

## Quality control of surfactants for oil and gas extraction intensification

*M.M. Chuiko\*, L.A. Vytvytska, I.M. Stankovska*

*Ivano-Frankivsk National Technical University of Oil and Gas;  
15, Karpatska Str., Ivano-Frankivsk, 76019, Ukraine*

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### Abstract

The method of express control of the degree of rocks wetting by surfactants solutions and formation fluids while intensification of oil and gas extraction by controlling and regulating the interphase parameters at the formation fluid-rock – surfactant water solution interface in the process of bottom hole zone treatment has been suggested.

The basis of the proposed method is the dependence of the change in the impedance of the capacitive cell, which contains the studied fluids and specimens of the rock, on their wettability properties, which, in turn, determine the rate of dispersion of the solution on the investigated surface. The main informative parameter of the proposed method is the rate of impedance change, which is determined by the angle of inclination of the graphic dependences of the change of impedance in time when the solution of surfactant is being spread on the solid surface. To implement the developed impedance control method, a device was developed and a method of grading the degree of wettability for a comprehensive evaluation of the quality of surfactants and the selection of such surfactants that have the most optimal wetting properties for specifically-taken oil and gas rocks has been developed.

Keywords: *impedance, liquid velocity, quality control, surface-active substances (surfactants), wettability.*

Due to changes in the structure of the energy market of Ukraine, the depletion of oil fields, rising energy prices and the growth of competition, oil and gas sector enterprises, in particular oil and gas production companies, must ensure their own competitiveness.

This can be achieved through the introduction of modern approaches to production management, in particular, WCM systems (world-class production), which involve application of management, modern technology and continuous improvement of the production process through phased quality control, cost reduction, optimization of each technological operation and search for the most functional methods of efficient production at each stage.

As far as nowadays due to the depletion of oil and gas bearing strata, the problem of intensification of oil and gas production is a pressing issue, then the improvement of one of the stages of oil and gas extraction (contouring of the deposit) requires the control of the quality of surfactants used to intensify oil and gas extraction.

The behavior of the liquid on the solid surface determines the wetting properties of all the media involved in the interaction. Therefore, in order to control the wetting process, it is expedient to consider the surface properties of not every phase in particular, but of the entire system in the complex, and to control

the dynamics of the process of fluid leakage on the hard surface of the rock. Along with a large number of methods for determining the surface tension of liquids, measurement of this parameter for solids is carried out approximately, and the quantitative assessment is very approximate, since a significant number of parameters are affected. Measurement of the marginal angle of wetting using existing methods is carried out in a static mode, which prevents the ability to control the dynamics of fluid dispersion of the surface of a solid, that is, to carry out an express control of the wetting process.

Investigation of wettability parameters such as surface tensions at the interfaces of the contacting phases of the solid-liquid-gas system, the marginal wetting angle, adhesion, and free surface energy formed the basis of many research papers by a number of scientists, the first of which were: Huck, Zhoren, Jung, Laplace and others. Gibbs suggested thermodynamic approach for describing wettability properties. The latter in conjunction with Rebinder's work contributed to the development of the surfactant production industry. Also, wettability issues have been studied and practiced by such well-known scientists as Frumkin, Deryugin, Zikman, Fooks, Neyman.

Spreading rate has been actively studied lately as a characteristic of the kinetic regularity of wetting. This interest is due to the fact that very often the rate of interaction between a solid and a liquid depends on the rate of spreading.

Nowadays the most common oil and gas production intensification method includes treating of the bottom hole zone of the well with surfactant solutions (surfactants). In this case, the control of the

\* Corresponding author:  
myrosyachuyko@gmail.com

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efficiency of the treatment – is, first of all, control of the process of wetting of rocks with formation fluids and solutions of surfactants. This process requires the rapid control of the degree of wettability of the working solution of oil-bearing rocks for the comprehensive assessment of the quality of surfactants and the determination of their optimal concentration, which allows maximize the volume of production.

Therefore, a methodology for grading the quality of different types of surfactants and selecting their optimal concentration for the treatment of bottom hole zones of layers from specific deposits is suggested. The criterion for the gradation is the rate of dispersion of the solution of surfactant and formation fluid in the pores of the rock. This physical quantity depends on several variables: the wettability of porous rocks, the surface tensions of liquids and solids, the viscosity of liquids, and also the roughness of the surface of porous rocks. Due to the existence of interconnections between the parameters on which the reliability of control depends, there is a need for the development of a method for a comprehensive assessment of the quality of wetting of rocks by liquids.

