Control of surface active agents content in aqueous environment by measuring surface tension

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Received: 21.06.2013 Accepted: 10.10.2013

Abstract

Surface tention (ST) is a physical-chemical parameter that informs about the presence of surface-active agents (surfactants) in the aqueous environment. The article proposes to obtain experimentally ST (IST) time dependence of the controlled aqueous environment and to judge by the equilibrium ST value (EST) about the surfactant concentration in such an environment, based on the previously received calibration dependence of EST on the concentration of respective surfactant in the aqueous environment. EST dependence of controlled aqueous environment is recommended to get though ST measurements by pulsing meniscus method based on the measurement of maximum pressure in the bubble (MPB) without its separation. The essence of pulsing meniscus method has been described. The advantage of this method over usual MPB method is that in the process of obtaining IST dependence and EST value one should use the same air meniscus surface at the end of metering capillary submerged in the sample of the investigated aqueous environment. It considerably speeds up the process of getting IST dependence and EST value of aqueous environment. The article contains a block diagram, appearance and work description of a device that implements pulsing meniscus method with the application of microcontrollers and hydraulic damper of depth of the metering capillary submersion in the controlled aqueous environment. Calculation of ST value on the basis of the measured maximum pressure drop $\Delta p_{\rm max}$ in the meniscus pulsation process could be accomplished by one of the proposed dependences and methods (M. Cantor, R. Feustel, E. Schrödinger, J. Dugne, S. Sudgen, R. Bendure, I. Kisil). Recommended ranges of values for the parameter $\Delta \rho g r / \Delta p_{max}$ have been demonstrated, where relative methodological error of the calculation results of ST values will not exceed 0.1%, where $\Delta \rho$ is the densities difference of the controlled aqueous environment and air, g is the acceleration of free fall and *r* is an outlet radius of the device metering capillary.

Key Words: aqueous environment, concentration, control, maximum pressure in the bubble, measurement, pulsing meniscus, surface-active agent, surface tension.

Introduction

At present, surface active agents (surfactants) are used almost in all branches of industry, agriculture, everyday life, medicine etc. The main property of surfactants is their ability to influence the interaction between the contacting phases. This fact enables their usage as cleaning agents, as auxiliary materials in technological processes of ore flotation, oil and gas extraction, well drilling and also in production of synthetic fibers, rubber, plastic etc. However, a widespread usage of surfactant resulted in the increase of their production volume. Constant renewal of their range causes the pollution of aqueous environment (rivers, reservoirs, industrial wastewater, groundwater etc.). It should be mentioned that most industrial enterprises and community facilities do not have proper

* Corresponding author: Zarichna@nung.edu.ua devices and systems to treat wastewater from surfactant content. Taking into account surfactant high hazard to human health they should be revealed in surrounding aqueous environment in time.

Well-known methods and devices applied for the assessment of surfactant presence in aqueous environment are mainly adapted to the laboratory conditions, require a lot of time for the preparation and carrying out of each analysis, have high cost and are not suitable for practical environmental monitoring of surfactant content in surrounding aqueous environment, especially when the concentrations are up to 0.01% [1, 2].

Photometric, chromatographic and chemical methods are used to control surfactant content in various aqueous environments of different manufactures.

Photometric method of surfactant content control in water is based on the extraction of surfactant ion pairs with different dyes from water samples by chloroform and determination of surfactant concentration according to the fluorescence intensity of the obtained extract recorded by fluorimeter. Photometric method is rather accurate, but it requires expensive and accurate equipment as well as laboratory conditions for carrying out appropriate control processes.

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Chromatographic method of surfactant concentration assessment in water permits to determine total surfactant content in the aquatic environment and its qualitative composition. Chromatographic method is suitable only for studying of some surfactant types and also requires expensive and complex equipment and laboratory measurement conditions. Analysis should be performed by a person with appropriate qualifications. In addition, there are always surfactant losses due to their adsorption on the chromatograph inner parts.

State Environmental Inspectorate controls surfactant content in wastewater of enterprises and in various aqueous environments by using mainly chemical analysis of water samples. Chemical analysis methods as well as photometric are long term and require skilled professionals and lots of expensive reagents. Moreover, the latter should be different for various surfactant types.

