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# THEORETICAL PRINCIPLES OF CONTROLLING THE CONCENTRATION OF ORGANICS IN A WATER ENVIRONMENT

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***Abstract.*** *Argued possibility of controlling the concentration of organic inclusions by determining the dynamics of the interphase tension of the phase interface: water medium - air. To implement the process of measuring the dynamics of interphase tension, a new method is proposed - based on the change in pressure in the pulsating meniscus. The theoretical justification of this method consists in the development, on the basis of the Young-Laplace capillarity equation, of a mathematical model of the pulsation process of the gas meniscus at the end of a knife capillary vertically immersed in a liquid in the vicinity of the maximum in a closed gas system. According to the results of simulation of the process of pulsation of the meniscus, the conditions for the occurrence of the phenomenon of hysteresis with jump-like transitions when the volume of the meniscus increases and decreases are theoretically substantiated.*

***Key words:*** *anthropogenic load, organic inclusions, surface tension, capillary surface, hysteresis, liquid meniscus, pulsation, modeling, mathematical model.*

## Introduction.

Increased anthropogenic loads in the locations of industrial facilities have led to the fact that the problem of timely detection and assessment of the level of pollution of water bodies for further localization of sources of pollution and prevention of negative environmental consequences has become especially relevant today.

Possibilities of a practical solution to the specified problem were limited due to the lack of sufficient modern technical means of automated operational control of the ecological state of the aquatic environment.

The exceptional importance of obtaining reliable and operational information about the general content of organic inclusions in drinking, natural and waste water in combination with the shortcomings of the standard method determines the relevance of this study, aimed at studying the operational method of controlling water pollution by organic substances.

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Most organic compounds (surfactants) have surface-active properties: alcohols, acids, amines, hydroperoxides, ketones, ethers, salts of carboxylic acids, etc. [1]. Thus, information on the content of surfactants in water can also serve as an integral assessment of the degree of its purity in terms of organic inclusions.To control organics by measuring the dynamic or equilibrium surface tension at the liquid-gas interface, currently, interphase tensometry is used, which is a very sensitive method of analyzing small concentrations of surfactants [2].

Modern methods, which are based on the analysis of the shape of a drop or a bubble, have practically no restrictions on the time of monitoring the adsorption process, which makes it possible to determine microconcentrations of organic inclusions [3]. However, they have a number of significant drawbacks: the effect of liquid evaporation on the change in the volume of the meniscus of the bubble during a long research process; the impossibility of operative control of the concentration of organic matter; impossibility of use in automated control systems.

To eliminate these shortcomings, a new method of determining the dynamic surface tension based on the measured pressure in the pulsating meniscus is proposed.

The essence of the method is that by direct and reverse gas supply to the bubble, the process of pulsation of the meniscus is realized in the vicinity of the maximum pressure in it, the value of which is uniquely determined by the surface tension at each cycle. The effect is that the bubble at each cycle does not burst after passing the maximum pressure, but goes into a new steady state of equilibrium, that is, the process of adsorption of surface-active substances is carried out on the same surface of the phase interface.

The possibility of implementing the proposed method is theoretically substantiated by developing a mathematical model of the pulsation process of the liquid meniscus in the vicinity of the maximum pressure in a system closed with respect to the amount of the gas phase [2].

**Capillary surface modeling**

Based on the Young-Laplace capillarity equation [4], the mathematical model of the capillary surface of a lying drop meniscus has the form:

$$\begin{cases} \frac{d\varphi}{dL_a} = K_a - \frac{\sin\varphi}{x_a} + z_a, \quad \frac{dx_a}{dL_a} = \cos\varphi, \quad \frac{dz_a}{dL_a} = \sin\varphi, \\ \frac{dV_a}{dL_a} = \pi x_a^2 \sin\varphi, \quad \frac{dS_a}{dL_a} = 2\pi x_a. \end{cases},$$

where $\varphi$ − is the angle between the normal to the capillary surface and the axis of symmetry; $K_a$ − Gaussian curvature at the umbilical point; $x_a$ – horizontal coordinate; $z_a$ − is the distance from the umbilical point to the edge of the capillary at the moment of maximum pressure; $S_a$ − is the surface area of the meniscus; $V_a$ − is the volume of the bubble.

