Effects of hydrodynamic impact on water from the viewpoint of cluster theory. Surface tension

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Abstract. Variation of surface tension coefficient $\sigma$ of distilled water under high-energy impact (hydrodynamic cavitation) was studied by the ring separation method. Force impacts on surface tension of water have been studied experimentally. Conditions have been found under which the surface tension coefficient $\sigma$ decreases to 20\%. The paper explains the produced results on the basis of cluster theory of water structure. The experimentally produced relaxation time of the surface tension of cavitation-activated distilled water to initial value has been found to be 3.5 hours.

1. Introduction

The paper studies variation of surface tension of distilled water in rotary type hydrodynamic generator in cavitation mode.

Surface tension is a phenomenon demonstrating difference of interaction forces between molecules on the surface and in the depth of a substance. Among the phenomena taking place at the phase interface of great practical significance are the phenomena of wetting and spreading. Conditions of wetting the surface of a solid body with fluid play a big part in the process of water penetration into porous bodies, soils, grounds. Important are wetting conditions in flotation processes widely used in extraction of mineral resources. The surface tension affects wettability, i.e. the degree of interaction between the contacting phases. Investigation of the effect of various physical, chemical, physical-chemical factors on the structure-energy state of water is urgently needed because this determines its reactivity when interacting with other substances. In progress are experimental studies investigating effect of various external factors, such as magnetization, effect of electric charge, exposure to microwave radiation, aeration and ozonization, enrichment with metal ions on surface tension. These effects can change (increase or decrease) the surface tension of water; the decrease of the coefficient substantially depends, at that, on the kind and degree of the effect. Surface tension depends on the nature of liquid and the phase bordering it, on the value of pressure and temperature [1, 2].

One of the lines of research aimed to create technical means to implement energy-efficient technologies is associated with the method of producing high-power discrete pulse energy in process liquid flow employing cavitation modes. Hydrodynamic cavitation is an efficient factor providing for development of novel technological processes based on thermodynamically nonequilibrium bubble medium. This is the result of effect of shock waves near collapsing cavitation bubbles and cumulative microjets formed by nonsymmetrical collapse of the bubbles. When the bubbles collapse in a local volume close to it and inside it fields of high temperature ($10^3 – 10^4$ K) and pressure ($\approx 1000$ MPa) form. This is the region where various chemical reactions and phase transformations may take place.
In [3] the authors study the use of cavitation effects in various processes. Intensification of mass transfer in «solid phase–liquid» system with account of cavitation destruction of the solid phase, changes in physical and chemical properties of the liquid phase are considered.

Cavitation intensity in hydrodynamic generators from the viewpoint of the quantity of cavitation bubbles and the energy of bubble collapse is estimated in [4].

2. Experimental techniques
Experiments were carried out on two hydrodynamic devices. They rotary-turbulizing apparatus (hydrodynamic generators HG1, HG2), in which at high angular speeds the liquid is separated from the blades to give rise to cavitation effects. The cavitation flow is specified by dimensionless parameter – cavitation index $\chi$: at $\chi > 1$ the flow is precavitation, one-phase; $\chi \sim 1$ the flow is cavitation, two-phase; $\chi < 1$ is the sheet cavitation, i.e. steady separation of the cavitation cavity from the solid flow; $\chi <\!\!< 1$ is the supercavitation.

HG1 generator is a mixing device housing a smooth-bored steel barrel (process chamber, reactor) with a stirrer-cavitator in the form of an impeller with flat wedge profile. Design of the second HG2 generator is identical to the first one. Technical characteristics and operation modes are given in table 1.

| Technical characteristics | HG1 generator | HG2 generator |
|---------------------------|--------------|--------------|
| Reactor volume, ml        | 300          | 3000         |
| Working volume V, ml      | 100          | 1000         |
| Reactor diameter, $10^{-2}$ m | 5           | 30           |
| Impeller diameter, $10^{-2}$ m | 1.5        | 13           |
| Motor power, kW           | 1            | 4            |
| Rotor-cavitator           | Two-blade impeller | Four-blade impeller |
| Wedge expansion angle, °  | 10 – 90      | 30           |
| Rotor speed, rpm          | up to 15000  | up to 4000   |
| Reactor and impeller material | Stainless steel | Iron         |

Operation of generators in cavitation mode: HG1 generator – impeller with wedge expansion angle 60°, angular speed of the rotor 10000 rpm, HG2 generator – impeller with wedge expansion angle 30°, angular speed of the rotor 2280 rpm, cavitation indices $\chi=0.05$ and 0.01, respectively. The distilled water used for five days after production was in a slightly open glass vessel.

