Formation of clathrate structures in surface layers of heavily diluted aqueous solutions

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Abstract. The paper presents the results of experimental studies related to the formation of clathrate structures in highly diluted hydrophilic aqueous solutions. A method based on the interference of laser beams transmitted through a water lens of various configurations is applied. It is shown that the studied solutions have properties associated with the self-organization of the structure in clathrate states due to the cooperative effect of changes in the inhomogeneous network of hydrogen bonds. It is found that in the range of small concentrations of dissolved substances in aqueous solutions, in spite of some stabilization of the structures in the formed clathrates depending on the number of interacting molecules, the formation of associates of various shapes is possible. An increase in the content of dissolved substances in aqueous solutions leads to the destruction of the ordered structure, and the excess molecules of the hydrophilic substance, combined together, form complex aggregates or their “islands”.

1. Introduction

The paper presents the results of vertical laser sensing of drops of hydrophilic substances highly diluted in water, which made it possible to detect clathrate nano-formations in various combinations, the nature of which is still insufficiently clear. The processes of the formation of macroscopic, spatially ordered inhomogeneities (clusters, associates and clathrates) that spontaneously arise in the boundary layers of aqueous solutions is studied. The phenomenon of the appearance of new physicochemical, spectral, diffraction, refractometric and other effects related to heterogeneity in the changing inhomogeneous structure of the surface layers of these solutions has been poorly studied. The main problem that determines the importance of these studies is that when conducting many biophysical experiments and interpreting their results, water and aqueous solutions considered to macroscopically homogeneous systems. However, the processes of formation of clusters and clathrates based on them in the surface layers of these solutions are not fully understood and the mechanism of their formation is not clear. Despite the fact that in recent years a lot of attention has paid to research related to the cluster structure of water and aqueous solutions, the problem of evaporating liquid droplets into the surrounding air has not lost its relevance.

The increased interest in the processes of self-organization in drying drops of liquids [1] has led to the need to develop and apply various methods for this process diagnostics. The study of liquid
evaporation using a microscope by usual method makes it possible to obtain information only about the shape of the drop, but does not allow to study changes in the structure of the drop surface layer [2–4].

Modern technology allows to visualize various structures in aqueous solutions, the existence of which previously could not even assumed. The development of laser technology and computer technology provides an opportunity to take a fresh look at optical research methods. For example, the development and creation of semiconductor lasers of various radiation and power ranges made it possible to obtain rather narrow collimated (low divergent) beams and created new research opportunities in optical gradient refractometry and interferometry. 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 of analysing the received information.

The formation of elliptic diffraction umbilic in a water drop was considered in details in works of M.V. Berry et al. from the point of view of the theory of catastrophes [1]. However, in these studies, attention wasn’t 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 current stage of development of laser technology and computer technology allows us to take a fresh look at optical research methods, known for a long time. For example, the development and creation of semiconductor lasers of various radiation and power ranges made it possible to obtain rather narrow collimated (low divergent) beams and created new research opportunities in optical gradient refractometry and interferometry. 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 of analysing the received information.

2. The relevance of the work

The interaction of water with various substances, and in particular with alcohols, from the point of view of changing the structure of their aqueous solutions has not studied. In this connection, this study is relevant both from a purely scientific point of view and from the point of view of the practical application of these solutions in pharmacology, medicine and the food industry.

As is well known, water and alcohols are associated liquids in which the association is due to the presence of hydrogen bonds between the hydrogen atoms of one molecule and the oxygen atoms of another molecule. In this case, the energy of hydrogen bonds is much weaker than the energy of covalent bonds between oxygen and hydrogen [6]. Structural formations in water can decay and re-form in various combinations. As shown in [7], dual water molecules having two hydrogen bonds are more stable. Unlike water, in ethanol, glycerin and their aqueous solutions, associates can be formed not only in the form of flat hexagons, rings, but also in the form of chains [7–8]. Thus, their aqueous solutions are mixed complex formations or aggregates, the study of the mechanisms of formation of which is of particular interest to researchers. It is assumed that bulk of the water in ethanol, glycerin, and their aqueous solutions preserves the tetrahedral structure. Molecules of ethanol and glycerol having a larger size, when embedded in the structure of water, violate it, while the embedding of water molecules into their structure is not accompanied by a significant change in the latter. When a small amount of ethanol or glycerol dissolved, the water structure still preserved, although it undergoes a slight deformation. With a further increase in the concentration of soluble substances, the water structure is broken. In the region of average concentrations of solute in water, upon evaporation of a droplet, a dynamic equilibrium of associates of identical molecules, aggregates of various molecules and single molecules of dissolved hydrophilic substance and water is established, i.e., the structure of the system is stabilized.

3. Experimental part

The selection of solutions of dissolved substances in aqueous solutions carried out of the results of refractometric and polarimetric measurements. As a result, purified water and highly diluted solutions of ethanol and glycerol chosen to conduct studies of changes in the clathrate structures of the surface layer.
To visualize clathrate structures and/or their associates in the surface layer of these aqueous solutions, we used a projection microscope-based setup described in detail in [1, 7]. In the process of research, we used cells of various configurations (triangular, square and pentagonal) and of different sizes \(a = 1.5 - 7\) mm in order to make sure that the solutions formed in the surface layers do not depend on the shape of the cells in which they placed. The qualitative dynamics of changes in clathrate structures in the surface layers of aqueous solutions is observed in drops of a triangular shape. A semiconductor laser with a wavelength of \(\lambda = 409\) nm and a power of about 40 mW was used as a source [7–8]. The diameter of laser beam incident on a triangular cell with the test solution is 15 – 18 mm. Due to the relatively low power density of the radiation incident on the droplet and the low absorption coefficient of transparent liquids for a wavelength of 409 nm, the heating of a droplet of an evaporating liquid by laser radiation can be neglected. Fragments of sections of the obtained fractal-cluster structures of the surface layer of the solution during the time of its evaporation increased by \(4 \times 10^2 - 10^3\) times. For better visualization of fixed structures images were converted to black and white.

