

## DEVICE FOR STUDY OF DYNAMIC SURFACE TENSION OF AQUEOUS SURFACTANT SOLUTIONS

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**Abstract.** Theoretical bases of fixed spinning drop method for the study of dynamic interfacial tension of aqueous surfactant solutions on the border with other immiscible liquids in water are considered. The block diagram and appearance of the device, which implements the method of fixed spinning drop are given. There are provided the results of research of the dynamic interfacial tension between the base oil and aqueous solutions of surfactants Tipol and Savenol of different concentrations used for intensification of oil and gas extraction.

**Keywords:** spinning drop method, surfactant, dynamic interfacial tension, aqueous solution, device

### PRZYRZĄD DO BADANIA DYNAMICZNEGO NAPIĘCIA POWIERZCHNIOWEGO WODNYCH ROZTWORÓW SUBSTANCJI POWIERZCHNIOWO CZYNNYCH

**Streszczenie.** Rozpatrzone podstawy teoretyczne metody stałych kropli wirujących w badaniu międzyfazowego dynamicznego napięcia wodnych roztworów środków powierzchniowo czynnych na granicy ich zetknięcia z innymi płynami. Zaprezentowano schemat blokowy i wygląd urządzenia wykorzystującego prezentowaną metodę oraz wyniki badań dynamicznego napięcia międzyfazowego wodnych roztworów Tipolu i Savenolu dla różnych koncentracji stężenia używanych do intensyfikacji wydobywania ropy naftowej i gazu.

**Słowa kluczowe:** metoda kropli wirujących, substancja powierzchniowo czynna, dynamiczne napięcie na granicy faz, roztwór wodny, przyrząd

#### Introduction

The essence of the classical spinning drop (SD) method for measuring interfacial tension (IT)  $\sigma$  at the interface of two immiscible liquids is measuring of the appropriate size of easier liquid drop that is placed in a horizontal tube that rotates around its axis [2, 7]. Thus IT  $\sigma$  is calculated as follows [2]:

$$\sigma = \Delta\rho\omega^2 R^3 / 4, \quad (1)$$

where  $\Delta\rho$  – difference of contacting liquids densities,  $\omega$  – angular velocity,  $R$  – largest radius SD.

Method SD is the one of known methods for measuring low values IT (up to 1 mN/m) [7], that may occur on the interface between aqueous surfactants solutions (SS) – base oil in oil and gas extraction technology [6], production of surfactants [1] etc.

However, the dependence (1) has already methodological error of about 1%, even assuming that the length of SD is greater than its radius  $R$  in four times or more [2]. In addition the drop constantly moves along the horizontal axis of the rotating glass tube and measurement of  $R$  is made only in one point of SD. The situation influences on the accuracy of the measurement  $\sigma$ .

Note that IT  $\sigma$  decreases during the time  $t$  of the interface presence between the aqueous SS – other studied liquid phases. Such dependence IT  $\sigma$  vs.  $t$  is called dynamic IT (DIT) and the result of its study makes possible to determine the time and concentration of surfactant in some technological process. It effects on the quality of the process.

The reservations about the classical method of SD significantly complicate receipt of the DIT at the border of two immiscible liquids and lead to significant errors in the results of this study. The purpose of this paper is to substantiate the modified SD method for study the DIT, namely fixed spinning drop method (FSD).

#### 1. Theoretical part

The FSD method is that in a sealed horizontal glass tube with a heavier fluid (aqueous surfactant solution) is injected an easier drop of liquid. The one end of the drop is fixed to the surface of the cork tube. Then the tube is put in rotation mode around of its horizontal axis and the full or partial contour of the FSD is experimentally obtained.

Calculated theoretical contour of the FSD should vary with the minimal deviation from the experimental contour. It is assumed, that parameters of theoretically calculated contour (including rotating capillary constant  $c = \sqrt[3]{\sigma/\Delta\rho\omega^2}$ ) correspond to the parameters of experimental contour. Therefore the IT calculated

using of theoretical contour is equal to the IT between the studied liquids with known values of  $\omega$  and  $\Delta\rho$ .

The SD is fixed by its one side on the end of corresponding cork. Moreover, the wetting angle of the cork surface by oil in the medium of aqueous surfactant should be equal zero.