Taking into account the above-mentioned information, the necessity to develop methods for surfactant content control without these deficiencies has appeared. The best solution to this problem is a method based on the measurement of surface tension (ST) at the distribution limit of controlled aqueous environment and air.

Surfactants presence in aqueous environment is detected by ST decrease at the phase distribution limit of controlled aqueous environment and air [3]. Moreover, the character of ST variation from the moment of creation of phase distribution surface to the achievement of ST equilibrium value has a distinct dynamic nature, which is determined by chemical composition and surfactant concentration in the controlled aqueous environment.

Fluids without surfactant presence, including clean water, do not show such ST variation with time. Thus, the dynamics of water ST at the distribution limit with air can serve as an indicator of surfactant content in it. For determining surfactants in water or aqueous solutions it is sufficient to measure ST of studies liquids fixing ST values in time. ST decrease with time accurately indicates the presence of surfactants in the tested liquid.

A necessity conditioned by the above-mentioned facts is to study ST dynamics of controlled liquid at its distribution limit with air (dependence of ST at the phase distribution limit on the time of its existence) and, consequently, develop certain methods for such studies.

At present all known instruments devoted to the ST dynamic study at the distribution limit of liquid environment – air are produced in Germany, USA, Russia, Ukraine. They are mainly intended for laboratory operation conditions, have high cost and are practically not suitable for on-line control of surfactant content in natural water environments directly in the field conditions. Therefore, the main task now is to develop a new methodology for surfactant concentration control based on the study of ST dynamics at the distribution limit of controlled aqueous environment – air that would have sufficient accuracy of ST study results and high efficiency of control procedure.

Theoretical part

ST measurement at the distribution limit of controlled aqueous environment – air can be conducted by many methods with the help of corresponding devices [3].

Among methods that study ST dynamics, the best one is the method of maximum pressure in the gas bubble (MPB). Classical Laplace formula for capillary surfaces, which describes the connection between physical and geometrical parameters of a two-phase system [4] underlays MPB method as well as many other methods connected with ST study:

$$\Delta p = \sigma_{\rm lg} \left(\frac{1}{R_{\rm l}} + \frac{1}{R_{\rm 2}} \right),\tag{1}$$

where Δp is the difference of internal and external pressures that influence capillary axisymmetric surface of two phases distribution in a certain point; R_1 , R_2 is the curvature radii of the capillary surface at this point in mutually perpendicular planes; σ_{lg} is the ST at the distribution limit of liquid-gas.

In the Laplace equation (1) there is a possibility to find ST σ_{lg} , if you know Δp and geometric parameters of capillary surface R_1 , R_2 . The external pressure is a hydrostatic one connected with the depth of gas bubble location in the investigated aqueous environment and the internal pressure is represented by a capillary pressure, which is always directed to the center of capillary surface curvature. It manifests as of liquid column rise in a capillary submerged in fluid.

Analyzing equation (1), one should notice that one of the values measured easily in practice is a pressure drop Δp . If it is measured, then to find ST σ_{lg} one should know curvature radii R_1 and R_2 of the gas bubble surface at one of its points.

However, the curvature radii R_1 and R_2 are the functions of capillary constant of the aqueous environment $a^2 = \frac{\sigma_{lg}}{\Delta \rho g}$, of edge radius of the lower capillary end r, where gas bubble meniscus is located (capillary outlet radius), where $\Delta \rho$ is the difference of densities of aqueous environment and bubble air, g acceleration of free fall. It is impossible to find values R_1 and R_2 within the process of ST measurement σ_{lg} by experiments. While implementing MPB method it has been proposed to measure maximum pressure drop $\Delta p_{\rm max}$ that occurs during gas bubble formation in the liquid from the lower orifice of metering capillary submerged into investigated fluid to a depth h. The obeliscal point (meniscus vertex) here, where $R_1 = R_2 = R_0$, should be taken as a characteristic point of bubble capillary surface. Taking into account all these facts the dependence (1) will be the following:

$$\Delta p_{\max} = \frac{2\sigma_{\lg}}{R_0} + \Delta \rho g (H+h) , \qquad (2)$$

where *H* is a distance from the obeliscal bubble point to the capillary lower end at the moment of maximum pressure drop Δp_{max} ; R_0 is the radius of bubble meniscus curvature at this moment.