Examples of the recorded fractal-cluster structures of the surface layers of the studied aqueous solutions of twice purified water, ethanol, and glycerol at room temperature during the drying of drops of a triangular configuration \((a = 2.5\) mm) are presented in the figures below.

**Figure 1.** Slices of the structures of clathrates formed in the surface layer of purified water at room temperature during the drying process of a drop of triangular configuration \((a = 2.5\) mm)

**Figure 2.** Slices of the structures of clathrates of an aqueous solution of hydrogen peroxide at room temperature during drying of a drop of a triangular configuration \((a = 2.5\) mm)

**Figure 3.** Slices of the structures of clathrates of an aqueous solution of ethanol at room temperature during drying of a drop of a triangular configuration \((a = 2.5\) mm)

**Figure 4.** Clathrate structures of an aqueous glycerol solution fixed under the same conditions
From the presented photographs of clathrate structures (Figs. 2–4), it’s seen that the structures of the surface layers of the studied solutions differ significantly from each other. The schemes of possible mechanisms for the formation of fractal-cluster structures in the surface water layers and aqueous ethanol solutions were described in detail in [7–8], in which significant differences in the processes of cluster formation and evolution in the surface layers of aqueous-alcoholic solutions were revealed in comparison with water structures.

At low contents of ethanol or glycerol, their molecules are embedded into the interstitial cavity of the water lattice without causing destruction of its structure. A similar mechanism of dissolution continues only to a certain critical concentration, after which saturation occurs. A further increase in the content of both ethanol and glycerol leads to the destruction of the ordered structure of water with embedded solute molecules and a transition to a disordered structure in which excess molecules join together to form aggregates or islands in the form of closed formations or chains. These units can freely move next to each other forming a mobile fluid. Even with a slight decrease in temperature the ordering becomes more and more, and the aggregates become larger and larger.

The effects observed in the dissolution of ethanol or glycerol in water are due to the complex supramolecular structure of both the water itself and the substances dissolved in it. When dissolved in water their molecules with their hydrocarbon part are located in the voids of the water structure, while the oxides of hydroxyl groups replace one of the frame water molecules.

Figure 5. Scheme of the interaction of ethanol with water

Clusters of structured aqueous solutions of ethanol or glycerol, in turn, do not exist separately. They gather in associates (or, in our case, equivalently, clathrates) of clusters [9–10].

Associates, unlike clusters, do not have a stable structure, and have many modifications. Clusters and ethanol or glycerol clathrates formed on their basis in water are not always strictly hexagonal. In the best case, the angles between the vertex molecules are not equal to 120°, because most often there are not enough peaks for their formation.

Figure 6. Possible patterns of clathrate formation in the surface layer of twice-purified water (a) and aqueous solutions of ethanol (b) and glycerol (c) (horizontal projection)

4. Conclusion

Thus, in this work, we applied the interference method for visualizing fractal-cluster structures and their clathrates (associates) in the surface layers of highly dilute aqueous solutions at room temperature. Fragments of the obtained structures of the surface layers of the solutions allowed us to make the following assumptions:

1. The tetrahedralization of highly diluted aqueous solutions of ethanol or glycerol is apparently associated with the hybridization of carbon in solution.
2. With an increase in hydrocarbon radicals solubility in water decreases and the hydrophobicity of the molecule increases. In this case, ethanol or glycerol molecules exhibit the ability to intermolecular association due to hydrogen bonding. In aqueous solutions hydrogen bonds are formed not only between ethanol or glycerol molecules, but also between their molecules and water molecules. Alcohol, like water, are able to form intermolecular hydrogen bonds due to a partial negative charge on the oxygen atom of one molecule (one of the lone pairs of oxygen electrons) and a partial positive charge on hydrogen to the other.

![Figure 7. Some of the possible intermolecular hydrogen bonds in water (a) and solutions of ethanol and glycerol (b, c) ![Figure 8. A possible mechanism for the formation of clusters of ethanol and glycerol in aqueous solutions

3. There are two kinds of molecules in water, one of which forms a tetrahedral framework, and the other fills its cavities. Therefore, as a result of studies and identification of the fixed structures of clathrates (associates), it can assume that ethanol or glycerol molecules in aqueous solutions form either clusters of various types or chains connected to each other via hydrogen bonds.

The amount of hydrates of a certain type depends on the concentration of water in ethanol or glycerol.
Figure 9. Formation of spatial clathrates in highly diluted aqueous solutions of ethanol or glycerol

4. The effects observed in the dissolution of ethanol or glycerol in water are due to the complex supramolecular structure of both: water itself and soluble substances. When dissolved in water, alcohol molecules with their hydrocarbon part are located in the voids of the water structure, while the oxygen of the hydroxyl groups replace one of the frame water molecules. The processes considered by us, apparently, occur due to the fact, that the associates or clathrates of ethanol or glycerol in water can decompose and re-form in various combinations.

Below models of associates (clathrates) formed from elementary tetrahedra in alcohol-containing aqueous solutions are demonstrated.

Figure 10. Mechanisms of the possible formation of “islands” of clathrates in the surface layer of an aqueous solution of ethanol or glycerol

Thus, in this work, clathrates (associates) of various shapes in the surface layer of purified water and aqueous solutions of hydrogen peroxide, ethanol and glycerol at room temperature are visualized.

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