3)_{\text{et}}$  interaction between the oxygen of a water molecule and the methyl-ethyl group of an ethanol molecule at the ethanol concentration  $x_{\text{et}} = 0.005$  and at the temperatures  $T = 10$  and  $30$  °C

interaction has tendencies typical of the RDF for the  $\text{O}_{\text{et}}-\text{H}_{\text{et}}$  interaction.

— At the concentrations within the range of  $0.2 < x_{\text{et}} < 0.25$ , the broadening of the first RDF maximum and the enlarging of the first hydration sphere occur, which may be explained by the increase of the number of fluctuations connected to a reconstruction of the local network of bonds between ethanol molecules. We note that, at those concentrations and only at a temperature of about 20 °C, the following features are observed: the form of the RDF curve drastically changes, namely, the amplitude of the first RDF maximum decreases; and a second maximum emerges, which evidences for the increasing role of long-range interactions between ethanol molecules.

— At the concentrations within the range of  $0.25 < x_{\text{et}} < 0.5$ , the first RDF maximum almost disappears, while the second RDF maximum, which is connected to the long-range interactions without the formation of hydrogen bonds, grows.

Thus, at the temperatures  $T = 5 \div 20$  °C and the concentrations  $x_{\text{et}} = 0.005 \div 0.2$ , the reconstruction of the hydrogen bond network in the ethanol aqueous solution occurs owing to the break of the hydrogen bonds between water molecules and the formation of new hydrogen bonds with ethanol or other water molecules. According to Franks' concept [10], the modification of the hydrogen bond network is a consequence of the formation of clusters from hydrophobic molecules. If the

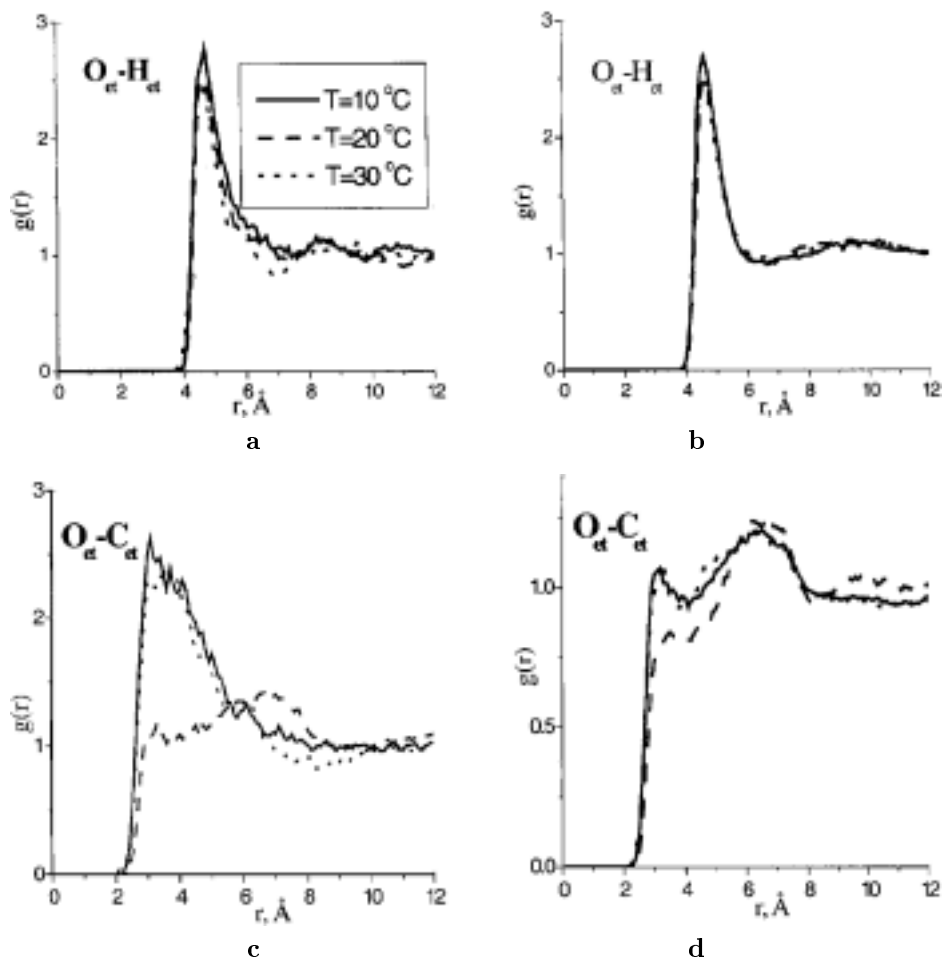


Fig. 3. RDFs for the  $O_{et}-H_{et}$  interaction between the oxygen of an ethanol molecule and the hydrogen of the other ethanol molecule at the ethanol concentrations  $x_{et} = 0.005$  (a) and  $0.5$  (b), and for the  $O_{et}-C_{et}$  interaction between the oxygen of an ethanol molecule and the methyl-ethyl group of the other ethanol molecule at  $x_{et} = 0.2$  (c) and  $0.5$  (d) for various temperatures

concentration increases further ( $0.2 < x_{et} < 0.25$ ) and the temperature rises to about  $20\text{ }^{\circ}\text{C}$ , stable formations including ethanol molecules appear due to the hydrophobic properties of the latter. In the range of the ethanol concentration of  $0.25 < x_{et} < 0.5$  and at the temperatures  $T = 20 \div 30\text{ }^{\circ}\text{C}$ , the ethanol aqueous solution consists of stable formations including both water and ethanol molecules. It was found that the RDF for the  $O_{et}-C_{et}$  interaction, where the methyl-ethyl group of the ethanol molecule takes part, is more sensitive to the temperature variations in the investigated range of concentration than the RDF for the  $O_{et}-H_{et}$  interaction, where the hydroxyl group of the ethanol molecule is engaged.

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РОЗРАХУНКИ МЕТОДОМ МОНТЕ-КАРЛО  
СТРУКТУРНИХ ОСОБЛИВОСТЕЙ ВОДНИХ  
РОЗЧИНІВ ЕТИЛОВОГО СПИРТУ ПРИ РІЗНИХ  
КОНЦЕНТРАЦІЯХ ТА ТЕМПЕРАТУРАХ

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Резюме

Метод Монте-Карло використаний для вивчення процесів гідрофобної гідратації етанолу у воді в інтервалі температур

від 5 до 35 °С з мольною часткою етанолу від  $x_{et}=0,005$  до  $x_{et}=0,5$ . З комп'ютерного експерименту отримані радіальні функції розподілу для взаємодій між молекулами різних компонент розчину, на основі яких проаналізовано вплив температури та концентрації молекул етанолу на зміну локальної структури розчину.