IMPROVED METHOD OF ROTATING DROP

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The scope of use of surfactants is currently quite wide. Aqueous solutions of surfactants are widely used to increase oil and gas production in Ukraine. They are used to process bottomhole zones of production and injection wells, as well as to maintain formation pressures at oil fields. The defining parameters of surfactant solutions include the following: surface tension (at the interface of the liquid and gaseous phases), interfacial tension (at the interface of two insoluble liquid phases) and the edge wetting angle (at the contact of the three phases). The use of methods and measuring instruments is relevant for the assessment of surfactant solutions in specific technological operations.

The interfacial tension of liquids is determined using the rotating drop method, which is known as the Vonnegut method. The essence of the method is as follows. A drop of lighter liquid $\alpha$ is inside the liquid $\beta$, which is in a sealed tube (Fig. 1). The tube with liquids rotates around a horizontal axis. Heavier fluid is pushed to the periphery, and a drop of lighter fluid - to the axis of rotation due to centrifugal forces. A drop of lighter liquid takes an elongated shape along the axis of rotation. This process takes place against the forces of interfacial tension, which try to make a drop with a smaller surface area. Interfacial tension is determined from the following dependence [1,2]:

$$\sigma = \frac{\Delta \rho \omega^2 D^3}{32}$$

where:
- $\Delta \rho$ – the difference in density of liquids;
- $\omega$ – rotation speed;
- $D$ – droplet diameter.

Fig. 1. The profile of the drop when rotating around the horizontal axis
The disadvantage of this method is the need to achieve significant speeds of the tube (up to 10,000 rpm), so that the length of the drop was four times its diameter; sensitivity to vibrations of the device; the complexity of the procedure of the experiment; the need to spend time to equalize the velocities of liquids after the formation of a drop (i.e., to achieve gyrostatic equilibrium).

A method is proposed in which the drop is squeezed through a hole in the cork during rotation. This drop is fixed at one end on the vertical wall of the cork (Fig. 2). The interfacial tension is calculated using expression (1), to which was added a correction factor $F$:

$$
\sigma = \frac{\Delta \rho \omega^2 D^3}{32} \cdot F.
$$

(2)

The coefficient $F$ can be defined as a functional dependence on different parameters of the drop or their combination. Obviously, it is convenient to use parameters that are easily determined in the experiment. Such parameters are the diameter $D$ and the droplet length $L_{\text{max}}$. The diameter of the drop can be measured in any of its cross sections, but it is most convenient to measure the diameter in the middle of the profile of the drop.

The relationship between $F$ and $D$, $L_{\text{max}}$ was checked by calculating the correlation coefficients between them. Different shapes of the rotating drop with a given interfacial tension $\sigma$ were calculated. For each shape, the interfacial tension $\sigma_s$ was calculated according to formula (1) and the coefficient $F$ according to the following expression:

$$
F = \frac{\sigma}{\sigma_s}.
$$

(3)

$L_{\text{max}}$, $D$ were determined from the calculated contours of rotating drops. Correlation coefficients $C$ between $F$ and $L_{\text{max}}$ were calculated: $C_{F, L_{\text{max}}} = -0.577$, as well as $F$ and $D$: $C_{F,D} = -0.157$. As can be seen from the results of the application of only one parameter does not allow to unambiguously establish the relationship between $F$ and the size of the drop. It was found that when applying the ratio $D/L_{\text{max}}$ there is a correlation with $F$: $C_{F,D/L_{\text{max}}} = 0.962$. Therefore, $F$ can be represented as a function of $D/L_{\text{max}}$.

To find the dependence of $F(D/L_{\text{max}})$, their values for different shapes were calculated (Table 1). As can be seen from the table for drops with $D/L_{\text{max}} < 0.2$ (i.e., the length of the drop should be 5 times the diameter in the middle part) it is possible to use formula (1), the relative methodological error will not exceed 0.1%.
The data in table 1 were approximated by a 4th order polynomial. The expression for calculating the interfacial tension is written as follows:

$$\sigma = \Delta \rho \omega^2 D^3 \cdot \left(-0.0136 \cdot \left(\frac{D}{L_{\text{max}}}ight)^4 + 0.0305 \cdot \left(\frac{D}{L_{\text{max}}}ight)^3 + 0.186 \cdot \left(\frac{D}{L_{\text{max}}}ight)^2 - 0.145 \cdot \frac{D}{L_{\text{max}}} + 1.02\right)$$

The results of measurements of Vonnegut interfacial tension and the proposed methods are shown in table 2. The results show a good repeatability of the values of interfacial tension between the considered methods, which confirms the effectiveness of the developed method.

### Table 1

| $F$ | $D/L_{\text{max}}$ | $F$ | $D/L_{\text{max}}$ | $F$ | $D/L_{\text{max}}$ | $F$ | $D/L_{\text{max}}$ |
|-----|------------------|-----|------------------|-----|------------------|-----|------------------|
| 1.001039 | 0.22196 | 1.002179 | 0.418705 | 1.035984 | 0.789224 | 1.415196 | 1.822904 |
| 1.001007 | 0.236717 | 1.010066 | 0.594264 | 1.074951 | 0.978523 | 1.570379 | 2.12858 |
| 1.00121 | 0.324853 | 1.035984 | 0.78922 | 1.169168 | 1.271022 | 1.757722 | 2.474972 |
| 1.002179 | 0.418704 | 1.035984 | 0.789223 | 1.281753 | 1.542066 | 1.757728 | 2.474969 |

### Table 2

| Experiment number | Interfacial tension, mN/m |
|-------------------|---------------------------|
|                   | Vonnegut’s method | The proposed method |
| 1                 | 0.2                   | 0.198               |
| 2                 | 0.214                 | 0.203               |
| 3                 | 0.217                 | 0.228               |

**Conclusions.** The proposed method has a number of advantages. The formation of a drop during the rotation of liquids in gyrostatic equilibrium allows to determine the interfacial tension of liquids with a small delay in time (not more than 0.3 s), which can be used to study the dynamic interfacial tension. No need to use high speeds of the tube with liquids simplifies the measurement procedure and the design of the device.

### References:

[1]. Viades-Trejo, Josefina, Gracia-Fadrique, Jesús. (2007). Spinning drop method: From Young–Laplace to Vonnegut. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 302. 549-552.

[2]. Drelich J., Fang, Ch., White C. I. (2002). Measurement of interfacial tension in fluid-fluid systems. In Encyclopedia of Surface and Colloid Science, A. Hubbard, Ed., 3152-3166.