For a comprehensive assessment of a solid wetting process, it is advisable to consider the change and redistribution of charges of liquid and rocks. In this case, this system can be considered as a capacitive cell, and the process of liquid spreading on the surface of the rock should be evaluated by changing the parameters of this cell. In the process of surface wetting due to changes in the size and shape of the drop, the velocity of the latter is proportional to the change in the total dielectric permittivity of the capacitive cell. The test fluid and sample breed are between the covers of the condenser, forming a capacitive cell.

For the theoretical substantiation of this method, the processes that take place in the capacitive cell during the dispersal of the fluid and the surfactant solution on the rock formation have been considered.

The capacity of the condenser with the dielectric is determined by the sum of the various polarization mechanisms.

The adhesion  $W_a$  on the interface solid body-liquid is determined by the parameters of intermolecular interaction and is numerically described by the following dependence:

$$W_a = \sigma_{mz} + \sigma_{pz} - \sigma_{mp}, \quad (1)$$

which, using the Jung equation, can be presented as follows:

$$W_a = \sigma_{pz} (1 + \cos \theta). \quad (2)$$

It should be noted that at the interface of the solid body – the liquid contact area of the liquid with solids may be different, so the work performed is found by multiplying the work of adhesion to the area of their contact [1].

$$W = W_a S. \quad (3)$$

Also, taking into account that the dispersion forces determine the polarization properties of dielectrics, the relationship between the microstructure of the dielectric

and the macroscopic surface energy is presented as follows [2]:

$$W = \frac{2N^2 h e \sqrt{sZ} (\sqrt{\alpha})^3}{64\sqrt{m} r^2}, \quad (4)$$

where  $N$  is the concentration of molecules;  $h$  is the Planck's constant ( $h = 6.6262 \cdot 10^{-34} J \cdot s$ ),  $e$  is the charge of the electrone ( $e = 1.6022 \cdot 10^{-19} C$ ),  $m$  is the electrone mass ( $m = 9.1095 \cdot 10^{-31} kg$ ),  $s$  is the valence,  $Z$  is the the number of free electrons,  $\alpha$  is the polarization,  $r$  is the intermolecular distance.

In its turn, there is a relationship between the polarization of the molecule  $\alpha$  and the dielectric permeability of the medium, which is described by the Clausius-Mosotti formula [3]:

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{\alpha N_A}{3\epsilon_0}, \quad (5)$$

where  $\epsilon$  is the dielectric permeability,  $M$  is the molar mass of substance,  $\rho$  is the density of substance,  $N_A$  is the Avogadro's number ( $N_A = 6.022 \cdot 10^{23} mol^{-1}$ ),  $\epsilon_0$  is the absolute dielectric permeability ( $\epsilon_0 = 8.8542 \cdot 10^{-12} F/m$ ).

From this equation, we can get  $\alpha$ , which is as follows:

$$\alpha = \frac{3\epsilon_0 M (\epsilon - 1)}{N_A \rho (\epsilon + 2)}. \quad (6)$$

Since the characteristics of the interaction between the contacting phases are determined by surface properties, which are numerically determined by their surface energy, and the work of adhesion consists in overcoming this energy for the formation of individual surfaces, one can equate equations (1) and (2) and substituting equation (6) for:

$$\sigma_{pz} (1 + \cos \theta) \cdot S = \frac{2N^2 h e \sqrt{sZ} \left( \sqrt{\frac{3\epsilon_0 M (\epsilon - 1)}{N_A \rho (\epsilon + 2)}} \right)^3}{64\sqrt{m} r^2}. \quad (7)$$

From the above mentioned dependence we obtain equality, which shows the connection between the marginal angle of wetting and the dielectric permeability  $\epsilon$  and the surface tension of the liquid  $\sigma_{pz}$ :

$$\cos \theta = \frac{N^2 h e \sqrt{sZ} \left( \sqrt{\frac{3\epsilon_0 M (\epsilon - 1)}{N_A \rho (\epsilon + 2)}} \right)^3}{32\sqrt{m} r^2 \sigma_{pz} S} - 1. \quad (8)$$