It should be pointed out that values H and R_0 depend on a^2 and r. Measurement of values H and R_0 is almost impossible within the process of σ_{lg} determination by the MPB method. In this case a number of dependences and methods of σ_{lg} conversion according to (2), providing h=0 can be actually used, depending on the desired methodological error. They are the following:

dependence of M Cantor [5]

$$\sigma_{\rm lg} = \frac{\Delta p_{\rm max} r}{2} \left(1 - \frac{2\Delta \rho g r}{3\Delta p_{\rm max}} - \left(\frac{\Delta \rho g r}{\Delta p_{\rm max}} \right)^2 \right); \qquad (3)$$

dependence of R. Feustel [6]

$$\sigma_{\rm lg} = \frac{\Delta p_{\rm max} r}{2} \left(1 - \frac{2\Delta \rho g r}{3\Delta p_{\rm max}} - \frac{1}{3} \left(\frac{\Delta \rho g r}{\Delta p_{\rm max}} \right)^2 \right); \quad (4)$$

dependence of E. Schrödinger [7]

$$\sigma_{\rm lg} = \frac{\Delta p_{\rm max} r}{2} \left(1 - \frac{2\Delta \rho g r}{\Delta p_{\rm max}} - \frac{1}{6} \left(\frac{\Delta \rho g r}{\Delta p_{\rm max}} \right)^2 \right); \quad (5)$$

iterative dependence of J. Dugne [8]

$$\frac{\Delta p_{\max}}{\Delta \rho g a} = \frac{2}{r/a} + 0.6679 \frac{r}{a} + 0.0853 \left(\frac{r}{a}\right)^3; \quad (6)$$

iterative method of S. Sugden with the application of a certain table [9, 10];

iterative dependence of R. Bendure [11]

$$\sigma_{\rm lg} = \frac{\Delta p_{\rm max}/r}{2} \sum_{i=0}^{5} B_i \left(\frac{r}{a\sqrt{2}}\right)^i,\tag{7}$$

where $B_0 = 0.99951$; $B_1 = 0.01359$; $B_2 = -0.69498$; $B_3 = 0.11133$; $B_4 = -0.56447$; $B_5 = -0.20156$;

dependence of I. Kisil [12]

$$\sigma_{\rm lg} = \Delta p_{\rm max} r \sum_{i=0}^{5} C_i \left(\frac{\Delta \rho g r}{\Delta p_{\rm max}} \right)^i, \qquad (8)$$

where $C_0 = 0.500152$; $C_1 = -0.354452$; $C_2 = 0.272662$; $C_3 = -1.953555$; $C_4 = 3.520689$; $C_5 = -1.852359$.

The analysis of the relative methodological errors $\delta_{met.}$ of the above-mentioned dependences and methods [12] shows that to achieve values $\delta_{met.} \leq 0.1\%$ the range of permitted values $\frac{\Delta \rho gr}{\Delta p_{max}}$ at the application of these dependences and methods should correspond to the data listed in Table 1.

Thus, analyzing a received value
$$\frac{\Delta \rho g r}{\Delta p_{\text{max}}}$$
 based or

the values $\Delta \rho$, g, r and measured Δp_{max} excluding hydrostatic pressure in the investigated liquid at the capillary lower end, on the basis of data listed in Table 1 an appropriate dependency or method can be chosen for σ_{lg} calculation by MPB method that will give methodological error no more than 0.1%.

Table 1 – Range of recommended values $\frac{\Delta \rho g r}{\Delta p_{\text{max}}}$ for the

above-mentioned dependences and methods of $\sigma_{\scriptscriptstyle lg}$

calculation in order to receive their methodological errors $\delta_{met.} \leq 0.1\%$

Dependence,	Recommended range
methods	of values
R. Bendure [11]	0-0.002
M. Cantor [5]	0-0.035
R. Feustel [6]	0-0.047
S. Sagden [9, 10]	0-0.123
E. Schrödinger [7]	0-0.154
J. Dugne [8]	0-0.532
I. Kisil [12]	0–0.639

Illustrative changes in time *t* of pressure Δp within the process of gas bubbles formation in a liquid without surfactants and a liquid with surfactants are shown in Fig. 1. Here the curves 1 and 3 demonstrate greater amount of air supply into the bubbles within the process of their formation, than it is demonstrated by the curves 2 and 4.





