Giant water clusters: where are they from?

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Abstract: A new mechanism for the formation and destruction of giant water clusters described in the literature is proposed. We have earlier suggested that the clusters are associates of liquid crystal spheres (LCS), each of which is formed around a seed particle, a microcrystal of sodium chloride. In this paper, we show that the ingress of LCS in water from the surrounding air is highly likely. When a certain threshold of the ionic strength of a solution is exceeded (for example, in the process of evaporation of a portion of water), the LCS begin to “melt”, passing into free water, and the salt crystals dissolve, ensuring re-growth of larger crystals as a precipitate on the substrate. A schematic diagram of the dynamics of phase transitions in water containing LCS during evaporation is proposed.

Keywords: free and bound water; giant water clusters; liquid crystal shells; salt microcrystals

1. Introduction

The structure and dynamics of water has been a top debatable topic for more than a decade [1-5]. To explain a number of its anomalous properties, a two-phase water concept has been developed [6,7]. The reasons for the anomalous physical properties of water are traditionally sought at the atomic-molecular level, in the nanometer space, and on the picosecond time scale. However, recent data allow considering water as a micro-dispersed system. To the best of our knowledge, giant (millimeter-sized) clusters in a thin layer of water were detected for the first time using the IR spectroscopy [8] and were assumed to have liquid crystal nature. Subsequently, supramolecular water complexes ranging in size from 10 to 100 μm were visualized using laser interferometry [9,10] and small-angle light scattering [11,12]. The nature of these clusters is still controversial. The authors of [13] used dielectrometry and the resonance method to show that with an increase in the frequency of reactive current from 1 to 300 kHz, the electrical capacitance of distilled water decreases several fold. With increasing concentration of NaCl aqueous solutions, their electrical capacity increases several fold. The authors suggested that these changes in distilled water are due to the presence of interconnected associates in it. Changes in NaCl solutions, according to the authors, depend on the ratio of the number and size of water associates and the degree of hydration of ions. A decrease in the content of water aggregates (r ≤ 5 μm) under the action of an external constant magnetic field with a magnetic induction of 1.5 T for 30 minutes was also noted in [12].

In our previous studies by the method of acoustic impedancemetry, we identified slow (near-hour) self-oscillation processes in colloidal liquids [14] and proposed a mechanism for their implementation [15]. It is based on periodic phase transitions between the free and bound (liquid crystal) water of the hydration shells of the dispersed phase, which manifests itself in fluctuations in the density of the liquid. These transitions are regulated and coordinated in the whole volume by
osmotic pressure changing as a result of these transitions. Morphologically, these processes manifest themselves as the growth and destruction of spherical structures of micron size (50 - 250 μm), transparent in a liquid medium and visible in it due to the “contouring” by the particles of the dispersed phase. In-phase with the growth and destruction of water microstructures, the surface tension of the test solution fluctuates at the “liquid – air” boundary. Liquid crystal water spheres exhibit the properties of a viscous liquid and evaporate at temperatures above 200 °C [16].

The fact of formation of a quasi-crystalline phase of water at hydrophilic surfaces (both moving [17-19] and stationary [20-22]) has been repeatedly recorded over the past 100 years and experimentally confirmed by many independent researchers. Those discoveries have made an immeasurable contribution to the development of hydrodynamics and biology. To study the phenomenon in laboratory, Nafion - fluorocarbon polymer membranes, including hydrophilic sulfone groups, are commonly used as an example of hydrophilic surface [22,23]. When immersed in water, an “exclusion zone” (EZ) – a water layer with a more dense molecular packing than free water – is formed in 10 to 60 minutes. The width of this layer can reach 500 μm. At the same time, other ions and dispersed particles are displaced from the close-packed water zone. The growth of “exclusion zones” near the surface of metals and glass was also noted [23,24]. In recent years the concept of the molecular structure of the “exclusion zone” has evolved from multi-layered packing of water dipoles [21,22] to a layered structure of flat sheets of hexagonal cells formed by water molecules, where the sheets, unlike crystalline ice, are interconnected by weak electrostatic interaction rather than by rigid hydrogen contacts [23,25]. This ensures that the sheets glide relative to each other, as a result of which the “exclusion zone” behaves like a viscous liquid. It is noteworthy that, in accordance with the study [26], during the melting of ice, an LC phase of water first forms and then free water. Based on the results of our work [14–16], we continued to study the origin and areas of existence of LCS when considering the phase transformations of water in the process of its evaporation. The structure and atomic composition of materials were analyzed by the method of X-ray diffraction and secondary ion mass spectrometry (SIMS).

