
HYDROPHOBIC HYDRATION IN A STRONGLY DILUTED WATER SOLUTION OF PROPANOL

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The Monte-Carlo method is used for the investigation of processes of hydrophobic hydration of propanol in water in the temperature range 283–313 K at the propanol concentration $x_{\text{Pr}}=0.004$ ppm. The radial distribution functions for interactions between molecules of different components of the solution are obtained from a computer experiment and used to analyze the influence of the temperature on the variation of the liquid local structure.

1. Introduction

Nowadays, the importance of investigating the structure and thermodynamic properties of liquids and their mixtures has grown up considerably. The study of the interconnection between the molecular structure and the macroscopic behavior of liquids allows one to understand the influence of the medium on the local structure and the activity of molecules of a liquid. The analysis of the existing structure-sensitive methods of investigating the condensed state results in the conclusion that neither of them appears to be sufficiently complete. The statistical theory of simple liquids establishes the interconnection between the equilibrium properties and the molecular structure of these liquids in the general form that supposes a detailed description only in separate cases. In turn, the computer simulation gives a possibility to investigate many-component liquids on the molecular level and to clarify the contribution of separate interactions to the variation of structural and energy characteristics of a solution. A special attention in the study of many-component solutions is devoted to the examination of water solutions of both polar and nonpolar molecules that serve as a basis for the analysis of the influence of hydrophilic and hydrophobic interactions on a change of the liquid local structure.

It is known that the introduction of hydrophilic or hydrophobic molecules to water results in the variation of the liquid local structure [1] and the formation of a network of hydrogen bonds between the introduced molecules and water ones. A lot of physical-chemical investigations provide calorimetric and dielectric data for the “inorganic alcohol – water” systems that indicate the hydrophobic character of interactions in them [2]. Unfortunately, the main attention in these investigations is paid to the simplest “methyl alcohol – water” system [3–5]. Detailed researches of the processes of hydrophobic and hydrophilic hydration for more complicated molecules are practically absent. Thus, the interatomic interaction between water molecules in water solutions of nonelectrolytes remains insufficiently investigated; for today, there is no final model of processes of intermolecular interaction in water solutions, so that the question about the interaction between molecules of different sorts remains open.

In the present work, we performed a systematic investigation of the influence of hydrophobic properties of an introduced molecule on the local structure of water solutions. As a polar molecule, we used a molecule of propyl alcohol that played a role of a “structure-forming marker” when studying the peculiarities of the formation of a local liquid structure in a wide temperature range.

2. Investigation Technique

The information on the local liquid structure can be obtained both experimentally and theoretically. With the help of the Monte-Carlo method, we calculated the radial distribution functions (RDF) of molecules in liquid that provide information on interatomic

bond distances and numbers of the nearest neighbors surrounding a molecule. The local liquid structure was investigated, by analyzing the radial distribution functions [6] that determined the probability density of the location of an atom as a function of the distance from some arbitrarily chosen atom. It is worth noting that the position of the first RDF maximum represents the interatomic bond distance, while those of the first and the second minima determine the dimensions of the first and the second hydration spheres. The first hydration sphere represents the area restricted by a layer with the radius numerically equal to the position of the first RDF minimum. The second hydration sphere is the area between the first and the second RDF minima [7]. Analyzing the network of hydrogen bonds between molecules, we used the following criterion: the distance between the nearest neighboring oxygen atoms in a water molecule must not exceed 3.5 Å. The hydrogen bond between neighboring molecules was chosen so that to have the minimal length O...H (hydrogen bond length) among all possible intermolecular distances. The hydrogen bond distance for pure water was determined from the results of neutron experiments, and it equals 2.5–2.8 Å [8].