As shown in the Fig. 1,*a* pressure drops Δp_{max} are equal in the liquid without surfactants at different air supply into the bubbles (smaller intervals between two successively formed bubbles). The same phenomenon can be observed with minimal pressure drops Δp_{min} at the time of bubbles separation from the capillary bottom end. In the liquid with surfactants the pressure drops

 Δp_{max1} at greater amount of air supply into bubbles (smaller intervals between bubbles) are bigger than at lower air supply into bubbles $\Delta p_{\text{max 2}}$. The pressure drops $\Delta p_{\min 1}$ and $\Delta p_{\min 2}$ are changed accordingly. It can be explained by the fact that during the time t_{ℓ} (life) of pressure increase in the bubble located at the capillary bottom end in the liquid with surfactants there is a surfactant adsorption at the distribution limit of the air bubble meniscus. The more the intervals between formed bubbles the bigger is the amount of adsorbed surfactant on the bubble meniscus surface than at smaller intervals between bubbles. It reduces $\sigma_{l\sigma}$ and accordingly, due to (1) or (2) reduces Δp_{max} . This process cannot be observed in the liquids without surfactants (Fig. 1, a), so the pressure Δp_{max} remains the same at different air supply into bubbles within their formation (different intervals between two successively formed bubbles).

Time interval from the moment of pressure value Δp_{max} to the moment of pressure value Δp_{min} is a time of spontaneous bubble formation. It is usually called the time of bubble "death" t_d . The adsorption process is believed to occur at this time t_d , that is, the dependence will be $\sigma_{\text{lg}} = f(t_\ell)$ for different values t_ℓ till σ_{lg} equilibrium value is obtained, in other words such a value σ_{lg} that will not change (decrease) with the t_ℓ increase.

To obtain the dependence $\sigma_{lg} = f(t_\ell)$ by MPB method with the formation of air bubble separated from the capillary bottom end, it is necessary to create such bubbles by increasing the time interval between them till ST equilibrium value is reached.

In order to decrease time for obtaining a specified dependency it has been proposed to avoid air bubbles formation after the maximum pressure drop Δp_{max} is reached. Then the capillary surface should be immediately returned to one of its states, having existed before the appearance of maximum pressure and the pressure inside should be increased again to reach a maximum pressure drop and etc. Due to this process the dependence $\sigma_{lg} = f(t_{\ell})$ can be studies with the help of one surface, considering that the time t_{ℓ} will represent the whole period of one distribution surface existence of the controlled aqueous environment and air. It will significantly reduce the time for obtaining the dependence $\sigma_{lg} = f(t_{\ell})$ and simplify the device necessary for the fulfillment of pulsing meniscus method.

To achieve this mode, the air volume of the device measuring circuit should be considerably decreased and as soon as the maximum pressure drop Δp_{max} is reached, the system of air intake from the meniscus should be put into operation, avoiding formation of air bubbles and their separation from the lower end of the capillary.

Experimental part

Based on the considerations given above a device block diagram has been developed to study ST dynamics of the surfactant aqueous solutions, which is depicted on Figure 2 and contains the following blocks and units.



- 1 investigated liquid; 2 metering capillary;
 3 hydrostatic pressure compensator;
 4 differential pressure sensor;
- 5 analog-digital converter; 6 microcontroller;
 - 7 diaphragm vessel; 8 hydraulic cylinder;
- 9 transfer mechanism; 10 stepping motor;
- 11 -stepping motor driver; 12 -power unit;
 - 13 plug for blow-off; 14 keyboard;
- 15 memory expansion unit; 16 indication unit

Figure 2 – Block diagram of the device to study ST dynamics of surfactant aqueous solutions

A vessel contains the investigated aqueous environment 1 where the metering capillary 2 and hydrostatic pressure compensator 3 (compensator of the capillary 2 submersion depth) are submersed to the same depth.

The basic element of the device is a calibrated metering knife capillary, the lower end of which is submersed into the investigated solution 3 and the upper end is connected with diaphragm vessel 6. To avoid chemical interaction of the capillary material and surfactant solution that can lead to the distortion of measurement results, the capillary should be manufactured from inert (chemically resistant) materials.

Quartz glass has been selected as a material for the metering capillary. Capillary lower end is manufactured in the shape of a knife cut to avoid the influence of wetting angle by the aqueous environment of capillary material. The internal capillary hole has the radius size r = 0.5 mm.