In the proposed method, the FSD is formed in the process of tube rotating with heavier fluid (fig. 1). Glass tube 1 is divided into two parts by cork 3 with a hole. The tube is filled by heavier fluid 2 and is rotated with frequency  $\omega$ . The drop 4 is injected through the hole in the cork 3 into rotated tube with the liquid 2, which is heavy that the liquid of drop 4. One end of drop 4 is fixed on the front wall of cork 3. This makes impossible drop moving along the axis of rotation tube under the influence of destabilizing factors. In rotation of the strictly horizontal tube the FSD 4 takes the position along the axis of rotation of the tube 1. The edge of the drop is held on a solid front surface of cork due to the forces of adhesion. In such case the spinning drop of the lighter liquid has shape like as shown on Fig. 1.

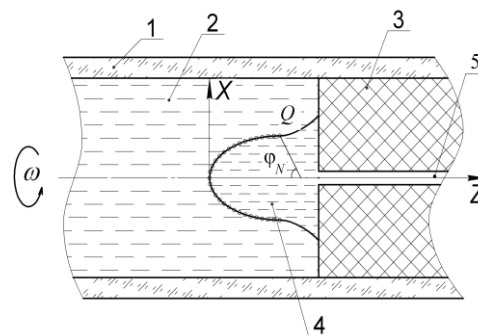


Fig. 1. The shape of FSD of lighter liquid on a solid end of cork inside the rotating tube with heavier liquid: glass tube (1); heavier liquid (2); cork (3); drop of base oil (4); hole (5)

Determination of the IT on the border of two liquids  $\sigma$  is done by following basic procedures:

- getting a set of coordinates of the FSD's contour from its experimental photography;
- calculation of the set of theoretical contours of FSD using of some dependencies, taking into account known physical, chemical, and other parameters which effect on these contours;
- development of similarity criteria for theoretical and experimental obtained contours of the FSD;
- choosing theoretical contour which has the smallest deviation from the experimental contour of the FSD.

Calculation of theoretical contours of FSD is based on the following system of differential equations solution [5]:

$$\begin{cases} \frac{d\varphi}{dl} = K_c - \frac{x_c^2}{2} - \frac{\sin \varphi}{x_c}, \\ \frac{dx_c}{dl} = \cos \varphi, \\ \frac{dz_c}{dl} = \sin \varphi, \end{cases} \quad (2)$$

where  $x_c=x_1/c$ ,  $z_c=z_1/c$  – are the dimensionless points of coordinates of theoretical contours of the FSD;  $x_1, z_1$  – are the dimension points of coordinates of theoretical contour of the FSD;  $K_c = K_1 \cdot c$ ,  $K_1$  – are dimensionless and dimension surface curvatures of the FSD on its apex;  $l_c=l_1/c$ ,  $l_1$  – are dimensionless and dimension lengths of the arches of the meridian profile of FSD from its apex to the point on the FSD surface;  $\varphi$  – is the angle between the normal to the surface of FSD and the axis Z.

The solution of the system (2) is provided by one of the numerical methods (of Runge-Kutta and Adams–Moulton). This method allows to get values  $x_c$  and  $z_c$  for different values of angle  $\varphi$  and given contour shape parameter  $K_c$  corresponding to experimentally obtained contour of the FSD. While measuring the IT  $\sigma$  by FSD method,  $K_c$  parameter can vary in a range from 0 to  $3/\sqrt[3]{4}$ .

It should be noted that we calculate the real coordinates ( $x, z$ ) of the FSD contour taking into account the optical zoom factor  $M$ , which is created by glass tube with a test liquid, thus:

$$\begin{cases} x = \frac{x_v}{M(x_v)}, \\ z = z_v, \end{cases} \quad (3)$$

where  $x_v, z_v$  – are the coordinates of theoretical contours of spinning drop obtained from its experimental image. The dependence of  $M(x_v)$  is calculated according to the procedure described in [4].

Calculation of theoretical contours of the FSD is performed by iterative method of “golden section” [3]. In this case two theoretical contours are calculated with given the initial values of curvature  $K_c$  for each type of contour:

$$K_{c1}=B-0,61(B-A), K_{c2}=A+0,61(B-A), \quad (4)$$

where  $A$  and  $B$  are the limits of change  $K_c$  on each iteration.

