Structural features of the near-surface layers of highly diluted aqueous solutions

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Abstract. Particular importance currently is given to highly diluted aqueous solutions due to the fact that not only the presence of clusters, but also more complex structures – associates, bastons, etc., have been found in them. However, 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 aqueous solutions is not fully understood. 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. We studied droplets of distilled micellar water, hydrogen peroxide, an aqueous solution of glycerol, ethanol, etc. At low concentrations of hydrophilic substances in aqueous solutions their molecules are embedded into the interstices of the water lattice without causing destruction of its structure. It is found that the dissolution mechanism continued only to a certain critical concentration after which “saturation” occurred. A further 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 present work is devoted to the study of formation of macroscopic, spatially ordered inhomogeneities (clusters, associates and clathrates) which spontaneously arise in the boundary layers of aqueous solutions of ethanol and glycerol. 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 are considered to be macroscopically homogeneous systems. However, the processes of the formation of clusters and clathrates based on them in the surface layers of water-alcohol 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 been paid to researches of cluster structure of water and aqueous solutions, the problem of evaporating liquid droplets has not lost its relevance. Especially important is highly diluted aqueous solutions due to the fact that not only the presence of clusters, but also more complex structures – associates, bastons, emulons, etc., were found in them.

The increased interest in the processes of self-organization in drying drops of liquids has led to the need to develop and apply various methods for this process diagnostics [1]. The study of liquid evaporation using a microscope by the 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 surface layer. The formation of elliptic and hyperbolic diffraction umbilics 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 [2–4], as well as our work [5]. However, in these studies attention wasn’t paid to the fine structure of the resulting caustics. Modern technology makes it possible to visualize various structures in aqueous solutions, the existence of which previously could not even be assumed. The development of laser technology and computer technology allows us 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.

2. Experimental part
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 reform in various combinations. As shown in [7–10] dual water molecules with 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 [11–13]. Thus, their aqueous solutions are mixed complex formations or aggregates, the study of the formation mechanisms of which is of particular interest of researchers. It was 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 alcohol or glycerol is dissolved, the water structure is 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 alcohol and water molecules is established, i.e., the structure of the system is stabilized. At high concentrations of dissolved substances in the studied solution, the structure of these substances, with included in them water molecules, predominates. Mixing alcohol and glycerin with water is accompanied by heat and contraction (compression) of the mixture. The reason for the compression is the formation of associative bonds, which leads to the densification of molecules and a decrease in the total volume of the system.

The selection of aqueous solutions of dissolved substances was carried out on the basis of measurements of the dependence of the refractive index of the solution (Fig. 1), the surface tension coefficient (Fig. 2) and the angular rotation of the plane of polarization (Fig. 3) of the surface layers on the concentration of dissolved substances in water.

To visualize clathrate structures in the near-surface layer of aqueous solutions of ethanol or glycerol we modernized a setup based on a projection microscope [1,11], with which an expanded laser beam passing through a layer of a drop (4) of an aqueous solution placed in the triangular cell (5) located on the stage (3) was projected by a 20-x micro lens (6) onto the SMOR – high-resolution receiving matrix (7) and the resulting picture of the structure was recorded by personal computer (8). In the process of research we applied drops of solutions of various configurations (triangular, square and pentagonal) and of different sizes (a = 1.5 mm, a = 2.0 mm, a = 2.5 mm, a = 3 mm, a = 3.5 mm and a = 7 mm) in order to ensure that the solutions formed in the surface layers do not depend on the shape of the cells in which they were placed. A semiconductor laser with a wavelength of \(\lambda = 409\) nm and a power of about 40 mW was used as a source [11–13]. The diameter of a laser beam incident on a triangular cell with the test solution was about 15 – 18 mm. (Fig. 4). Due to the relatively low power density of the incident radiation and the low absorption coefficient of water and other 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 clathrate structures of the surface layer of the
solution were increased in $4 \cdot 10^2 - 2 \cdot 10^3$ times. For better visualization of fixed structures images were converted to black and white.

**Figure 1.** The dependence of the refractive index of an aqueous solution of ethyl alcohol on its concentration.

**Figure 2.** The dependence of the surface tension coefficient on the concentration of ethanol in an aqueous solution.

**Figure 3.** The dependence of the angular rotation of polarization plane of ethanol aqueous solutions on its concentration.

**Figure 4.** The scheme of the experimental setup (a) for visualization of clathrate structures, the location of sections and photos of some structures in the surface layer of alcohol-containing aqueous solutions (b) when laser radiation passes through a triangular cell with a solution: 1 – laser radiation beam; 2 – radiation attenuating filters; 3 – a glass slide; 4 – a drop of solution; 5 – triangular cell; 6 – micro lens; 7 – receiving matrix of a digital microscope; 8 – laptop (PC).

Examples of some recorded clathrates structures of the surface layers of aqueous solutions of ethanol and glycerol at room temperature during drying of a drop of a triangular configuration ($a = 3.5$ mm) are presented in the figures below.
Figure 5. Slices of the structures of clathrates of an aqueous solution of ethanol at room temperature.

From the presented experimentally obtained pictures (Fig. 5, 6) it can be seen that the clathrate structures of the surface layer of an aqueous solution of glycerol significantly differ from the structures of an aqueous solution of ethanol. The schemes of possible mechanisms for the formation of clathrate structures in the surface water layers and aqueous ethanol solutions were described in detail in [11 –13], in which significant differences in the processes of cluster and clathrate formation and evolution were revealed.

Figure 6. Clathrate structures of an aqueous solution of glycerol fixed under the same conditions.

At low contents of alcohol 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 alcohol content leads to the destruction of the ordered structure of water with embedded alcohol molecules and a transition to a disordered structure in which the excess alcohol molecules join together to form aggregates or islands of alcohol in the form of closed formations or chains (Fig. 7). 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.

Figure 7. Possible patterns of clathrate formation in the surface layer of aqueous solutions of ethanol (a) and glycerol (b) (horizontal projection).

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

3. Discussion
In presented work we applied a simple method for visualizing clathrates (associates) structures in the surface layer of highly diluted aqueous solutions of ethanol and glycerol at room temperature. Fragments of the obtained structures allowed us to make the following assumptions:
1. The tetrahedraization of highly diluted aqueous solutions of ethanol or glycerol is apparently associated with the hybridization of carbon in solution.
2. With an increase in the hydrocarbon radical, 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 bond. In aqueous solutions hydrogen bonds are formed not only between ethanol or glycerol molecules, but also between their molecules and water molecules (Fig. 8). The amount of hydrates formed of a certain type depends on the concentration of water in solution.

Figure 8. The mechanisms of the possible attachment of ethanol molecules to the water cluster and its incorporation (a), as well as the formation of “islands” of clathrates in the surface layer of an aqueous glycerol solution (b).

3. Since there are two types of molecules in water, one of which forms a tetrahedral framework, and the other – fills its cavities, thus, as a result of studies and identification of the fixed structures of clathrates (associates), it can be assumed that ethanol molecules in the aqueous solution form either clusters of various types or chains connected to each other via hydrogen bonds (Fig. 9).

The presence of hydroxyl groups causes the similarity of glycerol with monohydric alcohols; therefore, it enters the same reactions, but with the participation of three hydroxyl groups.

Figure 9. Intermolecular hydrogen bond in an aqueous solution of ethanol and 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 atoms of the hydroxyl groups replace one of the frame water molecules (Fig. 10).

Figure 10. Possible models of clathrate formation in aqueous solutions of ethanol (a) and glycerol (b).

The processes considered in this paper, 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.
4. References

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