The surface tension coefficient $\sigma$ (mN/m) was found by the ring separation method based on measurements of the force required to separate a wire ring from the liquid surface, accuracy ~ 3%. The experiment was carried out immediately after production of the distilled water, every point is the average of five measurements during 5 – 7 min. The content of dissolved oxygen in the water samples under study before and after cavitation treatment was measured on MARK-210 analyzer. Electric conductivity $S$, pH, oxidation-reduction potential (ORP) and temperature $T$ were measured with Water Test instrument of Hanna Instruments, which makes possible to measure these parameters in the following ranges: $\text{pH}=(0\div14)$; $S=(0\div2000)$ μS; $\text{ORP}=(1000\div10000)$ mV; $T=(0\div60)$ °C.

3. Experimental results and discussion

The value of $\sigma$ for water treated in HG1 and HG2 generators with different exposure time $\tau$ is given in table 2 and in figure 1.

| $\tau$, c | $T$, °C | $\sigma$, mN/m | $S$, μS | pH | ORP, mV |
|-----------|--------|----------------|--------|----|---------|
| HG1b      | HG2c   | HG1           | HG2    | HG1 | HG2     | HG1 | HG2    |
| Δa,% | 0  | 25.44 | 22.93 | 72.00 | 72.00 | 126.0 | 121.33 | 7.72 | 7.37 | 154.8 | 143.67 |
|------|----|-------|-------|-------|-------|-------|--------|------|------|--------|--------|
| 30   | 24.72 | 31.17 | 69.26 | 67.62 | 128.2 | 142.33 | 7.88 | 7.67 | 149.0 | 98.00 |
| 60   | 25.64 | 33.57 | 68.61 | -     | 131.4 | 157.00 | 7.96 | 7.83 | 139.8 | 90.67 |
| 90   | 25.72 | 35.63 | 68.24 | 67.04 | 126.8 | 160.33 | 8.04 | 7.87 | 138.8 | 115.00 |
| 120  | 26.44 | 38.83 | -     | 66.23 | 130.0 | 173.33 | 7.98 | 7.93 | 135.0 | 110.67 |
| 150  | 26.86 | -     | 66.32 | -     | 130.8 | -     | 8.06 | -   | 126.6 | -     |
| 180  | 29.62 | -     | 65.16 | -     | 138.6 | -     | 8.04 | -   | 123.8 | -     |
| 210  | 29.40 | -     | 62.34 | -     | 139.0 | -     | 8.02 | -   | 124.6 | -     |
| 240  | 27.28 | -     | 60.16 | -     | 138.2 | -     | 7.91 | -   | 135.0 | -     |
| 270  | 29.68 | -     | 57.48 | -     | 141.8 | -     | 8.12 | -   | 134.0 | -     |
| 300  | 28.60 | -     | 56.37 | -     | 137.8 | -     | 8.08 | -   | 145.2 | -     |
| Δa, % | 12 | 69 | 22 | 8 | 9 | 43 | 5 | 8 | 6 | 23 |

\[ Δ \] - difference between final and initial values in per cent.

\[ b \] Working liquid volume \( V_1 = 100 \text{ ml} \).

\[ c \] Working liquid volume \( V_2 = 1000 \text{ ml} \).

It can be seen that in certain modes of hydrodynamic flows and cavitation treatment time it is possible to achieve considerable decrease of \( \sigma \) of water (22% and 8%).

**Figure 1.** Surface tension coefficient \( \sigma \) vs cavitation treatment time \( \tau \): 1 – HG1 generator, 2 – HG2 generator.

Temperature of water \( T \) increases with treatment time \( \tau \). This is connected with bubble pulsation followed by collapse of the cavitation bubble. The water treated in HG2 is heated more intensively than in HG1 generator. Surface tension depends on temperature.