3. Model

In the calculations, we used the model of three force centers for propanol and water molecules, where atoms of oxygen O, hydrogen H, and the C₃H₇ group were presented by separate force centers [9]. It was considered that interatomic bonds in the molecules were rigid, whereas the intermolecular interaction was pairwise and additive. In the course of calculations, the interaction between the force centers with participation of a propanol molecule was described by the optimized potential for liquid systems (OPLS). In order to describe the interaction between water molecules, we used the SPC/E model of water. The geometrical parameters of the molecules used in our calculations, the charges, and the parameters σ and ε , as well as the charges at the force centers, were presented by the Jorgansen group in [10,11]. The parameters σ and ε for the interaction between water and propanol atoms were calculated by using the Lorentz–Berthelot mixing rule [6].

4. Details of the Computer Experiment

In the computer experiment, the water–propanol solution was presented by 124 water molecules and one propanol molecule. The “water–propanol” system

was simulated at temperatures of 283, 293, 303, and 313 K; at these temperatures, its densities corresponded to the experimental ones [2]. The interaction between atoms was calculated with the help of (2). In order to generate a new configuration of the ensemble, we chose an arbitrary molecule, rotated it around one of its axes within ± 0.15 degrees and after that shifted its coordinate center within ± 0.15 Å. The use of such a technique of generating the new configurations allows us to obtain about 50% of successful changes of the configuration. All calculations were performed according to the following scheme: 2×10^6 steps for equilibration of the system in the NVT ensemble, the next 10^6 steps for obtaining the structural data, and the following 3×10^6 steps for obtaining the energy properties of the investigated system.

5. Radial Distribution Functions for the “Water–propanol” System at Various Temperatures

We calculated the RDFs for all possible interactions in the “water – propanol molecule” system. The obtained functions characterize the structural changes that take place in the system after the introduction of a propanol molecule to water at temperatures of 283, 293, 303, and 313 K.

When analyzing the interactions in a strongly diluted solution of propyl alcohol (concentration $x_{pr} \sim 0.004$), a special attention was paid to the interactions between the hydrophilic or hydrophobic parts of the propanol molecule and oxygen of the water molecule. It is due to the fact that interactions of such a kind can result in the formation of hydrogen bonds between the interacting atoms, which in turn causes variations of the network of hydrogen bonds between water molecules in the neighborhood of the introduced propanol molecule, as well as changes in the liquid local structure [13]. Thus, the highest attention is attracted by interactions participating in the formation of hydrogen bonds between molecules of water and those of the introduced substance, as well as hydrogen bonds between water molecules of O_W–H_W type in the first and the second hydration spheres. Hydrogen bonds between propanol and water molecules can be formed due to the following interactions: firstly, the interaction between oxygen of the water molecule and hydrogen of the propanol molecule O_W–H_P; secondly, the interaction between oxygen of the water molecule and the alkyl-methyl group of the propanol molecule C₃H₇ (O_W–C_P bond); and the

interaction between hydrogen of the water molecule and oxygen of the propanol molecule.

Figure 1 presents the obtained RDFs for the interaction between oxygen of the propanol molecule and hydrogen of the water molecule O_P-H_W . The first RDF maximum lies in the neighborhood of 2.5 Å and can be associated with a hydrogen bond formed due to this kind of interactions. The second maximum that corresponds to long-range interactions without formation of a hydrogen bond lies close to 4.5 Å. With increasing temperature, no variations of the position of the first RDF maximum were observed. Thus, the temperature does not influence the distance of hydrogen bonds formed due to the interaction between oxygen of the propanol molecule and hydrogen of the water molecule.

Figure 2,*a* shows the obtained results for the interaction between oxygen of the water molecule and the methyl-ethyl chain C_3H_7 of the propanol molecule C_P-O_W . The first RDF maximum that can result in the formation of a hydrogen bond is fixed at 2.7 Å. In the same way as in the case of the O_P-H_W interaction, the second maximum is located in the neighborhood of 4.5 Å that coincides with the distance between the nearest neighbors for the water molecule. It is worth noting that, at temperatures of 283–313 K, the values of the second maximum considerably (by a factor of 2) exceed those of the RDF for the first maximum, which testifies to the fact that the important role in this case is played by interactions at large distances. This indicates that, firstly, the interaction between an atom of the C_3H_7 group of the propanol molecule and oxygen of the water molecule is of the same nature as the interaction between water molecules, and, secondly, the behavior of the second hydration sphere is determining for the formation of a local structure around the C_3H_7 group of the propanol molecule.