Hydrostatic pressure compensator 3, the lower part of which is submersed in the investigated aqueous environment 1 and mounted at the same level with the metering capillary 2 and the upper part of which is connected to the differential pressure sensor 4, is used

N₂	Surfactant name	Concentration dependence on EST
1	Savenol	$c(\sigma) = 1.066 - 54.64\sigma + 946.1\sigma^2 - 5494\sigma^3$
2	Zhyrynoks	$c(\sigma) = 2.848 - 125.8\sigma + 1857\sigma^2 - 9159\sigma^3$
3	Tipol	$c(\sigma) = 0.05304 - 1.025\sigma + 1.105\sigma^2 + 35.57\sigma^3$
4	Gala	$c(\sigma) = 0.03517 - 0.9558\sigma + 5.345\sigma^2 + 17.55\sigma^3$
5	Fairy	$c(\sigma) = 0.05227 - 1.137\sigma - 0.7621\sigma^2 + 91.69\sigma^3$
6	BYK LPD 6296	$c(\sigma) = 14.87 - 345\sigma + 1481\sigma^2 + 6049\sigma^3$
7	Isopropanol	$c(\sigma) = -16.35 + 1593\sigma - 3.418 \cdot 10^4 \sigma^2 + 2.115 \cdot 10^5 \sigma^3$
8	Ripoks	$c(\sigma) = -90.97 + 6184\sigma - 1.36 \cdot 10^5 \sigma^2 + 9.762 \cdot 10^5 \sigma^3$

Table 2 – Approximative dependences of surfactant solution concentration on equilibrium surface tension of different surfactants

for the pressure compensation of hydrostatic column submersed in liquid, which provides independent measurement results from the depth of capillary submersion.

Differential pressure sensor 4 is designed to measure pressure differences in the capillary 2 and hydrostatic pressure compensator 3. Differential pressure sensor MPXV7002DP CASE1351-01 manufactured by the company Free scale semiconductor with a measuring range of pressure drop \pm 2kPa is produced in the integrated form together with previous amplifier and thermal compensation circuit. The error of pressure drop measurement given by this device does not exceed 1.5%.

Analog-digital converter 5 is used to convert direct current signal from the differential pressure sensor 4 and transfer this signal in digital code to the microcontroller 6, where it is considered as a constituent part.

According to the developed program embedded in it, microcontroller 6 controls all external electronic nodes of the device such as keyboard for data input 14, indication unit 16, stepping motor 10 and internal integrated electronic nodes such as analog-digital converter 5. It also conducts certain computational operations connected with measuring process and calculation of value σ_{pe} according to the selected dependence or method. In our case the application of dependence (8) is foreseen.

Diaphragm vessel 7, a part of the device pneumatic system, is designed to change its internal volume and, consequently, the gas pressure inside the system due to the membrane deformation. Due to this a bubble is formed at the end of metering capillary 2. The internal spaces of metering capillary 2 and differential pressure sensor 4 are connected between each other by diaphragm vessel, which has the ability to join a plug for blow-off 13 to clean the capillary from the residue of the investigated liquid.

Hydraulic cylinder 8 is used to create pressure for diaphragm deformation in the vessel 7. Transfer mechanism 9 converts the rotary motion of stepping motor to the translational motion of the hydraulic cylinder 8 rod. Stepping motor 10 is designed to operate the hydraulic cylinder 8 rod. Stepping motor driver 11 is a distributive-power block designed to operate the stepping motor 10 and is run by directing pulses of microcontroller 6.

Power unit 12 supplies direct current with stabilized voltage to all electronic units of the device.

Plug 13 closes the hole of diaphragm vessel 7 to which the blowing-off node of the metering capillary is connected. The blowing-off node should be used to clean the capillary from liquid residue before and after the measurement process.

The keyboard 14 is designed to input control commands for the microcontroller. Memory expansion unit 15 is devoted for storing of measurement results.

To assess surfactant concentration in aqueous environment on the basis of the determined equilibrium ST value one should use appropriate preliminary received approximative dependences of surfactant concentration in water on equilibrium ST of corresponding surfactant original solution. At present there are such dependences for two domestic and six industrial surfactants. These dependences are represented in Table 2 and entered into microcontroller 6 memory. To determine surfactant concentration in aqueous environment an operator selects appropriate dependence on the control panel taking into account previously received information about the presence of this or that surfactant in the controlled aqueous environment.

