Structural features of aqueous solutions of alcohols

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Introduction

Recently, more and more attention has been drawn to the study of the mechanisms that regulate hydrophobic and hydrophilic interactions in water, since they determine the main causes of the behaviour of aqueous solutions of biological macromolecules. The study of processes in bio-solutions is in close connection with studies of their structure, macroscopic behaviour, and thermodynamic properties. The presence of hydrophilic (hydroxyl OH groups) and hydrophobic groups (methyl and ethyl groups) in monohydric alcohols makes it possible to consider them as simple model systems for obtaining information about the behaviour of biomolecules in water. The use of molecular modelling of aqueous solutions of alcohols makes it possible, on the one hand, to develop a methodology for studying the behaviour of biomolecules in water. On the other hand, the analysis of the energy and structural characteristics of alcohol solutions at different concentrations makes it possible to determine the causes of the anomalous behaviour of the physicochemical properties of alcohols at different concentration. In addition to the above, when carrying out studies of the concentration-structural features of aqueous solutions of monohydric alcohols by the Monte Carlo method, we achieved the following goals: to study the effect of the hydrophilic properties of alcohols on the change in the structural characteristics of aqueous solutions at various concentrations of alcohol; build model representations for the structure of aqueous solutions of alcohols at various concentrations.

Methods and Results

Computer experiment

Aqueous solutions of alcohols were modeled by the Monte Carlo method in the NVT ensemble at densities with the corresponding experimental solution densities at given concentrations of alcohols at T=300K [1]. System consists of 256 molecules in the cubic box with the periodic boundary conditions. Initial configuration is formed in cubic box of 18.6Å length. Intermolecular interactions are calculated according to (1). Maximum trial displacements are ± 0.15Å and maximum rotations are ± 15°, 2×10^6 of Monte Carlo steps for the equilibration of the system, 10^6 Monte Carlo steps for obtaining structural properties and 5×10^5 of steps for obtaining energy properties ware used. Short range intra-atomic interactions in liquid can be specified by Lennard-Jones potential and long range interactions, which are described by Columbic potential:

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

Parameters of *LJ* potential σ and ε are taken from the papers [2,3]. Methyl and ethyl groups of the alcohol molecule are assumed to be single interacting sites. SPC/E model is used for water molecules. The total energy of intermolecular interaction $<E_{total}>$ of solution can be represented by the sum of three components: interaction energy between the molecules of solvent, interaction energy between the molecules of the dissolved substance and interaction energy between the molecules of solvent and dissolved substance. In the case of the aqueous solution of propanol the total average energy of intermolecular interaction in the solution is:

$$<E_{total}>=<E_{LJ}>+<E_{coul}>=<E_{alcohol\text{-}alcohol}>+<E_{wat\text{-}alcohol}>+<E_{wat\text{-}wat}>,$$

where $<E_{alcohol\text{-}alcohol}>$– the total energy of interaction between the molecules of alcohol, $<E_{wat\text{-}wat}>$– the total energy of interaction between the molecules of water, $<E_{wat\text{-}alcohol}>$– the total energy of interaction between the molecules of water and alcohol.

Concentration dependence <Etotal >, <Ealcohol-alcohol >, <Ewat-wat > and <Ewat- alcohol> in alcohol-water solution at T = 300 K

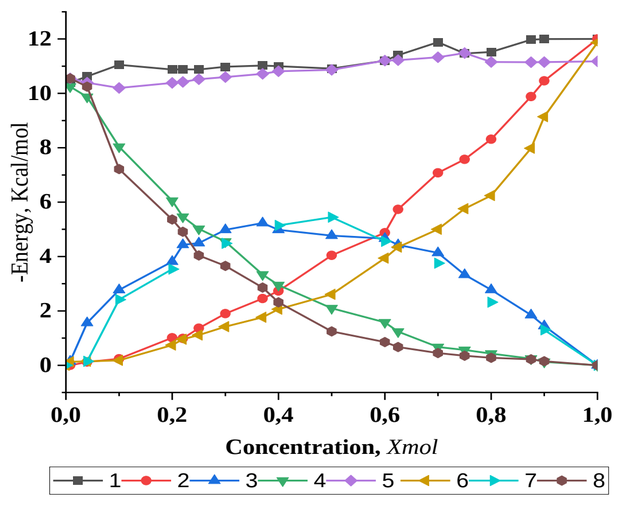

Fig.1 Concentration dependence <E sum > (1-ethanol, 5-propanol), <Ealcohol-alcohol> (2-ethanol, 7-propanol), <Ewat-wat> (4-ethanol, 8-propanol) and <Ewater- alcohols> (3-ethanol, 7-propanol) in water-alcohol solution at T = 300 K

Conclusions

Based on Monte Carlo studies, the following has been established:

- in an aqueous solution of ethyl and propyl alcohols at infinitesimal concentrations (below X< 0.05 in the case of ethyl alcohol and X< 0.04 in the case of propyl alcohol), the alcohol molecule does not change the percolation properties of the network of hydrogen bonds between water molecules;
- The value of the dipole moment of an alcohol molecule affects the structural characteristics of clusters of alcohol molecules in water at concentrations of X= (0.2 - 0.25).
- at concentrations of alcohol in water over X >0.3 the structure of clusters is rearranged from alcohol molecules into structures similar to reverse micelles. The number of alcohol molecules forming reverse micelles does not depend on the structure and dipole moment of alcohol molecules and is equal to 4. In this case, the structure of the alcohol molecule determines the number of water molecules surrounding the micelle.
- at concentrations Xpr = (0.6 - 0.8). rupture of micelles formed by alcohol molecules occurs. At these concentrations, there can also be free alcohol molecules, and half-chains of four alcohol molecules.

References

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