The analysis of the RDFs for the water-propanol solution in the case of the C_P-O_W interaction at various temperatures testifies to the following facts. First, the RDF value for the first maximum rises at temperatures of 293 and 303 K. At a temperature of 303 K, one observes an increase of the RDF values for the positions of the second maximum with a simultaneous decrease of the RDF values and the position of the second minimum. This fact allows one to assume that the system becomes more structured at this temperature. Second, the second hydration sphere at a temperature of 303 K has the maximal dimensions and halfwidth, which testifies to the increase of the role of fluctuation phenomena at this temperature. At higher and lower temperatures, the

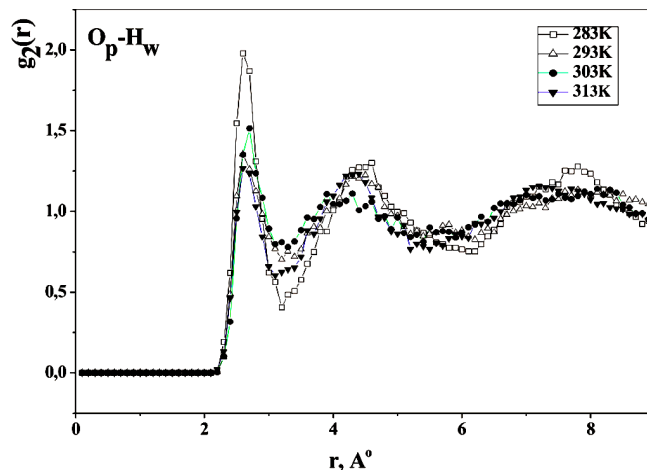


Fig. 1. Radial distribution functions for the interaction between the oxygen atom of propanol and hydrogen atom of water at various temperatures

RDF clearly shows the existence of the third hydration sphere that indicates a higher structuring of the system at these temperatures than that at 303 K. Third, at a temperature of 313 K, there exist an inessential shift of the position of the first maximum and a significant decrease of the RDF value. Moreover, the value of the position of the first minimum and the dimensions of the first hydration sphere grow. The size of the second hydration sphere r decreases and lies in the range 3.4–3.5 Å, which is an evidence of the compaction of the liquid local structure at large distances.

In the case of the interaction between oxygen of the water molecule and hydrogen of the propanol molecule H_P-O_W , an increase of the temperature does not influence the position and value of the first RDF maximum. It is worth noting that the position of the first peak for this kind of interactions is located close to 4.5 Å, which coincides with the distance between neighboring molecules in water. The temperature dependence is observed only for the second hydration sphere, namely, one registers a shift of the position of the second maximum and a change of the dimensions around 6.6 Å $< r < 9.6$ Å. The largest dimensions and the position of the peak 6.0 Å $< r < 9.6$ Å with a maximum close to 7.7 Å is typical of the second hydration sphere at a temperature of 293 K. A further increase of the temperature is accompanied with a decrease of the dimensions of the second hydration sphere. The position of the maximum lying in the neighborhood of 7.7 Å is also changed and becomes almost equal to the position of the RDF maximum at 293 K.