In the obtained dependence, some values are constants, and some are constant for a particular substance, therefore, to establish the relationship between the surface tension and dielectric properties, they can be replaced by such a coefficient:

$$k_{\alpha} = \frac{N^2 h e \sqrt{sZ} \left( \sqrt{\frac{3\epsilon_0 M}{N_A \rho}} \right)^3}{32 \sqrt{m} r^2} \quad (9)$$

Then the dependence (9) will be as follows:

$$\cos \theta = \frac{k_{\alpha} \left( \sqrt{\frac{\epsilon - 1}{\epsilon + 2}} \right)^3}{\sigma_{p^2} S} - 1 \quad (10)$$

The obtained dependence clearly reflects the relationship between the marginal angle of wetting and the surface tension of the fluid and its dielectric properties, which allows for taking into account the peculiarities of the interaction of the contacting media (the rate of dispersion) and theoretically justifies the ability to control the degree of wettability of the surface rock by dielectric properties of the liquid and solid.

Changing the impedance of the capacitive cell in time when the fluid is spilled characterizes the quality of the interaction of the solid-liquid system. It is proposed to establish the degree of fluid leakage by the studied rock surface by comparing the changes in the impedance changes when the fluid is rolled out, the solution of surfactant and reference liquid during their alternate application to the investigated surface under normal ambient conditions.

On the basis of the suggested capacitive control method, the device WDM-1 (wettability degree meter) has been developed. Its block diagram is given in Fig. 1.

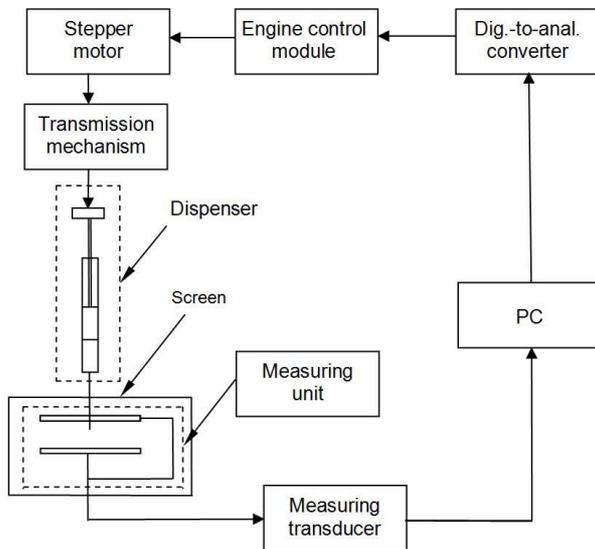


Figure 1 – WDM-1 block diagram

In the course of measurements, the reference and other controlled liquids are applied with constant flow to a controlled solid body sample which is located between the plates of the condenser (capacitive cell). The application of liquid to the surface of a solid is carried out with the help of a dispenser and a transfer mechanism, which turns the rotary motions of the engine into the translatory displacement of the piston of the dispenser. Engine control is carried out by a computer using a digital-analog converter and an engine

control unit. Impedance measurement is carried out simultaneously with the application of liquid on a solid body by a measuring retractor. The transformed and amplified signal from the converter is transmitted to the computer, in which signal is processed and the characteristics of the change of impedance in time is built. It should be noted that in each individual case, the purity of the surface and the dispenser must be examined.

The design of the device involves the rapid replacement of samples of the studied surfaces, as well as protection from the influence of external electric fields.

The measuring transducer is based on the microprocessor block type AD 3934.

The mechanical block of the device, including the measuring block, the dispenser and the transmission mechanism, is shown in Fig. 2.