On the first iteration value  $A$  is equal to 1, and  $B$  is equal to  $3/\sqrt[3]{4}$ . During following calculation of the theoretical contours, values of  $A$  and  $B$  should be changed in order to get theoretical contour that is the closest to the experimental one. These calculated theoretical contours are compared with experimental contour by the method of calculating the mean arithmetic value of the differences parameters  $Q$  for each theoretical contour as follows:

$$Q_{(1,2)} = \frac{\sum_{i=1}^N \left| \frac{x_i}{z_i} - \frac{x_{(1,2)j}}{z_{(1,2)j}} \right|}{N}, \quad (5)$$

where  $i, j$  are the points numbers of experimental and theoretical contours respectively,  $i=1 \div N, j=1 \div T$ ;  $N$  is the number of experimental points;  $T$  is the number of theoretical contour points. Indices (1, 2) indicate that the couple of coordinates are used for the 1st and 2nd theoretically calculated contours of FSD.

Parameter  $Q$  is calculated only for points for which the condition is valid:

$$\frac{z_{1i}}{z_{1N}} - \frac{z_j}{z_T} \rightarrow \min. \quad (6)$$

Using (5) we calculate the parameters of deviations of two theoretical contours from the experimental contour  $Q_1$  and  $Q_2$ . The values  $K_{c1}$  and  $K_{c2}$  are calculated as follows:

$$B = K_{c2}, K_{c2} = K_{c1}, K_{c1} = A + 0,3(B - A), \text{ if } Q_1 < Q_2, \quad (7)$$

$$A = K_{c1}, K_{c1} = K_{c2}, K_{c2} = A + 0,6(B - A), \text{ if } Q_1 > Q_2. \quad (8)$$

The procedure of calculating and comparing theoretical contours of fixed spinning drop with the experimental contour is repeated till the parameter  $Q$  reaches its minimal value.

The arithmetic average of interfacial tension for 10 points of the spinning drop contour is recommended to be taken as IT calculation result:

$$\sigma = \frac{\Delta\rho\omega^2}{10} \sum_{i=1}^{10} \left( \frac{x_{Ni}}{x_{cTi}} \right)^3, \quad (9)$$

where  $x_{Ni}$  and  $x_{cTi}$  – are points of corresponding experimental and theoretical contours of FSD, which are defined on profiles of these drops at a distance  $(0,6 \div 0,8)z_N$  from their apexes for the same values of the angle  $\varphi$ ;  $z_N$  – is the total length of experimental or theoretical contour.

In order to study the DIT of contacting liquids, described above the measuring procedure for IT is repeated within the required time interval.

The functional diagram of the device VMN-2, which realizes the proposed method of FSD is shown in Fig. 2.

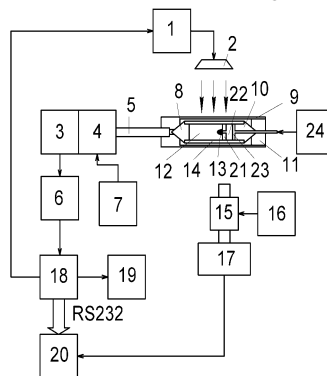


Fig. 2. Functional diagram of the device VMN-2: 1 – electronic key; 2 – illuminator; 3 – rotation sensor; 4 – engine; 5 – shaft of the engine; 6 – Schmitt trigger; 7 – engine control unit; 8, 10 – corks; 9 – patron; 11 – screw; 12 – heavier liquid; 13 – a drop of lighter liquid; 14 – a glass tube; 15 – lens; 16 – focusing unit; 17 – camera; 18 – microcontroller; 19 – display; 20 – PC; 21 – cork with a hole; 22 – lighter fluid; 23 – piston; 24 – unit of displacement piston rod

## 2. Experimental part

External view of the device VMN-2 for the study DIT, is shown in Fig. 3.

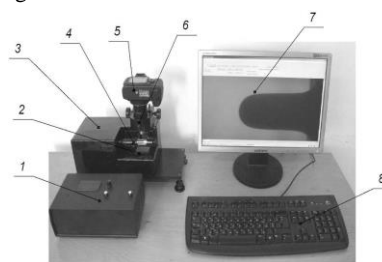


Fig. 3. The external view of device VMN-2: 1 – electronic unit; 2 – lighting unit; 3 – mechanical unit; 4 – patron; 5 – camera; 6 – focusing unit; 7 – PC monitor; 8 – keyboard