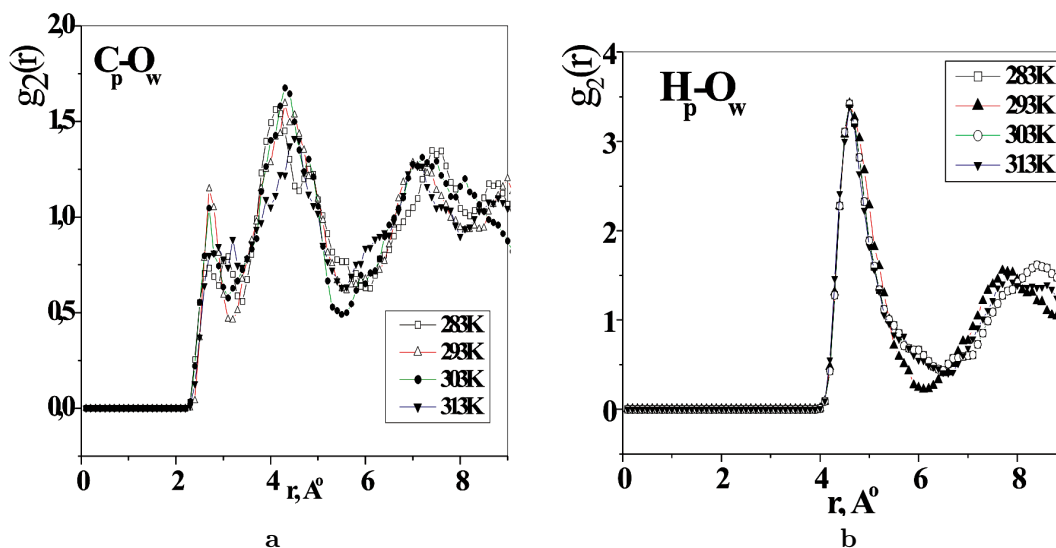


Fig. 2. Radial distribution functions in the “water–propanol” system at temperatures of 283, 293, 303, and 313 K

Thus, the analysis of the RDFs (Figs. 1 and 2) for the “water–propanol molecule” interaction demonstrates that the highest RDF value corresponds to the interaction between hydrogen of the propanol molecule and oxygen of the water molecule. That is, it is worth expecting that the probability density cloud for the interaction between atoms of water and propanol will be shifted to the region close to oxygen of the propanol molecule. Moreover, the majority of water molecules interacting with propanol will be possibly located in the neighborhood of the hydroxyl group of the propanol molecule. But, taking the hydrogen bond criterion into account, these interactions will not result in the formation of hydrogen bonds between the propanol and water molecules. One can see from the obtained RDFs that the change of the liquid local structure takes place only in the neighborhood of the C_3H_7 group of the propanol molecule. This agrees with the conception about the structure-forming properties of hydrophobic polar solvents, whose introduction to water results in the change of the network of hydrogen bonds between water molecules, which leads, in turn, to a local variation of the structure of the solvent in the vicinity of the introduced molecule [14].

It is worth noting that the variation of the network of hydrogen bonds between water molecules in the case of the introduction of a propanol molecule can be characterized by the number of the nearest neighbors (water molecules) around the propanol molecule that is proportional to the area under the first RDF maximum. The integration within the first RDF coordination

sphere for the O_P-H_W interaction allows one to determine how many hydrogen atoms of water molecules can be observed in the neighborhood of the oxygen atom of the propyl alcohol molecule. It is established that the oxygen atom of the propanol molecule is surrounded by $n = 4.6 \pm 0.2$ (at $T = 283$ K) hydrogen atoms of water molecules. In the case of the interaction between the ethyl-methyl group of the propanol molecule C_P-O_W and oxygen of the water molecule, the C_P-O_W group interacts on average with $n = 3.0 \pm 0.2$ (at $T = 283$ K) atoms of water molecules. The number of oxygen atoms of water molecules participating in the interaction with the hydroxyl group of the propanol molecule H_P-O_W is approximately equal to $n = 1.3 \pm 0.2$ (at $T = 283$ K).