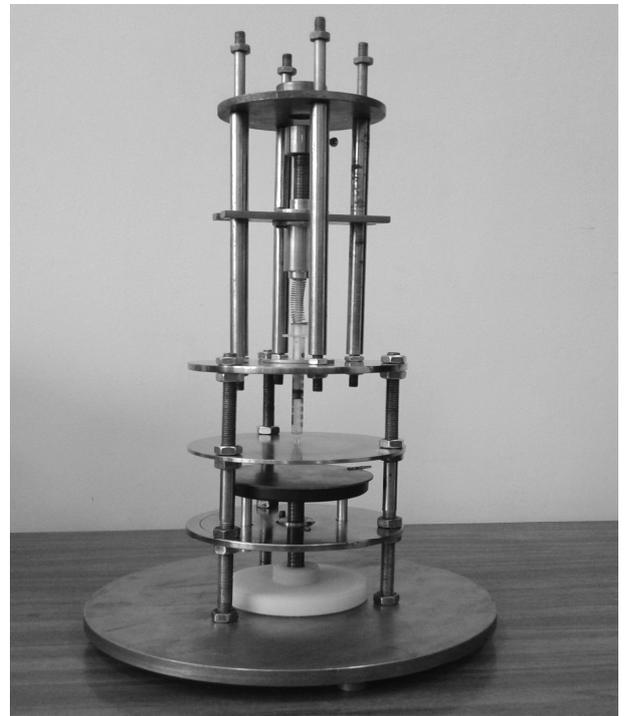


Figure 2 – Mechanical block of the device WDM-1

In the course of experimental studies, the wetting properties of pure liquids (water, alcohol) and water 10 % solution of surfactant (BYK LPD 6296) were tested when they were exposed to glass surfaces, glass fiber glass (PT) and rock pores. For all fluids, the sequence of the study was as follows: the impedance was first determined for the solid sample, and then the test fluid was applied with constant flow.

To determine the operating frequency of the measuring signal, we have defined the character of the dependence of the impedance change upon change in the medium permeability between the plates of the condenser by the introduction of a rock sample. Figure 3 shows the graphs of the dependence of the normalized values of impedance in time at the following frequency values: 1, 2, 3, 5, 7.5 and 10 kHz. Norm values are obtained while assigning absolute values of impedance

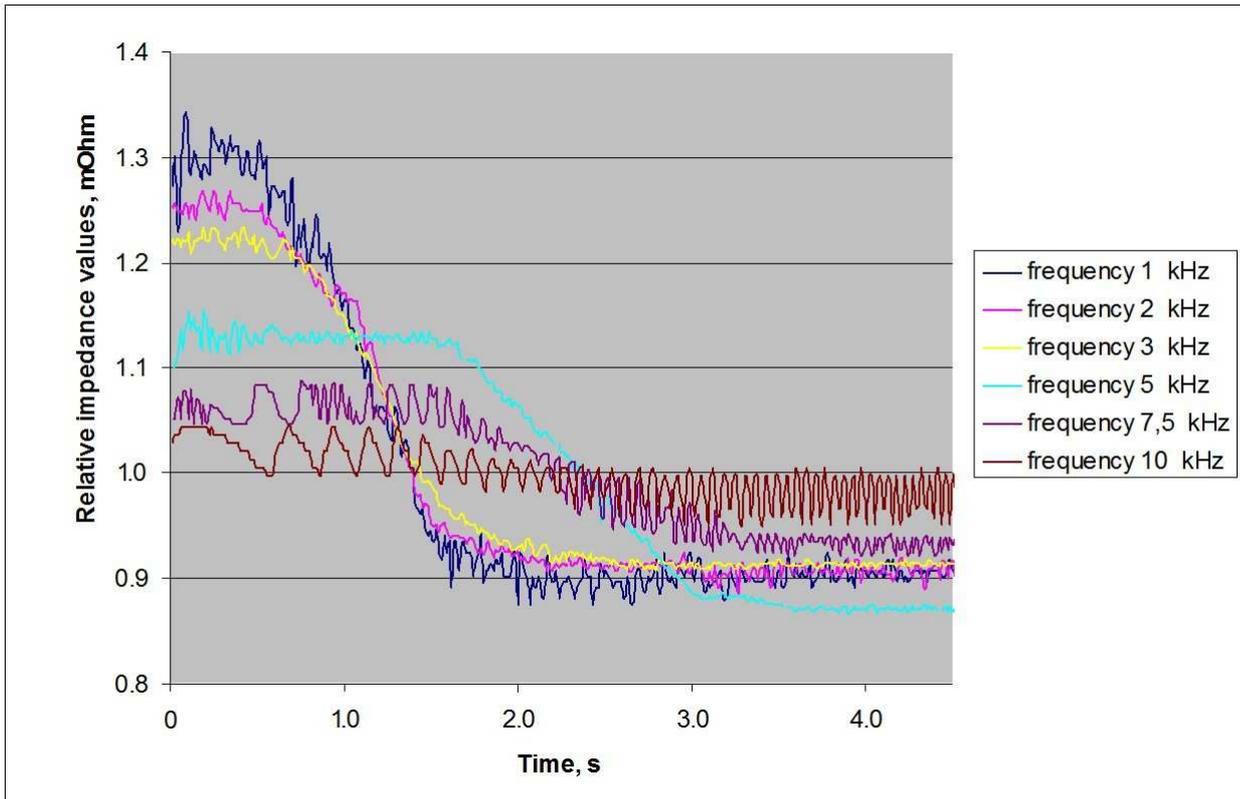


Figure 3 – The character of the change of the impedance of the capacitive cell when it is applied to the test sample at different frequencies of the measured signal

