STRUCTURE EFFECTS IN CONCENTRATED AQUEOUS SOLUTIONS OF ETHANOL

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The Monte Carlo method has been used to calculate structure and energy properties of the concentrated aqueous solutions of ethanol with mole fraction of ethanol from 0.5 to 0.9. On the basis of analysis of the concentration dependences of the radial distribution functions and energy properties of the solution, a model that describes intermolecular interaction mechanisms between water molecules in concentrated aqueous solutions of ethanol has been developed.

Introduction

Due to the important role in physics, chemistry, and biology, the hydrogen bonds are the focus of the numerous researches for many years [1]. Water and organic alcohols have their own unique place as model objects in these investigations. The simplest organic alcohols are representatives of the amphiphilic-like molecules, namely the molecules that can form complex structures (such as micelles, layered structures, and so on) in the strongly polar and non-polar solvents. It should be noted that the structure investigations of the amphiphilic solutions are focused on the studying of the balance between the non-polar (hydrophobic) and polar (hydrophilic) interactions in such mixtures. The amphiphilic-like substances are widely used in chemical industry and biology. In particular, the behavior of amphiphilic molecules is thoroughly studied when phenomena that occur in biological membranes are the object of the investigation.

It is known that in dilute aqueous alcohol solutions the hydrophobic interaction between the non-polar methyl group of an alcohol molecule and water is one of the dominant interactions [2]. At the same time, the role of this interaction in concentrated alcohol solutions is not yet clear. The earlier proposed models [3] are based on the assumption that there exist the unstable formations of alcohol or water molecules with the pseudocritical behavior due to fluctuations in the mixture.

In the case of concentrated alcohol solutions, both thermodynamical and bulk properties were studied [4]. At the same time, it should be noted that available experimental data give us information only about the averaged characteristics without taking into account the peculiarities in the interaction between particles in the system. From this point of view, the most effective techniques are the scattering of low-energy neutrons and computer calculations.

1. Model

In this work, we used the OPLS-model for ethanol [5] and the TIP4P-model for water [6]. These models allow us to investigate energy and spatial structure properties of both solutions and pure liquids. In addition, they are relatively easy and allow performing rather complicated calculations. The Monte Carlo experiment was carried out for the NVT-ensemble at temperature $T = 300$ K and a density of 1 g/cm^3. The system consisted of 124 molecules placed in a cubic cell with periodic boundary conditions. The initial system was formed as a cubic cell. The length of a cube edge was 18.6 Å. The intermolecular interaction was calculated taking into account the Lennard—Jones and Coulomb interactions [7]. It was assumed that the interaction between molecules is pairwise and additive. At every step, in order to make a new configuration, we randomly chose a single molecule. Then this molecule was rotated