Based on the theory of similarity, all the given parameters are reduced to the capillary constant $a^2 = \sigma/(\Delta\rho g)$.

The initial conditions at the umbilical point (when the arc length of the axial section of the meniscus $L_a$= 0) are set as follows:

$$\varphi = 0,\ x_a = 0,\ z_a = 0,\ S_a = 0,\ V_a = 0.$$

Dependence for dimensionless pressure $P_a$:

$$P_a = P/(\Delta\rho g a) = Ka + z/a = K_a + z_a,$$

where $P_a$ − pressure inside the bubble; $\Delta\rho$ − density difference of liquid - gas media, g – acceleration of free fall.

To represent the process of quasi-static formation of a gas bubble, the characteristics of the meniscus were chosen, which change monotonically with its growth and take predetermined discrete values. The volume of the meniscus $V_a$ and the angle between the normal to the capillary surface and the axis of symmetry $\varphi$ were taken as such characteristics. As the simulation results showed, other characteristics (height, area, arc length of the axial section of the meniscus) are not monotonic. The sequence of increasing discrete values of these characteristics corresponds to a set of capillary surfaces that reflects the quasi-static formation of a gas bubble for a given value of.

**Quasistatics of changes of the meniscus**

Modeling the cyclic process of meniscus volume changes near maximum pressure revealed that as the capillary constant and surface tension increase, the pressure inside the bubble rises at the same volume. However, with the next volume increase, the pressure decreases.

The simulation results show that the lower the surface tension of the substance, the smaller the maximum possible volume of the meniscus (Fig. 1)

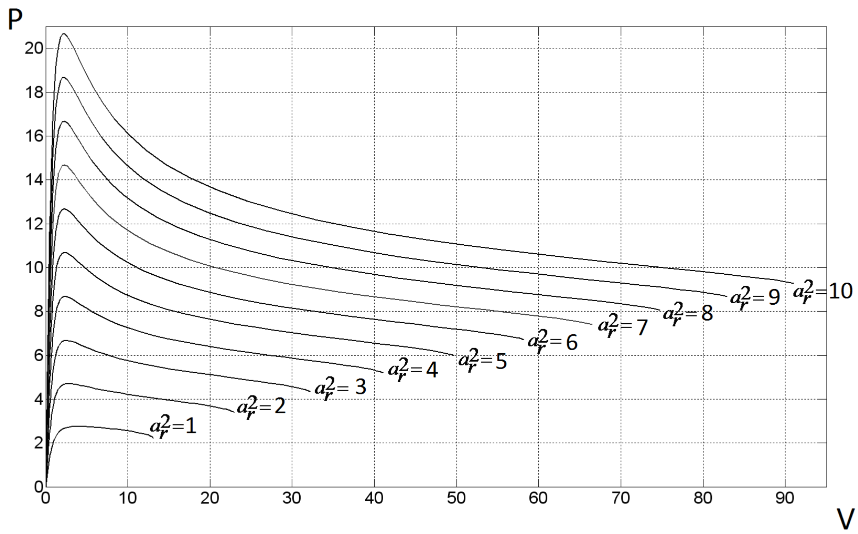


**Figure 1 – Dependence of pressure on volume over the entire range of its change**

*A source: own research*

For the theoretical study of the process of changing the capillary surface of the bubble, including its volume, a simplified simulation scheme was proposed (Fig.2).