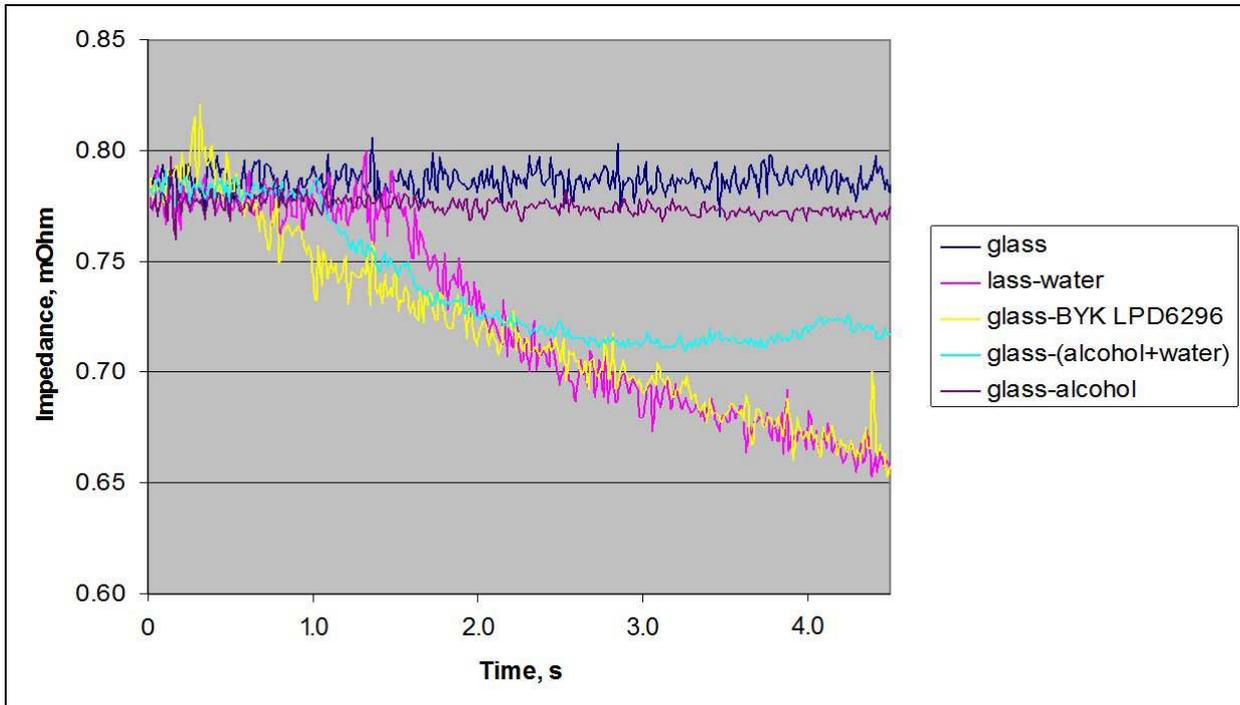


Figure 4 – Impedance change in time when applying fluids to a glass surface sample

to their mean arithmetic meanings. As it can be seen from the figure, at the frequency of the measuring signal of 3 kHz, its character of the change is clear and has the smallest spread of its values.

Therefore, subsequent studies of wettability were carried out at a frequency of 3 kHz. In Figs. 4–6 there are the smoothed graphs of the time dependences of the

impedance change when applied to the indicated fluids on the indicated surfaces. Smoothing of experimental dependencies was carried out using a linear filter at 5 points.