With increase in the temperature of the system, the number of the nearest neighbors in the case of the O_P-H_w interaction decreases to $n = 3.5 \pm 0.2$ (at $T = 323$ K). For the C_P-O_W interaction, the minimal number of neighbors $n = 2.2 \pm 0.2$ was registered at $T = 293$ K. A further increase of the temperature results in the rise of the number of the nearest neighbors (to 3.1 ± 0.2 at $T = 323$ K). In the case of the interaction between the hydroxyl H_P-O_W group of the propanol molecule and the oxygen atom of the water molecule, the number of the nearest neighbors rises with the temperature.

The obtained results allow us to assume that the number of water molecules participating in the formation of hydrogen bonds between atoms of the propanol molecule and atoms of water molecules surrounding it is determined by the interaction between the oxygen atom of water molecules and the methyl-

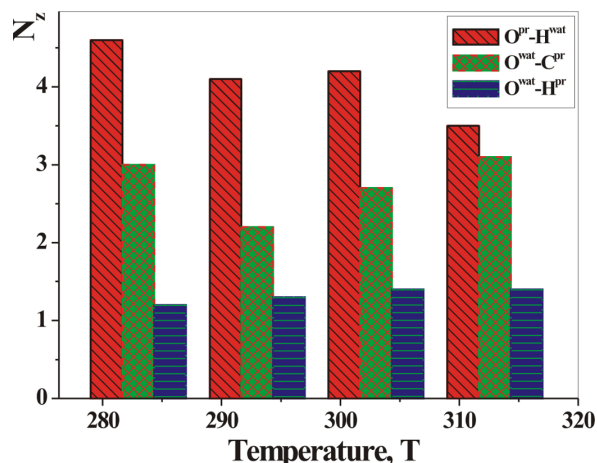


Fig. 3. Number of the nearest neighbors for interactions in the “water–propanol” system at various temperatures

ethyl group of the propanol molecule. The average number of hydrogen bonds formed between the propanol molecule and water molecules equals $n = 4.2 \pm 0.2$ (at $T = 283$ K). In the neighborhood of oxygen of the propanol molecule, one observes a structureless packing of water molecules insensitive to temperature variations. The latter influence, most of all, the interaction between the methyl-ethyl group of the propanol molecule and oxygen of the water molecule, which determines the hydrophobic character of the temperature dependence of variations of the liquid local structure.

6. Conclusions

The RDF calculations performed using the Monte-Carlo method for the “water–propyl alcohol molecule” system at the concentration $x_{pr} \sim 0.004$ allowed us to obtain information on the influence of the propanol molecule on the local structure of water in the temperature range 283–313 K. It is established that, at $T < 293$ K, each oxygen atom of the propanol molecule almost completely uses the opportunities for the establishment of hydrogen bonds with hydrogen atoms of water molecules. At these temperatures, there exists a free volume in the neighborhood of the hydroxyl group of the propanol molecule which is numerically equal to the size of a water molecule. Outside of this volume, the location of water molecules can be described with the help of the hard-sphere model [15]. The methyl-ethyl group of the propanol molecule almost completely uses the

opportunities for the formation of hydrogen bonds with water molecules and dominates in the variation of a liquid local structure in the solution. At temperatures $T > 293$ K, the number of the nearest neighbors for all types of interactions decreases. This fact testifies to the enhancement of the role of fluctuation phenomena at these temperatures and the compaction of a liquid local structure around the introduced molecule at large distances, which manifests itself in a decrease of the positions of the second and third RDF maxima.

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ГІДРОФОБНА ГІДРАТАЦІЯ У СИЛЬНО РОЗВЕДЕНОМУ ВОДНОМУ РОЗЧИНІ ПРОПАНОЛУ

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Резюме

Метод Монте-Карло використано для вивчення процесів гідрофобної гідратації пропанолу у воді в інтервалі температур від 283 до 313 К при концентрації пропанолу $x_{pr} = 0,004$ м.д. З комп'ютерного експерименту отримано радіальні функції розподілу для взаємодій між молекулами різних компонент розчину, на основі яких проаналізовано вплив температури на зміну локальної структури рідини.