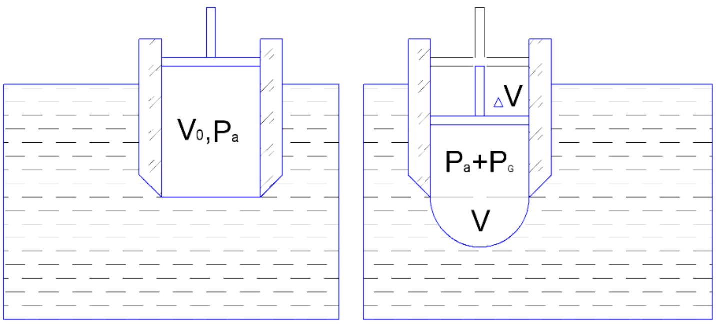


**Figure 2 - The process of squeezing out a gas bubble a) initial state, b) current state**

*A source: own research*

In Fig. 2 shows the process of changing the volume of the capillary surface of the bubble by moving the plunger forward (let's call this process squeezing). When the plunger moves down from the initial position (Fig. 2a), gas enters the meniscus, which leads to a change in its volume (Fig. 2b). When the plunger moves back, on the contrary, the gas phase passes from the meniscus to the supply system. From a thermodynamic point of view, the described process of changing the volume of a gas bubble is isothermal, since the volume of the liquid is many times greater than the volume of the gas bubble, and the heat capacity of the liquid is much greater than the heat capacity of the gas phase. In addition, the process takes place in a very small volume.

Since the hydraulic pressure of the liquid column $\Delta\rho gh$ is constant and insignificant compared to the atmospheric pressure $P_{atm}$, moreover, it is within the variation limits of $P_{atm}$, it can be neglected in the calculations and the dependence of the volume $\Delta V$ displaced by the piston (change in the volume of the supply system ) from the volume of the bubble $V$: $\Delta V = V + V_0 \frac{P_a}{P_a + P_\sigma}$.

For the proportionality of the research results as the initial volume of the system, it is advisable to take the volume with a multiple of k to the volume of the bubble at the moment of maximum pressure.

**Hysteresis of pulsation** of the menisc

Figure 3 shows the results of modeling the dependence of the possible states of the meniscus volume $V$ on the change in the volume of the supply system $\Delta V$ for small values of surface tension.

It was found that at small initial volumes, ambiguity of the dependence is not observed, and at larger values, three-valuedness is observed, which means the presence of hysteresis. With large values of the initial volume, the existence of a bubble after reaching the maximum pressure is impossible, since in order to achieve such a state, it is necessary to reduce $\Delta V$, which is practically impossible (the state is unstable). The hysteresis of the forward and reverse stroke occurs at sufficiently large values of the initial volume $V_0$, i.e., when, the hysteresis effect becomes more noticeable as it approaches the volume of the meniscus at the moment of maximum pressure.