2. Results

In our earlier work we showed based on optical microscopy that under natural conditions water is a dispersed system, in which the dispersed phase is represented by salt microcrystals surrounded by thick hydrated shells – liquid crystal spheres [27]. LCS were also present on the surface of dry glass and plastic. However, the origin of salt microcrystals in a liquid medium remained unknown. After free evaporation of a layer of distilled water ~ 2 mm thick from a glass Petri dish (d = 9 cm) under room conditions, a loose sediment remained at the bottom, which eventually turned into an array of salt crystals (Fig. 1). The electrical conductivity of distilled water used in this experiment was 36.5 μS / cm. Analysis of the crystals using an X-ray diffractometer unambiguously confirmed that it is sodium chloride (Fig. 2). That is, NaCl microcrystals were really “priming” for the formation of LCS. To test the possibility of salt ingress from the ambient air into water, the following experiment was carried out. 50 ml of distilled water from the same container was poured into two identical clean glass beakers. The end of a plastic tube connected to an aquarium compressor was immersed into one of the beakers. The input end of the tube was placed above the laboratory table in the working area. Laboratory air was passed through the water for 10 min, at a rate of 72 l / h (before the experiment, the compressor was idling for 20 min to clean air paths from possible internal contaminants). Thus, 12 l of air passed through 50 ml of water during the experiment. Both beakers (control and experimental) were left on the table at room conditions, covered with a flat lid, for a week to restore the structural balance. A week later the electrical conductivity of the control sample was 4.1 μS/cm, and of the experimental one 5.4 μS/cm. The microscopy of the droplets of the water samples tested on the glass slide also revealed the difference in the content and structure of the sediment (Fig. 3).
Fig. 1. Structures formed after drying of distilled water in a Petri dish (layer thickness ~ 2 mm): a - 7 days after the start of the experiment, b - 14 days after; c, d - large crystals grown from the sediment mass (a) one week after scraping it with a scalpel into a single mass. The width of the frames a, b - 3 mm, c, d - 1 mm.

Fig. 2. Diffraction pattern of crystals formed after evaporation of distilled water.
Fig. 3. Microphoto of water droplets dried on glass: a - control; b, c - after passing the air (c - dark-field image). Frame width: a, b - 3 mm, c - 1 mm.

Obviously, passage of air has led to severe water pollution. Moreover, salts constituted a large percentage of the microimpurities, which ensured an increase in the electrical conductivity of the sample. Thus, the aerosol origin of LCS is quite likely.

Secondary ion mass spectrometry was used to measure static mass spectra from the surface of a clean silicon wafer before and after evaporation on it of a drop of deionized water stored in the laboratory. In the dried drop of water, a strong increase in the intensity of all lines containing carbon and sulfur was noted (Fig. 4, 5).

Fig. 4. Intensity of the lines of positive secondary ions on the surface of silicon wafer before and after evaporation of a drop of deionized water on it (light and dark bars, respectively).

The radial distribution of ions over the spot of the dried drop was uneven (Fig. 6). In the central zone of the spot of the dried drop, the content of carbon, sulfur and chlorine prevailed, whereas lithium, sodium, potassium, magnesium, calcium and chlorine ions were more concentrated at the periphery. The presence of carbon and sulfur in a dried drop may indicate the presence of soot, which, like salt, could get into the water from the air.
Fig. 5. Intensity of the lines of negative secondary ions on the surface of silicon wafer before and after evaporation of a drop of deionized water on it (light and dark bars, respectively).

Fig. 6. The surface of the dried drop according to SIMS: a - image of a portion of the surface of Si on which there is a fragment of the perimeter of the dried drop of water (obtained by the integrated video camera of the TOF.SIMS-5 installation; frame size 1000x1000 μm²); b - lateral distribution of positive secondary ions on the Si surface, including the perimeter of the dried drop.

The dilution effect of small amounts of salts on colloidal structures has been actively discussed since the middle of the last century ([28], p. 50). Let us consider in more detail the evolution of structures on a glass slide when a portion of tap water (1 ml) containing micro-impurities dries out (Fig. 7). At the beginning of the drying of the water sample, part of the LCS, as a colloidal phase, is transferred by a capillary flow to the three-phase boundary [29] (Fig. 7, a-b). A progressive decrease in the concentration of free water is accompanied by an increase in the ionic strength of the solution. At the same time, part of the liquid crystal water surrounding the salt “seed” under the action of...
osmotic pressure melts, turning into free water and creating conditions for the growth of crystals with further evaporation of free water.