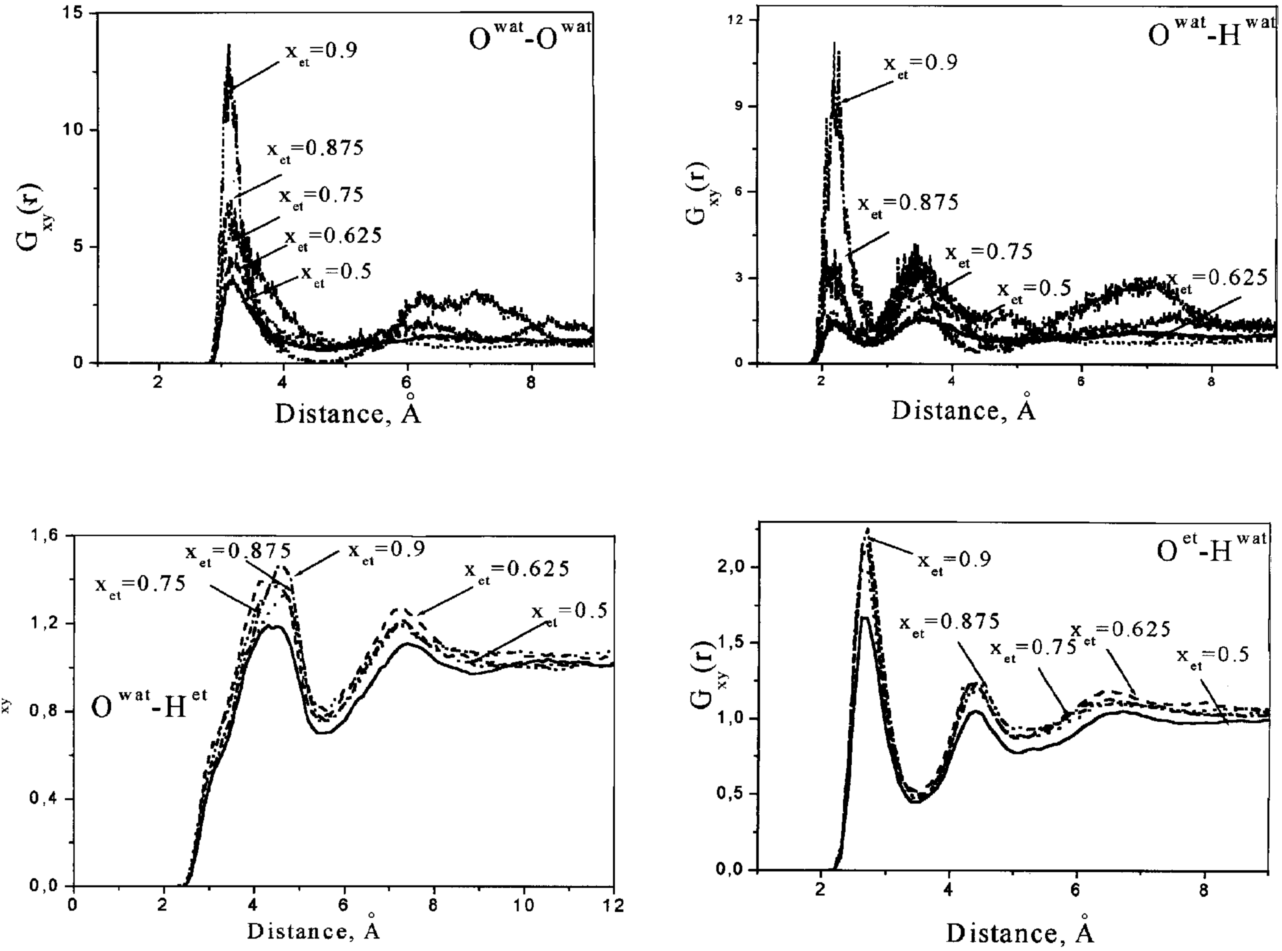

Fig.1. The radial distribution functions for aqueous solutions of ethanol of different concentrations at T = 300 K

around a random axis and shifted from its previous position. This procedure provided us about 50% good configuration changes. Shift and turn intervals were ±0.15Å and ±15°, correspondingly. All calculations were performed accordingly to the following scheme: $2{\cdot}10^6$ steps were carried out for equilibration of the NVT-ensemble, next 10^6 steps were carried out to obtain configuration data, and $5{\cdot}10^5$ steps were carried out to obtain energy properties of the system. We have investigated seven different aqueous solutions of ethanol with the mole fraction of ethanol $x_{\rm et}$ from 0.5 to 1.0.

2. Results and Analysis

In Fig.1, radial distribution functions (RDF) recovered from the computer experiment are shown for the interaction between molecules of water and ethanol in the concentration range 0.5—0.9 of the ethanol mole fraction. The characteristic shape of the RDF for $\rm O^{wat}-O^{wat}$ indicates that the interaction between water molecules is limited at distances more than 5Å. Note that a change of the size of the first hydration sphere (4.5Å) at low concentrations is less than the measurement inaccuracy ±0.01Å. Note that the abrupt widening of the RDF first peak is observed at $x_{\rm et}$=0.875. This widening, according to the ideas of the relationship between the increase of the number of fluctuations in liquid and a shape of the first peak of RDF, can be related with a reconstruction of the local network of intermolecular bonds between water molecules. At this concentration, a small increase of the size of the first hydration sphere up to 4.8Å is observed. We believe that it indicates the presence of clusters of water molecules in the solution. At $x_{\rm et}$=0.9, we observe the following particularities in the RDF behavior: an abrupt decrease of the RDF value for the first minimum whose position becomes 4.5Å again;

an increase of the RDF value for the first maximum and the essential contraction of the first peak. The obtained data are the evidence for the stabilization of the number of fluctuations and a much more solution structuring than those for the concentration $x_{\rm et}$=0.875. By integrating of the RDF of $\rm O^{wat} - O^{wat}$ within the first hydration sphere, it has been estimated that a water molecule has the greatest number of neighbors N_1=1.1±0.1 at concentration $x_{\rm et}$=0.875. At the further increase of the ethanol concentration in a solution, the amount of water molecules in the first hydration sphere decreases.