As it can be seen from the graphs, the curves of the impedance change for a set of controlled liquids, when spreading on the surface of a certain solid body sample,

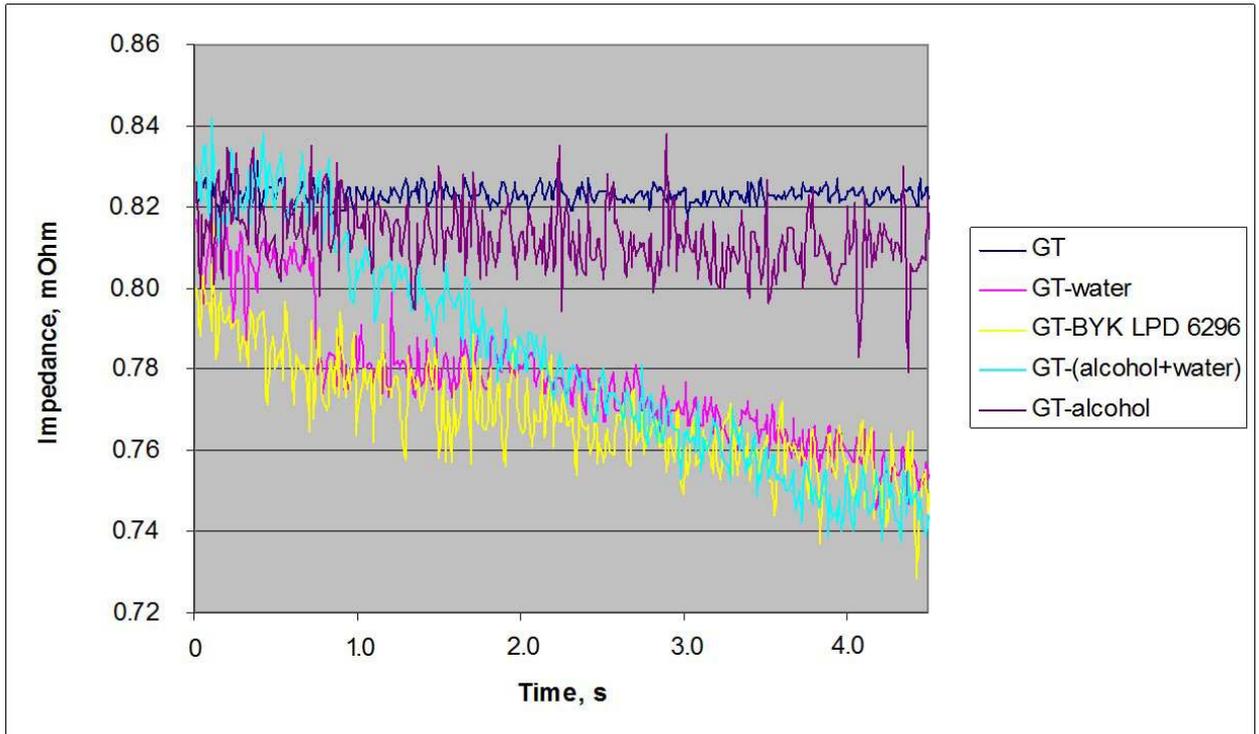


Figure 5 – Impedance change in time when applying fluids to a glass fiber sample

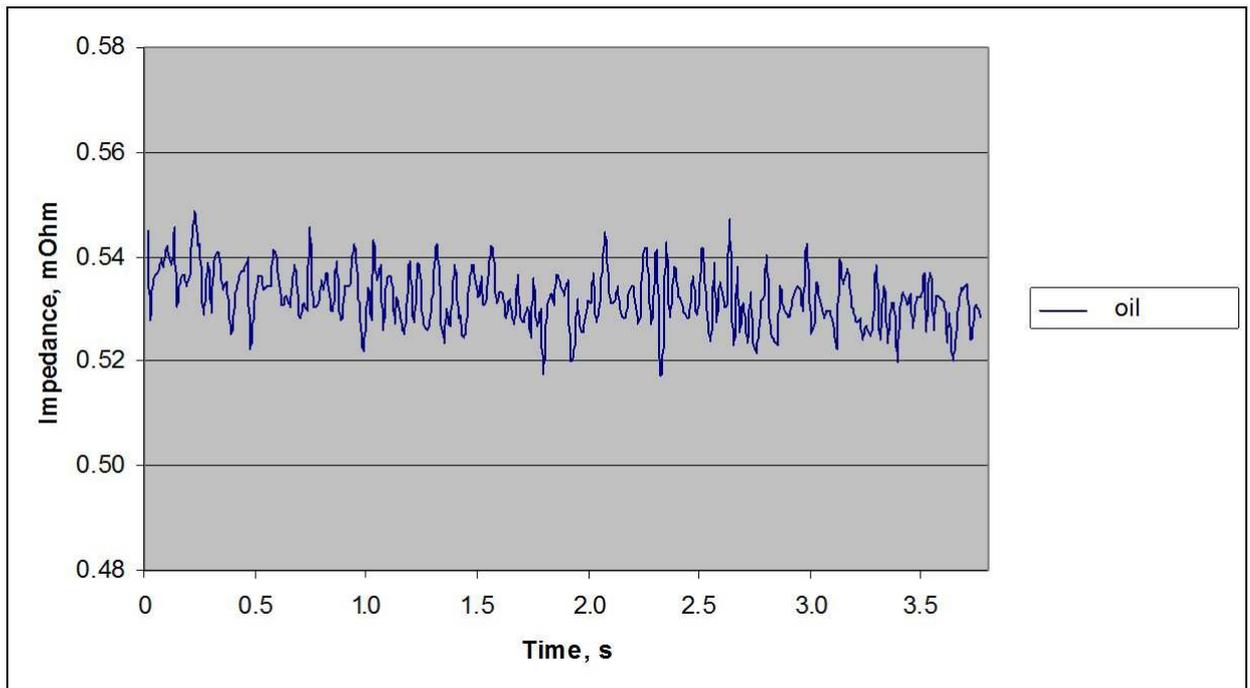


Figure 6 – Impedance change in time when applying oil to rocks samples

change their angle of inclination and the spread of measured values, depending on the surface moisture of the contacting media. From the graphs it is seen that with the decrease of the surface tension of the controlled liquid in the following sequence: water, water 10 % solution of surfactant (BYK LPD 6296), water 50 % solution of alcohol, alcohol – the angle of inclination of the curve and the spread of values decreases, which corresponds to reduction of the marginal angle of

wetting and for better wetting and spreading. Therefore, the graphic dependences obtained give an opportunity to assert that alcohol and surfactant solution have the best wetting properties while water is the worst one for the suggested solid body samples. While wetting the rocks by oil, wettability is low, with the addition of a surfactant solution, spreading is accelerating, which indicates a reduction of the marginal angle of wetting.

### Conclusions

The method being suggested is based on the dependence between the condenser impedance change and the change in the volume and form of the fluid under study when it is spat onto the surface of a solid, filling its interlayer space. This method of control makes it possible to select a liquid with the best wetting properties if compared with a particular solid body sample, taking into account the peculiarities of their interaction. At the same time, both media are investigated in their direct contact, since the behavior of the liquid applied to the solid depends on its actual physical