Metastable states of the fractal-cluster structure of alcohol-containing aqueous solutions

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Abstract. The paper presents the results of the study of fractal-cluster structures formed in the near-surface layer of alcohol-containing aqueous solutions. Water-ethanol mixture when changing the concentration of alcohol in water enters a new phase with a more dense packing of fluctuating structures. Molecules of alcohol, having a larger size than water molecules, when embedded in the structure of water, significantly violate it, as a result of which the structure of the system and its properties change. To visualize these structures in the surface layer of alcohol-containing aqueous solutions, the laser interferometry method was used in the work. It was found that in the range of average concentrations of alcohol in an aqueous solution, in spite of some stabilization of the structure of the system, the solutions in it have a substantial heterogeneity in the form of changing fractal-cluster structures. On the basis of the conducted studies, possible mechanisms for the transition of fractal-cluster water structures in the interaction with ethanol into spatial clathrates are shown.

1. Introduction

The formation of elliptic diffraction umbilic in a water drop from the point of view of the theory of catastrophes was considered in details in works of M.V. Berry et al. [1]. However, in these studies, attention was not paid to the fine structure of the resulting caustics. Despite the fact that in recent years a lot of investigations were paid to research related to the cluster structure of water, the task of evaporating a drop of liquid into the surrounding air has not lost relevance. The recently increased interest in self-organization processes in drying drops of liquids [2] has led to the need to develop and use various methods for diagnosing these processes. The study of the evaporation of a liquid using a microscope in the usual manner allows one to obtain information only about the shape of a drop, but does not allow one to investigate changes in the structure of the surface layer of the drop.

The current stage of development of laser technology and computer technology allows us to take a fresh look at optical methods of research, known for a long time. For example, the development and creation of semiconductor lasers of various radiation ranges and different powers advanced the development of interferometric methods far ahead, made it possible to obtain quite narrow collimated (low diverging) beams and created new research opportunities in optical gradient refractometry. The creation of matrix CCD photodetectors makes it possible to significantly improve the quality and
speed of obtaining and processing optical images and automate many processes for analyzing the received information.

The study of the properties of the near-surface layer of liquids is still relevant and is well shown in [3]. When studying the formation of caustics in a triangular water drop more than 15 years ago, we already noticed that as the drop dries, the structure of the surface layer of the water drop changes significantly [4].

However, the interaction of water with alcohols from the point of view of changing the structure of their aqueous solutions is practically not studied. In this connection, this study is relevant both from a purely scientific point of view and in terms of the practical application of these solutions in pharmacology, medicine and the food industry. As is well known, water and alcohols belong to associated fluids, in which the association is caused by the presence of hydrogen bonds between the hydrogen atoms of one molecule and the oxygen atoms of the other molecule. In this case, the energy of hydrogen bonds is much weaker than the energy of covalent bonds between oxygen and hydrogen [5]. Associates in water can decay and re-form in various combinations. As shown in [6], double water molecules having two hydrogen bonds are more stable. In contrast to water, ethyl alcohol and its aqueous solutions can form associates not only in the form of chains, but also in the form of flat rings [5]. Thus, water-alcohol solutions are considered as mixed associates, the study of the formation mechanisms of which is of particular interest to researchers.

The purpose of this work is to study the associate (clathrate) structures formed in the surface layer of alcohol-containing aqueous solutions.

2. Experimental part

It is assumed that most of the water retains a tetrahedral structure. Molecules of alcohol, having a larger size, when embedded in the structure of water violate it, while embedding of water molecules in the structure of alcohol is not accompanied by a significant change in the latter. When a small amount of alcohol is dissolved, the structure of the water still remains, although it undergoes a slight deformation. With a further increase in the concentration of alcohol, the structure of water is disturbed. In the area of average alcohol concentrations, a dynamic equilibrium of associates of identical molecules, aggregates of dissimilar molecules and single molecules of alcohol and water is established, and the structure of the system is stabilized. At high concentrations of alcohol in the solution, the structure of the alcohol with water molecules included in it prevails. Mixing alcohol with water is accompanied by the release of heat and the contraction (compression) of the mixture. The cause of compression is the formation of associative bonds, which leads to a condensation of molecules and a decrease in the total volume of the system. The selection of ethanol solutions in aqueous solutions was carried out on the basis of the results of refractometric measurements of the dependence of the change in the refractive index of the solution and the surface tension coefficient of the surface layer of the solution on the concentration of ethanol in distilled water. As a result, for the study of changes in the associate (clathrate) structure of the surface layer, solutions of alcohol-containing aqueous solutions were chosen at a concentration of ethanol in water of 30 mol %.