In [5] researchers studied properties of low concentrated wood soot (figure 2a) suspension treated in HG1 generator in cavitation mode. The soot was designated as «cavitation-activated carbon material – CACM». The size of soot globules was observed to decrease, at that \( \sim 15\% \).
Changes of soot globules were studied at micro-level by EPR and Moessbauer spectroscopy (figure 3).

EPR spectra were found to change the electron structure of carbon matrix of the globules which contains iron particle impurities. g-factor of carbon radical changed due to changes in the electron structure of carbon matrix. The coupling of earlier free in the wood soot electron with matrix changes.

According to Moessbauer spectroscopy data after hydrodynamic treatment the soot globule decreases the population fraction of carbide phase of iron. The produced data indicate powerful cavitation impact on dispersed part of soot suspensions. The impact on the dispersion part of the suspension, i.e. water, should be similar.

Nilsson and Pettersson published a review, which summarized the achievements of water research over the past few years [8]. Water on a large scale is homogeneous, but not homogeneous at the nanoscale, if we consider it not statically but dynamically, if at the same time we will monitor fluctuations between different types of formed structures. It turns out that water (up to boiling) is locally heterogeneous. In water short-lived fluctuations can form structures of low-density water, in which molecules prefer to gather in clusters that are loosely connected to each other, and more homogeneous high-density water.

The mechanism of water cluster deformation was considered in [9]. Depending on the changes in local density profile. The water nanocluster can be broken down into two regions. The region, where the water molecules behave like volumetric water is in internal part of the water cluster. The size of the cluster does not affect the position of water molecules in this region. The size of the cluster affects the properties of surface water molecules. For the cluster of larger size the average number of hydrogen bonds in surface water molecules is higher – this results in higher surface tension. The hydrogen bonds between surface molecules of water decrease with cluster size and decrease the surface tension. Therefore, destruction of the large water clusters and increasing number of smaller clusters under such modes (figure 2b) cause structural rearrangement of the water.

Dynamic behavior of surface water molecules in newly formed clusters cause not only changes in surface tension, but also in physical-chemical state of the cavitation-treated water on the whole. This is proved by measurements of properties of water treated in HG1 and HG2 generators in cavitation modes. In the distilled water the cavitation changes surface tension, pH value, electric conductivity, oxygen content (table 2, figure 4a). Besides, according to [10] as the temperature increases the density of cavitation-treated water \( \rho \) decreases. The power input in treatment in hydrodynamics generators is spent to heat the water, break H-bonds in the clusters and subsequent formation of \( \text{H}^+ \) and \( \text{OH}^- \) ions, \( \text{H}^* \) and \( \text{OH}^* \) radicals, decomposition products of hydrogen peroxide \( \text{H}_2\text{O}_2 \), active water molecules.
Figure 4. (a) Changes in Δ values of physical-chemical parameters of cavitation-treated water in HG1 and HG2 generators for 300 s and (b) relaxation of σ of water after cavitation treatment in HG1 for 1 – 30 s, 2 – 180 s, 3 – 210 s, 4 – 240 s.

Analysis of the data (figure 4a, table 2) specifying parameters of cavitation-activated water makes possible to evaluate structure-formation processes determined by changes in the number of surface water molecules in the clusters, free molecules forming by weakening and disruption of H-bonds of water.

Relaxation curves σ(t) for water treated in HG1 generator are given in figure 4b. Within the time ~ 210 min after the cavitation treatment the curves σ(t) group within the range of σ (68, 70) mN/m, but do not reach the original value of 72 mN/m. Deviation of σ from the original value ≈ 2 % remained for the following 2 days of observation. This is connected with water fluctuations. Therefore, the relaxation time of σ was evaluated as 210 min. This result is in agreement with conclusions in [10].

4. Conclusions
1. Variation of surface tension coefficient σ of distilled water under high-energy impact (hydrodynamic cavitation) in two hydrodynamic generators of the same type but of different power has been studied by the ring separation method.
2. Modes have been found at which the surface tension coefficient σ of distilled water decreased to 20%.
3. Changes in surface water tension at different temperatures and treatment time in the generator in cavitation mode have been compared with changes under analogous conditions of the physical-chemical parameters of water.
4. Experimental results produced on the basis of cluster theory of water structure are explained.
5. Experimentally obtained relaxation time of surface tension of cavitation-activated distilled water to original values is 3.5 hours.

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