and chemical parameters, and on the state of the solid surface (roughness, heterogeneity, pollution). Due to the short time of control, the error of determining the degree of wetting caused by the evaporation of the fluid decreases and the contrast of the liquid and solid surface, which is necessary for optical methods, loses its relevance.

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## Контроль якості поверхнево-активних речовин для інтенсифікації нафтогазовилучення

*М.М. Чуйко, Л.А. Витвицька, І.М. Станьковська*

*Івано-Франківський національний технічний університет нафти і газу;  
вул. Карпатська, 15, м. Івано-Франківськ, 76019, Україна*

Запропоновано метод експрес-контролю ступеня змочування розчинами поверхнево-активних речовин (ПАР) та пластовими флюїдами гірських порід при інтенсифікації нафтогазовилучення шляхом контролю і регулювання міжфазних параметрів на межі розділу пластовий флюїд – гірська порода – водний розчин ПАР у процесі оброблення привибійних зон пластових експлуатаційних свердловин.

В основу запропонованого методу покладено залежність зміни імпедансу ємнісної комірки, в якій знаходяться досліджувані рідини і зразок породи, від їх змочуючих властивостей, які, в свою чергу, визначають швидкість розтікання розчину досліджуваною поверхнею. Основним інформативним параметром запропонованого методу виступає швидкість зміни імпедансу, яка визначається кутом нахилу графічних залежностей зміни імпедансу в часі при розтікання розчину ПАР поверхнею твердого тіла. Для реалізації запропонованого імпедансного методу контролю виготовлено пристрій та розроблено методику градації ступеня змочуваності для комплексного оцінювання якості і підбору таких ПАР, які володіють найбільш оптимальними змочувальними властивостями стосовно конкретно взятих нафтогазоносних порід.

Ключові слова: *змочуваність, імпеданс, контроль якості, поверхнево-активні речовини, швидкість розтікання рідини.*