![Microscopic picture of structures in tap water dried on glass (1 ml) 5 days after application: a - melting of LCS and merging of the formed liquid droplets; b - growth of larger salt crystals. Frame width - 1 mm.](image)

After drying of 1 ml of distilled water with an electrical conductivity of 36.5 μS / cm, the beginning of salt erosion of the LCS at the interface was observed on a glass slide (Fig. 8, a, b). In the dried sample of water with a lower electrical conductivity (14.0 μS / cm), large aggregates of LCS settling on the substrate were found (Fig. 8, c, d).

![Structures on the glass after drying 1 ml of distilled water with electrical conductivity of 36.5 μS/cm (a, b) and 14 μS/cm (c, d). a, b - onset of salt erosion of LCS, which is indicated by the radial striation and scalloped edges of the structures; c, d - aggregates of LCS deposited on glass from the dried layer of liquid water. The width of each frame is 1.0 mm.](image)
Experimental data and available literature sources presented in this work allowed us to present a schematic diagram of the dynamics of phase transitions in water containing FSL with NaCl microcrystals as a “seed” when it evaporates from a solid substrate (Fig. 9).

Fig. 9. Schematic diagram of the dynamics of phase transitions in water containing LCS with NaCl microcrystals as a “seed” during its evaporation from a solid substrate, in the “Relative concentration - Time (%))” coordinates. Stage I - evaporation of free water and increase in osmotic pressure; Stage II - phase transition of LC-water into free water and reducing relative rate of evaporation; Stage III - growth of NaCl crystals. 1 - relative concentration of free water; 2 - relative concentration of LC-water; 3 - relative salt concentration.

3. Discussion

In our previous article [27], we already touched upon the discussion of the origin of salt microcrystals in water. In the present paper we report a more detailed study confirming their presence in ambient air and water under normal conditions. According to NASA, sea salt and dust are two of the most abundant aerosols [30]. Wind-driven spray from ocean waves flings sea salt aloft. The content of sodium chloride in sea water is 78%. The authors of [31-33] studied the lower atmosphere in Tokyo region using the lidar depolarization technique, Sun photometer measurements and the dipole discrete approximation method. They reported that the directly observed total depolarization ratio suddenly increased in the afternoon when the sea breeze became dominant and decreased rapidly in the evening. They showed that nonspherical particles, dust and crystallized sea-salt particles diffused in the troposphere. Their calculations showed that the diameter of crystallized NaCl particles was larger than 1 μm. Thus, we suppose that these particles can serve as primers for the condensation of atmospheric moisture forming hydration shells. This is a possible way for the formation of hydrated salt microcrystals in the atmosphere. The lower, main layer of the atmosphere (troposphere) contains more than 80% of the total mass of atmospheric air and about 90% of the total water vapor. In the troposphere, turbulence and convection are highly developed; clouds, cyclones and anticyclones arise. The temperature decreases with increasing height with an average vertical gradient of 0.65°/100 m [34]. Its upper limit in temperate latitudes is 10-12 km. Thus, if the temperature on the surface of the Earth is +25°C, then at an altitude of 10 km the temperature will be about +1.5°C. At temperatures below +0.15°C, NaCl x 2H₂O crystalline hydrates are formed [35]. Seawater freezing point is -1.8°C. Lowering the temperature of the solution has little effect on the solubility of NaCl, unlike most other salts (Fig. 10) [36].
This means that other salts crystallize earlier than NaCl when the solution cools. Thus, by natural recrystallization, seawater frees itself from most impurities and transforms into drops of pure NaCl water solution. Under suitable conditions, droplets form microcrystals. These microcrystals, fall into the lower layers of the troposphere, become part of other aerosol pollution, and enter the water again.