In the dependences listed in the Table 2 the value of equilibrium surface tension σ is measured in H/m, and concentration value $c(\sigma)$ is depicted in percents.

When study process is finished the operator can represent the research results on the device digital display, which may show ST dynamics in the corresponding aqueous environment, equilibrium ST value, determined concentration of a certain surfactant in the controlled aqueous environment.

An appearance of the developed device is represented on the Fig. 3.

In the process of device operation the stepping motor controlled by the microcontroller rotates shaft of transfer node, which then drives the hydraulic cylinder rod.





7 – compensator of liquid level;

8 – vessel with the investigated liquid

Figure 3 – Appearance of the device designed for the control of surfactant low concentrations by pulsing meniscus method

As a result, a working fluid (glycerol) is displaced from the hydraulic cylinder via connecting tube into the diaphragm vessel. Under the working fluid pressure the diaphragm deformation of this vessel is accomplished, which hermetically separates the diaphragm vessel into hydraulic and pneumatic parts. The diaphragm deformation is resulted in the decrease of the internal volume of device pneumatic part, the gas pressure inside is increasing accordingly and then a bubble is formed at the end of metering capillary in the investigated liquid.

Stepwise gas displacement through the capillary leads to the increase of bubbles at the capillary end. This process continues till the value of maximum pressure drop between meniscus pressure and hydrostatic pressure compensator is reached. Movable value of pressure drop is constantly measured by the differential pressure sensor and transferred through ACD to the microcontroller, which discretely in time records in memory a measured value of the pressure drop with clock frequency. The microcontroller constantly compares a movable pressure value with the previous one and if the comparing difference is negative, it determines the moment of maximum pressure.

After passing the state of maximum pressure drop the bubble volume increases very rapidly and the value of pressure drop unevenly decreases without bubble formation and separation from the capillary end.

At that moment the microcontroller produces a signal for the transition to the gas suction mode by

reverse rotation of the stepping motor and plunger movement back in the hydraulic cylinder accordingly. The pressures in the pneumatic part and, consequently, in the bubble decrease to a specified value. After that the microcontroller sends a signal to the stepping motor to change direction again for the pressure increase in the system. Moreover, during this process the microcontroller records the values of pressure drop $\Delta p_{\rm max}$.

Described measurement cycles are repeated till the value of maximum pressure drop becomes almost unchangeable that corresponds to the achievement of equilibrium ST at the distribution limit of aqueous environment – air.

The value of equilibrium ST is calculated on the basis of the obtained value of maximum pressure drop $\Delta p_{\rm max}$.

Conclusion

Control of surfactant content in aqueous environment (rivers, reservoirs, industrial wastewater, etc.) could be carried out on the basis of the measurement results of their ST at the distribution limit of the controlled aqueous environment – air by pulsing meniscus method based on the method of maximum pressure drop Δp_{max} measurement in the air bubble. Moreover, one and the same meniscus surface is used during the whole period of investigation - from the moment of its appearance to the achievement of equilibrium ST. A developed device based on the pulsing meniscus method with the application of microprocessor can be implemented directly in the field conditions for the express-control of surfactant concentration in the real samples from aqueous environments. Besides, with the application of this device there is a need to obtain preliminary calibration dependence between the concentration of corresponding surfactant in the aqueous environment, the presence of which will be for sure in the aqueous environment, and equilibrium ST. To calculate the equilibrium ST on the basis of the measured maximum pressure drops at the pulsing of the above-mentioned bubble meniscus, one of the mentioned dependences or methods should be used taking into account the value of the parameter $\Delta \rho g r / \Delta p_{\rm max}$. In order to achieve the methodological error of the ST calculation result no more than 0.1% the data listed in Table1 should be used.

References:

[1] Litovka, OV, Ponomarjov, KS 2010, 'Surface-active agents and methods applied for determining their concentration', *Construction Scientific Bulletin*, no. 60, pp. 105–109.

[2] State Standard of the Russian Federation 1999, *Drinking Water. Methods to determine surfactant content in drinking water*, ISO P 51211–98, International Organization for Standardization. Available from: www.gost-svarka.ru. [16 May 2013].