The RDF of $\rm O^{wat} - H^{wat}$ has two fundamentally important peaks, the first of them has maximum at 2.2Å and corresponds to the molecules bound by hydrogen bonds in the range 1.8—2.8 Å. The second peak that is in the range of the second hydration sphere has maximum in the vicinity 3.5Å and corresponds to the configurations of interacting particles which are not bound by the hydrogen bonds. It should be noted that, at concentration $x_{\rm et}$=0.75, the RDF behavior has the following peculiarities: the first peak of RDF is significantly higher than the second one; at $x_{\rm et}$=0.75, the minimum amount of neighbors (0.7±0.1) is observed for the interaction $\rm O^{wat} - H^{wat}$ in the range 1.8—2.5Å. The obtained results indicate that, at this concentration, the Coulomb interaction is dominant at long distances without formation of stable hydrogen bonds.

By integrating of the RDF of $\rm O^{wat} - H^{wat}$ in the range 1.8—2.5 Å, we estimated that each oxygen atom of a water molecule forms (the number of neighbors is 1.3±0.1) hydrogen bonds with hydrogens of water molecules at short distances at $x_{\rm et}$=0.875. At large concentrations of ethanol in water ($x_{\rm et}$=0.875 and more), the number of the nearest neighbors increases that indicates the increase of interaction between water molecules. Note that, at concentrations lower than $x_{\rm et}$=0.9, water molecules not completely use the possibility to form the maximal number of hydrogen bonds.

Let us consider the interaction between ethanol molecules and water ones. In this case, it is expedient to expect a formation of the following hydrogen bonds: $\rm O^{et} - H^{wat}$, $\rm H^{et} - O^{wat}$. The RDF for the $\rm O^{et} - H^{wat}$ interaction just as in case of the interaction between water molecules has two peaks; one of them is at 2.6 and another — at 3.6Å. By integrating the RDF in the range of the first hydration sphere, we estimated that, at an increase of the ethanol concentration in the solution, the number of water molecules, which form hydrogen bonds with oxygen in an ethanol molecule, increases as well. So, at concentration $x_{\rm et}$=0.875, the interaction between oxygen of ethanol (the number of neighbors is 1.6±0.1) and hydrogen of a water molecule, $\rm O^{et} - H^{wat}$, results in the formation of a hydrogen bond of 2.6Å in length. In the interaction of $\rm H^{et} - O^{wat}$ at the same concentration, more ethanol molecules (7.1±0.1 at $x_{\rm et}$=0.875) take part in comparison with the case of $\rm O^{et} - H^{wat}$ interaction. The obtained RDF for the $\rm H^{et} - O^{wat}$ interaction looks similar to RDF for the $\rm O^{wat} - H^{wat}$ interaction. The obtained result confirms the fact that the nature of the interaction of water molecules is the same as the interaction of water molecules with hydrogens of ethanol molecules. Concentrations values $0.5 < x_{\rm et} < 0.875$ obtained from the computer experiment, at which a change of the intermolecular interaction character between different molecules takes place, correlate with results of the analysis of Raman spectra [7]. According to the results of the spectral experiment in the concentration range $0.5 < x_{\rm et} < 0.75$, a gradual formation of the vibrating band with a maximum near 85 $\rm cm^{-1}$ occurs. The obtained vibration band is formed due to the interaction of two vibrations with maxima at 60 and 110 $\rm cm^{-1}$, correspondingly. The band with a maximum of 110 $\rm cm^{-1}$ corresponds to the intermolecular vibration of O—O of two hydrogen bonds between ethanol molecules, and the band with a maximum of 60 $\rm cm^{-1}$ is formed due to the O—O—O interaction of trimers of water molecules. With increase of the ethanol concentration in the solution, a shift of the envelope of these two bands to low frequencies occurs, which confirms the increase of the role of water trimers in the formation of a resulting vibration band, as well as the formation of water clusters and the decrease of the role of the interaction of ethanol molecules with water molecules. At concentrations $x_{\rm et} > 0.8$, the decrease of the half-width of the resulting spectral band with a maximum of 85 $\rm cm^{-1}$ is observed, which indicates the formation of both stable water clusters in a solution and stable ethanol clusters.

In Fig. 2, the concentration dependences of interaction energies in an aqueous solution of ethanol are shown. As follows from Fig. 2,*a*, the interaction energy between water molecules $E^{\rm wat} - E^{\rm wat}$ decreases with increase of the ethanol concentration in the solution. In turn, the interaction energy between the ethanol molecules $E^{\rm et} - E^{\rm et}$ increases with increase of the ethanol concentration. It is worth noting that the interaction energies $E^{\rm et} - E^{\rm et}$ and $E^{\rm wat} - E^{\rm wat}$ have identical values at $x_{\rm et}$=0.42. The average total interaction energy in the system, $E^{\rm total}$, has singularities close to $x_{\rm et}$=0.875. According to the Le Chatelier's principle [8], a decrease