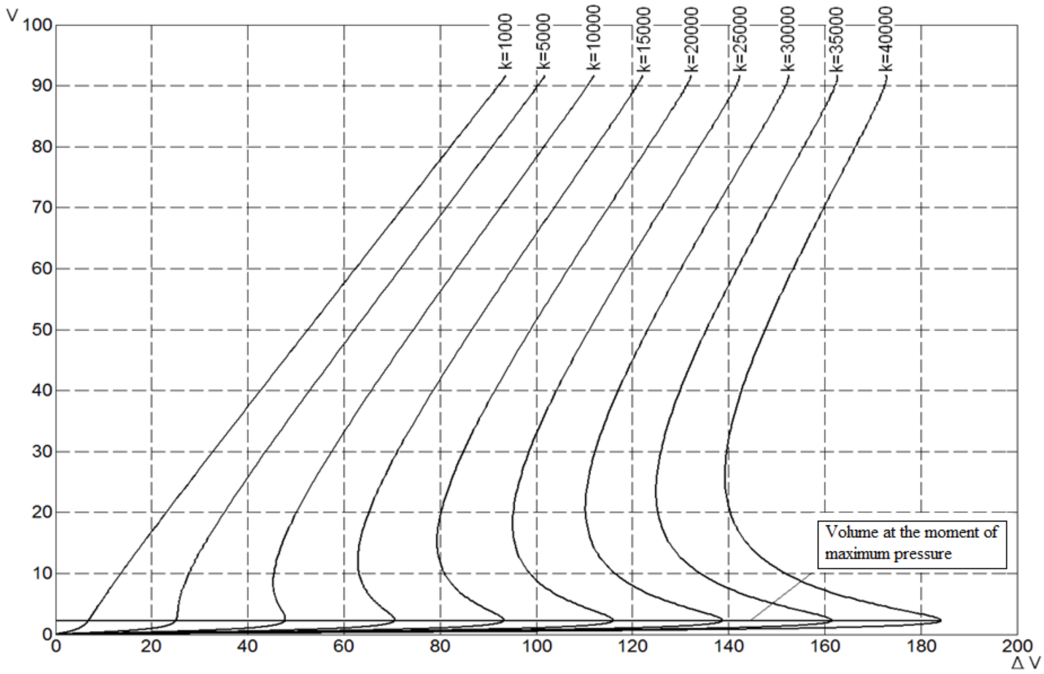


**Figure 3 - Dependence of the volume of the meniscus *V* on the change in the volume of the supply system *ΔV* for different values of the initial volume $V_0$ (k=500:500:50000; $a_r^2$=10, r =1mm, V-[мм³], $V_m$=2,2053 mm)**

*A source: own research*

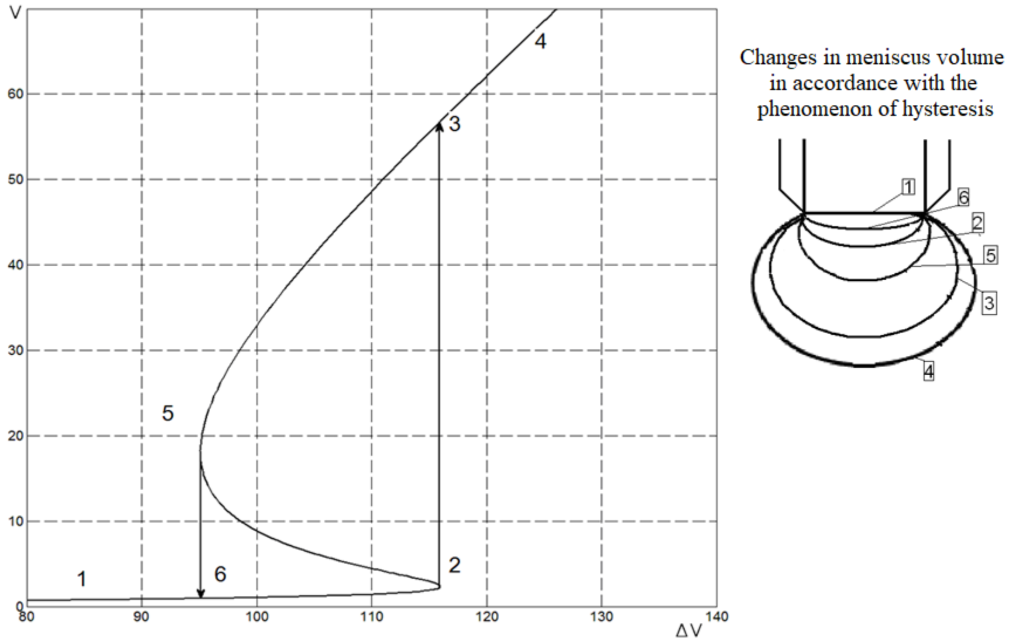


**Figure 4 − Hysteresis of the change in bubble volume from the volume of extrusion and retraction by the piston (increase 1-2-3-4, decrease 4-3-5-6-1)**

*A source: own research*

To examine the phenomenon of hysteresis in more detail, it is advisable to take one of the set of curves (Fig. 3) for K=2500, which is an example of a typical real dependence of V(ΔV). Figure 4 shows a fragment of this dependence with a pronounced bend and the corresponding visualization of the positions of the bubble volume.

**Summary and conclusions.**

As a result of numerical simulation, the following results were obtained:

- the theoretical foundations of the method of determining the concentration of surfactants based on the change in surface tension using the pulsating meniscus method were developed;
- a mathematical model of the process of pulsation of the meniscus in the vicinity of the maximum pressure was developed in order to study the characteristics of the process of controlling the concentration of surface-active substances;
- based on the results of modeling the process of bubble pulsation, theoretically substantiated and experimentally confirmed possibilities and conditions for the occurrence of the phenomenon of hysteresis with jump-like transitions during the extrusion and suction of the bubble
- the dependence of the given characteristics of the meniscus at the moment of maximum pressure depending on the capillary constant is deduced;
- limitations and recommendations regarding the instrumental and metrological characteristics of the implementation of the proposed method are theoretically substantiated;

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