In [27] we calculated that 1 ml of distilled water contains ~ 2.13 μg of NaCl. If we represent this mass in the form of cubic crystals with an edge length of 1 μm, then the number of such crystals in 1 ml of water will be about 1 million. This is a rough estimate of the number of crystallization centers that can be seen with an optical microscope. It was shown [11] that solutes in water are distributed inhomogeneously on large length scales. Regions of higher and lower solute concentration exist in solution and give scattering contrast sufficient for experimental observation. A detailed light scattering study showed that these regions can be characterized as close-to-spherical discrete domains of higher solute density in a less dense rest of solution. These domains do contain solvent inside and can be therefore characterized as loose associates (giant clusters, aggregates). Their size distributions are significantly broad, ranging up to several hundreds of nanometers. In the work [37] the authors used molecular dynamics simulations for studying aqueous ionic liquid (IL)/salt mixtures. The analysis of ion distributions, solvation, and mutual interactions in the course of the evolution reveals heterogeneity of all solutions due to ion segregation into mutually exclusive IL and salt domains, even in monophasic solutions (“ionic sociology”). The authors of the review [38] believe that the large-scale inhomogeneities in aqueous solutions seem to occur in a vast number of systems. And water was considered to be an active excitable medium in which appropriate conditions for self-organization can be established. The thixotropic phenomenon of water was also revealed by different experimental techniques. It may be triggered by large-scale ordering of water in the vicinity of nucleating solutes and hydrophilic surfaces.

In this work, we observed the dynamics of phase transitions in drying aqueous solutions to verify the earlier assumptions made about the nature of water-salt structures (giant clusters). The results of the observations allowed us to propose a scheme that fundamentally describes this dynamics in drying liquids. Additional research is needed to detail the process.

4. Materials and Methods

Tap, distilled and deionized water and aqueous solutions were used in the study. The experiments were performed under laboratory conditions at T = 22°-24° C, H = 73% -75%. The electrical conductivity of the solutions was measured with a MARK-603 conductometer (Russia).
“Crushed drop” preparations and smears for microscopic observations were prepared as previously described [15], using “ApexLab” slides (Cat. No. 7105) and “ApexLab” cover slides (24x24 mm). The samples were examined under a Levenhuk microscope with a computer-coupled video camera Levenhuk C-1400 NG using the ToupView program.

Air was passed through the water using a uniStar AIR 1000-1 aquarium compressor (2.5 W, 72 l/h) for 10 min. The X-ray diffraction experiment was performed on a Bruker D8 Discover X-ray diffractometer. The survey was carried out in a sliding incidence geometry (angle of incidence - 3°) with a Gebel mirror and a 0.6 mm gap on the primary beam. A 2θ scan was recorded with a Soller gap in front of the detector.

SIMS measurements were made on a TOF.SIMS-5 installation with a time-of-flight mass analyzer. We used cluster probe ions Bi3+ with an energy of 25 keV and a current of 1 pA in a single pulse. Separately, negative and positive secondary ions were recorded. Mass spectrometry of secondary ions (ionized sputtering products) allows surface and volumetric analysis of element concentrations to be performed. Using SIMS, a qualitative analysis of microstructures was carried out with reliable identification of all elements present with a sensitivity level of Nα > 10¹⁴-10¹⁶ at/cm³. In addition, the image of the surface in the secondary ions (lateral resolution of 0.1-0.50 microns) was obtained. The measurements were performed in the static SIMS mode, which ensures the nondestructive character of surface analysis.

5. Conclusions

The results of the study and analysis of the literature enable us to make the following conclusion. Aerosol contamination of water, which is almost impossible to avoid in real life, is accompanied by the appearance in the liquid medium of “giant clusters” - micro aggregates of LCS, each of which is formed around a salt microcrystal. Salt contained in LCS does not dissolve, as LC-water has insufficient dissolving ability. At a certain stage of water drying, when the osmotic pressure reaches a critical level, the LCS are eroded and "melt". The released microcrystals of salt obtain an opportunity for further growth and "Ostwald ripening". The methodological approach we used allows us to consistently explain the mechanism of the formation of "giant clusters" in bulk water described by other researchers. It is known that non-reagent energy impact on water leads to a uniform reversible change in its physicochemical properties: an increase in pH, a decrease in surface tension, an increase in the speed of ultrasound. All these changes can be associated with the destruction of the LCS aggregates (an increase in the dispersion and the interphase surface adsorbing protons) and a slow return to the initial state after the termination of the energy source. This assumption will be the subject for further research. The coexistence of liquid crystal and free phases of water in dynamic equilibrium explains, in our opinion, the anomalous characteristics of water as a physical object.

Supplementary Materials: Supplementary materials can be found at www.mdpi.com/xxx/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

LCS Liquid crystal spheres
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