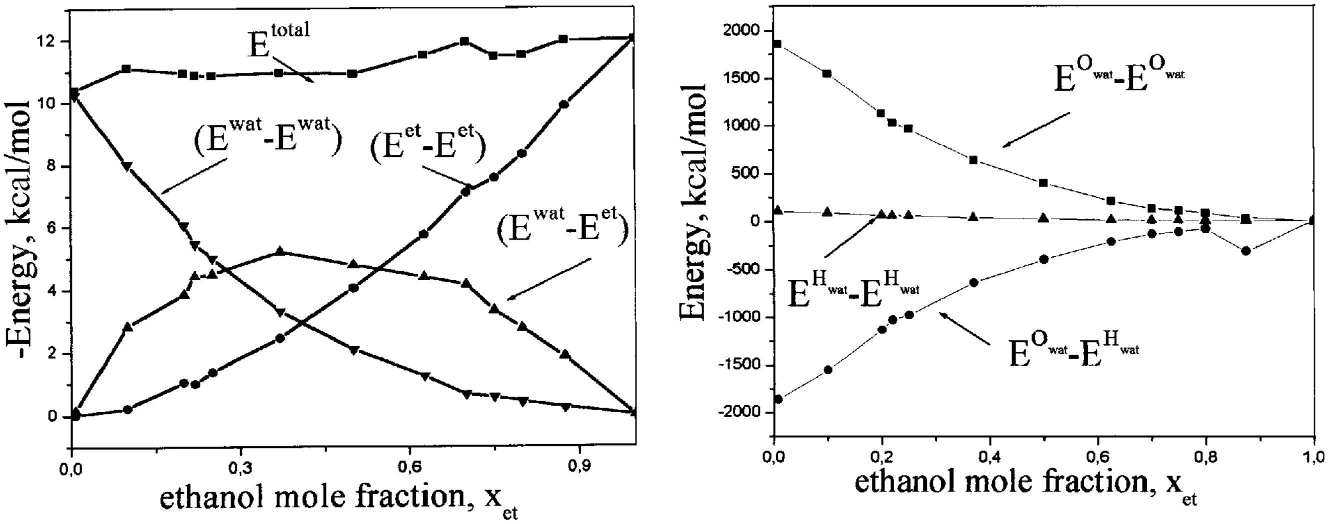

Fig. 2. The dependences of average interactions energies in aqueous solutions of ethanol on $x_{\rm et}$

of the average interaction energy in water solutions results in the increase of the aggregation of water interactions. In turn, the increase of the interaction between water molecules in an aqueous solution indicates that the hydrophobic interactions are dominant in the solution [9]. As shown in Fig. 2,*a*, the average interaction energy between water molecules $E^{\rm wat} - E^{\rm wat}$ decreases with increase of the ethanol concentration. In Fig. 2,*b*, the dependences of the average interaction energies between water molecules are shown: $E^{\rm O_{wat}} - E^{\rm O_{wat}}$, $E^{\rm O_{wat}} - E^{\rm H_{wat}}$, $E^{\rm H_{wat}} - E^{\rm H_{wat}}$. The average interaction energy $E^{\rm O_{wat}} - E^{\rm H_{wat}}$ has singularities at $x_{\rm et}$=0.875, which correlate with data obtained from the RDF analysis.

Conclusions

With increase of the ethanol concentration in water, one can observe a gradual increase of the role of Coulomb interactions between water molecules at relatively long distances without formation of stable hydrogen bonds between water molecules at $0.5 \leq x_{\rm et} \leq 0.75$. At the further increase of the ethanol concentration ($0.75 \leq x_{\rm et} \leq 0.875$), the interaction of water molecules increases and hydrogen bonds between water molecules are formed. In this case, water molecules don't realize completely the possibility of formation of the densest network of hydrogen bonds; it is associated with a great number of fluctuations and the reconstruction of a liquid local structure. At $x_{\rm et} > 0.9$, the number of fluctuations in liquid is stabilized, and water molecules take part in the formation of the maximal number of hydrogen bonds.

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СТРУКТУРНІ ЕФЕКТИ В КОНЦЕНТРОВАНИХ ВОДНИХ РОЗЧИНАХ ЕТИЛОВОГО СПИРТУ

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Резюме

Метод Монте-Карло застосовано для розрахунків структурних та енергетичних характеристик концентрованих водних розчинів етилового спирту, молярна частка якого змінювалась в діапазоні 0,5÷0,9. На основі аналізу концентраційних залежностей радіальних функцій розподілу та енергетичних характеристик розчину побудовано модель, яка описує механізми міжмолекулярних взаємодій між молекулами води в концентрованих водних розчинах етанолу.