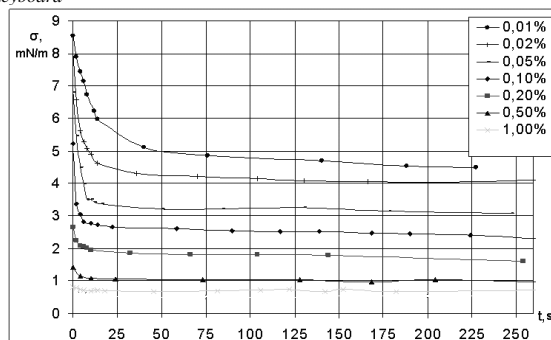


Fig. 4a. Research results of DIT of aqueous solutions of Tipol with different concentrations on border with the base oil of Perekopivsk's field of company "Okhtyrkanafogas"

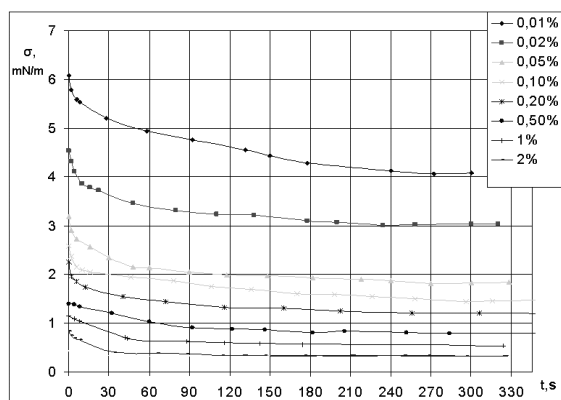


Fig. 4b. Research results of DIT of aqueous solutions of Savenol with different concentrations on border with the base oil of Perekopivsk's field of company "Okhtyrkanafogas"

The testing of the VMN-2 device was conducted by research of the DIT at the interface of aqueous solutions of Tipol and Savenol with the base oil from Perekopivsk's field by oil and gas extraction company "Okhtyrkanafogas".

The results of research of DIT of those SS for different concentrations are shown on Fig. 4.

### 3. Discussion

The time dependences of IT (Fig. 4) can be used to estimate the time required to achieve the desired value of tension at the interface of aqueous SS - investigated base oil. It allows more efficiently using surfactants in the relevant technical process for intensification of oil and gas extraction. As results show, the time required to establish equilibrium value of interfacial tension depends on the type of surfactant and its concentration in the aqueous solution and properties of the contacting base oil. For aqueous SS of low concentrations (0.01 ÷ 0.05)% time to set the equilibrium IT is 150 ÷ 300 s, and for solutions of higher concentration (1 ÷ 5)% it is equal 10 ÷ 60 s.

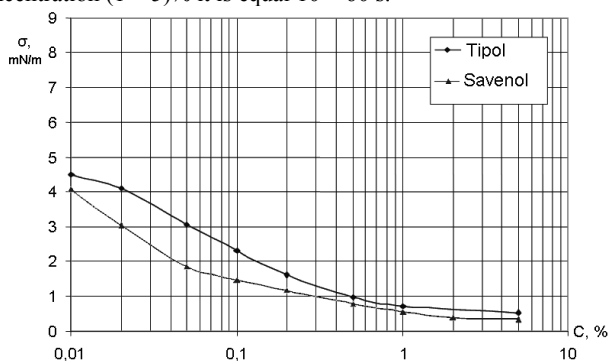


Fig. 5. Dependence of the equilibrium interfacial tension between aqueous solutions of Tipol and Savenol and the base oil of Perekopivsk's field of company "Okhtyrkanafogas" on the concentration of surfactant in solution

Based on the results shown above (Fig. 4) there were graphically obtained dependencies of equilibrium IT of aqueous SS on their concentration, which are shown on Fig. 5. These dependencies are used to evaluate the surface activity of the investigated surfactants and to determine the optimal concentration of surfactants in solution. As shown on Fig. 5, equilibrium value of IT of Savenol is lower for the same concentration Tipol and Savenol. It indicates higher surface activity of Savenol.

### 4. Conclusions

The method of fixed spinning drop for interfacial tension determination at the interface between two liquids has been proposed. This method can be used for the optimal choosing of type of surfactant and its concentration in aqueous solution for

various technological processes. Using the method of fixed spinning drop and the device that implements this method, dynamic interfacial tension of aqueous surfactants solutions has been studied at various concentrations, at the interface with the base oil of Perekopivsk field. Experimental studies have shown that the surfactant Savenol has higher surface activity in comparison with the surfactant Tipol.

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