To visualize fractal-cluster structures and their associates in the near-surface layer of alcohol-containing aqueous solutions, we modernized the experimental set-up based on a projection microscope [4,7]. With the help of a micro-lens (6), the expanded laser beam, passing through a layer of a drop (4) of an alcohol-containing aqueous solution placed in a triangular cell (5) located on the sample table (3), was projected onto an SMOR-high-resolution receiving matrix (7). The resulting picture of the structure was recorded in the memory of a personal computer (8). A semiconductor laser with a wavelength $\lambda = 0.409 \mu m$ and a power of about 40 mW was used as a source [4]. The diameter of the laser beam incident on a triangular cell with the test solution was of the order of 0.6 – 0.8 mm. The fragments of sections of the obtained fractal-cluster structures of the surface layer of the solution during the time of its evaporation increased 10 – 20 times. For better visualization of fixed structures, images were converted to black and white.
Figure 1. The experimental setup for visualization of fractal-cluster structures (a), the location of sections (b) and photos of some structures (c) in the surface layer of alcohol-containing aqueous solutions during the passage of laser radiation through a triangular cell with a solution. 1 – beam of laser radiation; 2 – radiation attenuating filters; 3 – glass slide; 4 – a drop of solution; 5 – triangular cell; 6 – micro lens; 7 – receiving matrix of a digital microscope; 8 – a laptop (PC).

Examples of some of the fixed associate (clathrate) structures of the surface layer of an alcohol-containing aqueous solution at an alcohol concentration in water of 30 mol % at room temperature in the process of drying triangular droplets are presented in the following figures and in possible models of their formation.

Figure 2. The structure of the associate (clathrate) of the hexagonal type of an aqueous solution of ethanol (a) and a possible model of the clusters of its constituents (b).
Figure 3. The structure of the associate (clathrate) formed from the tetrahedra of an aqueous solution of ethanol (a) and a possible model of the clusters of its constituents (b).

Figure 4. The structure of the associate (clathrate) of a closed type solution of ethyl alcohol in water (a) and a possible model of the clusters of its constituents (b).

Figure 5. The structure of the clathrate of three clusters of a closed type solution of ethyl alcohol in water (a) and its possible model (b).
Figure 6. The structure of the clathrate of three clusters of a closed type solution of ethyl alcohol in water (a) and its possible model (b).

Figure 7. The structure of the clathrate alcohol-containing aqueous solution in the form of a chain (a) and its possible model (b).

3. Conclusion
This work is an interdisciplinary study in which we applied a simple method for visualizing the associates (clathrates) of fractal-cluster structures in the surface layer of alcohol-containing aqueous solutions at room temperature. The fragments of the resulting fractal-cluster structures of the surface layer of the solution during the time of its evaporation made it possible to make the following assumptions:

1. Tetrahedron formation of aqueous solutions of alcohol is due, apparently, with the hybridization of carbon in solution.
2. With an increase in the hydrocarbon radical, the solubility in water decreases, the hydrophobicity of the molecule increases.

At the same time alcohols exhibit the ability to intermolecular association:

\[
\begin{align*}
\delta^+ & \delta^- \\
\delta^+ & \delta^- \\
\delta^+ & \delta^- \\
\end{align*}
\]

\[
\begin{align*}
H-O \cdots H-O \cdots H-O \cdots \\
R & R \\
R \\
\end{align*}
\]

The association of ethanol molecules is explained by the formation of intermolecular hydrogen bonds. On a possible scheme of formations, hydrogen bonds are indicated by dots, the letter R denotes a hydrocarbon radical.

In aqueous solutions, hydrogen bonds are formed not only between alcohol molecules, but also between ethanol and water molecules.
3. The addition of water molecules to the alcohol molecule with the formation of alcohol hydrates is described as following:

\[ C_2H_5OH + nH_2O = C_2H_5OH* nH_2O, \text{ where } n = 1, 3, 12. \]

The number of hydrates of a certain type depends on the concentration of water in alcohol.

![Figure 8](image)

**Figure 8.** The mechanism of possible addition of C₂H₅OH alcohol molecules to the water cluster (a) and its composition (b), R – C₂H₅OH.

4. Since there are two types of molecules in water, one of which forms a tetrahedral skeleton, and the other fills its cavities, as a result of studies and identification of the fixed structures of clathrates (associates), it can be assumed that the alcohol molecules in the aqueous solution form either clusters of various types or chains linked to each other via hydrogen bonds.

![Figure 9](image)

**Figure 9.** The chain of alcohol clusters in an aqueous solution.

5. The effects observed during the dissolution of alcohol in water are due to the complex supramolecular structure of both water itself and alcohol. When dissolved in water, alcohol molecules with their hydrocarbon part are located in the voids of the water structure, while the oxygen atoms of the hydroxyl groups replace one of the frame water molecules. Below are models of possible associates (clathrates) formed from elementary tetrahedra in alcohol-containing aqueous solutions.

![Figure 10](image)

**Figure 10.** Possible models (a) and the mechanism of clathrates formation in alcohol-containing aqueous solutions (b).

6. In water, there are two types of molecules, one of which forms a tetrahedral framework, and the other fills its cavities. Consequently, based on the research performed, it can be assumed that the
molecules of the alcohol in an aqueous solution form either clusters of different types or chains linked to each other by means of hydrogen bonds. These processes occur as a result of the breakdown of alcohol associates in water and the formation of new ones in various combinations.

Thus, in this work, we show the structure of clathrates (associates) in the surface layer of alcohol-containing aqueous solutions, which was visualized at room temperature and possible models of their formation are presented.

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