[3] Rusanov, AI, Prokhorov, VA 1994, *Interphase tensometry*, Chemistry, St.Petrsburg.

[4] Laplase, PS 1809, Theorie der Kraft, welcje in der Haarrohren und bei Annlichen Erscheiningenwirkt. Frei ubersetzt mit einigen Aninerkunden von Brandes und Giebert', *A. Phys. und Chim.*, Ed. 33, pp. 1–114.

[5] Cantor, M 1892, 'Uber Capillaritatsconstanten', Ann. Phys. u. Chem., vol. 47, pp. 399–421.
[6] Feustel, R 1905, 'Uber Kapillaritatskonstanten und

[6] Feustel, R 1905, 'Uber Kapillaritatskonstanten und ihre Bestimmung nach der Methode des Maximaldruckes kleiner Blasen', *Ann. Phys.*, pp. 61–92.

[7] Schrodinger, E, 1915, 'Notiz uber der Kapillardruck in Gasblasen', *Ann. Phys.*, vol. 46, pp. 413–418.

[8] Dugne, J 1971, Mesure de la tension superficiella par la methode de la pression maximale de bulle. Rapport CEA - R - 4240, Gif-sur-Vvette, Paris.

[9] Sugden, S 1922, The Determination of Surface Tension from the Maximum Pressure in Bubbles', *J. Chem. Soc. London*, vol. 121, pp. 858–866.

[10] Sugden, S 1924, 'The Determination of Surface Tension from the Maximum Pressure in Bubbles. Part. II', *J. Chem. Soc. London*, vol. 125, pp. 27–31.

[11] Bendure, RL 1971, 'Dynamic surface tension determination with the maximum bubble pressure method', *J. of Colloid and Interface science*, vol. 35, no. 2, pp. 238–248.

[12] Kisil, IS & Kisil, RI 2010, Measurement of surface properties at the phase distribution limit, Ivano-Frankivsk National Technical University of Oil and Gas, Ivano-Frankivsk.

УДК 532.6.08

Контроль вмісту поверхнево-активних речовин у водних середовищах шляхом вимірювання їх поверхневого натягу

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Вказано, що поверхневий натяг (ПН) є фізико-хімічним параметром, який інформує про наявність поверхневоактивних речовин (ПАР) у водних середовищах. Запропоновано експериментально одержувати часову залежність ПН (ДПН) контрольованого водного середовища і по рівноважному значенні ПН (РПН) судити про концентрацію ПАР у такому середовищі на основі попередньо отриманої градуювальної залежності РПН від концентрації відповідного ПАР у водному середовищі. Залежність ДПН контрольованого водного середовища рекомендується одержувати шляхом проведення вимірювань ПН методом пульсуючого меніска, який базується на вимірюванні максимального тиску у бульбашці (МТБ) без її відриву. Описано суть методу пульсуючого меніска, перевага якого перед звичайним методом МТБ полягає у тому, що у процесі одержання залежності ДПН і значення РПН використовується одна і та ж поверхня повітряного меніска на торці вимірюваного капіляра, зануреного у пробу досліджуваного водного середовища. Це суттєво прискорює процес одержання залежності ДПН і значення РПН водного середовища. Наведено структурну схему, зовнішній вигляд і опис роботи пристрою, який реалізує метод пульсуючого меніска з використанням мікроконтролера і гідрокомпенсатора глибини занурення вимірювального капіляра у контрольоване водне середовище. Розрахунок значення ПН на основі виміряного максимального перепаду тиску $\Delta p_{\rm max}$ у процесі пульсації меніска пропонується здійснити за допомогою однієї з наведених залежностей і методик (М. Кантора, Р. Фестеля, Е. Шредингера, Д. Дугне, С. Сагдена, Р. Бендуре, І. Кісіля). Наведено рекомендовані діапазони значень параметра $\Delta \rho_{gr}/\Delta p_{max}$, за яких відносна методична похибка одержаних результатів розрахунку значень ПН не буде перевищувати 0.1%, де $\Delta \rho$ – різниця густин контрольованого водного середовища і повітря, g – прискорення вільного падіння, *r* – радіус вихідного отвору вимірювального капіляру пристрою.

Ключові слова: вимірювання, водне середовище, контроль, концентрація, максимальний тиск у бульбашці, поверхневий натяг, поверхнево-активна речовина, пульсуючий меніск.