Advanced method for measuring slurry surface tension

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Abstract. The work is devoted to a method that makes it possible to level the influence of sedimentation on the surface tension of slurry. To do so the methods for measuring surface tension are used, where the sedimentation process is multidirectional relative to the surface under study. An analysis of the results shows that the proposed method can virtually eliminate the influence of sedimentation on the surface tension of dispersed systems with low kinetic stability. Using the proposed method, the concentration dependence of the surface tension of aqueous slurries of bentonite in the range of 0–20 mass% of the solid phase is studied.

1. Introduction
Bentonite is a clay mineral used in various fields of human activity. The range of bentonite use is very wide and extends from the food industry to the strengthening of hydraulic structures and preparation of drilling mud.

The analysis of the state of research of finely dispersed bentonite shows that there is a considerable amount of experimental and theoretical information on the crystal structure and the influence of lattice defects on a number of practically important properties [1–5].

In many cases, the surface properties of bentonite slurries are used. The methods of physical and chemical analysis are aimed at measuring and studying the surface properties of homogeneous substances. The existing practical request to study the surface properties of disperse systems remains unsatisfied. In particular, there is no reliable method for measuring the surface tension (ST) of slurries, which allows one to take into account the influence of sedimentation of particles on ST. Therefore, the development of reliable methods and techniques for measuring the ST of suspensions remains an urgent task.

2. Theoretical part
When developing a method that allows one to obtain reproducible ST magnitude, it is necessary to take into account that bentonite slurries differ in their complex chemical composition and structure, which makes it difficult to study a number of practically important properties [6–8].

In suspension, the following interfaces can be distinguished: solid particle – liquid, solid particle – air, liquid – air. The liquid – air interface is called the surface of the suspension, and it is the object of our study.
Bentonite slurry is a polydisperse system in the process of formation of which sedimentation is observed. As a result, there is a change in the content of particles of the solid phase in the surface layer, which has a significant influence on the magnitude of ST suspension.

It is generally accepted that solid phase particles do not significantly affect the ST magnitude of bentonite slurry. Therefore, the features of bentonite slurries on ST isotherms are usually associated with the composition of liquid phase, the presence of excess charges on the surface [9], and the influence of electrolytes [10]. However, the available experimental results indicate a significant influence of particles of bentonite solid phase on the ST magnitude [11–12].

Based on the features of surface formation characteristic of each method, the methods for measuring the ST of slurry can be divided into two groups. The first group includes methods in which the process of measuring ST is accompanied by sedimentation of solid phase particles on the surface (hanging drop technique, stalagmometric method). Indeed, when using these methods, coarse particles contained in a drop of slurry move to the surface.

The second group includes methods in which particles of the solid phase, as a result of sedimentation, leave the surface, i.e. the surface is depleted over time by coarsely dispersed particles (lying-drop techniques, maximum pressure in a gas bubble or in a drop, capillary method of surface tension measurement, and so on).

Therefore, when using any of the above methods for measuring ST, the researcher will encounter problems caused by the dynamic nature of the composition of the surface layer, which leads to the dependence of ST on the time of formation of droplet surface. Therefore, before proceeding with the development of a methodology for measuring the ST of slurries, it is necessary to find out what this dependence is and how to take it into account when measuring the ST of slurry.

### 3. Methods and materials

Samples of slurry of bentonite were prepared in distilled water by gravimetric method. To achieve the optimum degree of dispersion and reduce the measurement accuracy caused by sedimentation, after thorough mechanical grinding, bentonite was transferred to a dispersion medium and was subjected to stirring for 1–1.5 hours (magnetic stirrer; slow heating). After that, the prepared slurry was placed into storage for a certain time. As experience shows, to achieve a sufficient degree of dispersion required for measuring the bentonite ST, two days of exposure of a solid phase in the dispersion medium at room temperature should be sufficient. The measurements were carried out using the methods of a lying and a hanging drop on DSA-100 Analyzer [13].

### 4. Results

Using these two methods, the time dependence of the ST of bentonite slurry was investigated. The measurement results are presented in Figure 1 and 2.

As is clear from these Figures, when measuring the ST by the lying-drop technique, an increase in ST is observed over time (Figure 1), and in the hanging drop technique (Figure 2), the ST decreases with time. With an increase in the concentration of the solid phase, the linear time dependence of the ST remains to be unchanged; however, the angular coefficient (positive for lying-drop technique and negative for the hanging drop technique) grows in absolute magnitude. Such a change in the magnitude of ST is due to the fact that in the lying-drop technique, the concentration of solid phase particles in the surface decreases, which leads to an increase in ST approaching the magnitude of ST of water. As a result of sedimentation, in the hanging drop technique the surface, on the contrary, is enriched with particles of the solid phase and a decrease in the magnitude of ST is observed.

There is a question of how to level the influence of sedimentation on the results of measuring the ST of slurry. How to extrapolate the obtained results to the results that could be obtained in zero gravity? The analysis and generalization of the results allowed us to develop the following methodology.
Figure 1. Time dependence of ST of bentonite slurry with different content of solid phase at 298 K (lying-drop technique)

Figure 2. Time dependence of ST of bentonite slurry with different content of solid phase at 298 K (hanging drop technique)

The essence of the proposed methodology for measuring the ST of slurry is that the ST is measured in two ways, i.e. by the technique of hanging and a lying drop [14]. The process of sedimentation when using these two measurement techniques occurs in the opposite directions. In the first case, the surface of the droplet is enriched with particles of the solid phase and in the second it is depleted. As a result, the time dependences of ST in these two cases show opposite changes: when using the hanging drop technique, a linear (within the limits of measurement accuracy) decrease in ST is observed (Figure 2), the ST of the lying droplet increases linearly with time (Figure 1). Moreover, the time dependences of ST are the same in absolute magnitude.

The superposition of the ST results obtained using indicated measurement techniques, where the time dependences of ST are equal in absolute magnitude but are differently directed relative to the surface under study, allows one to minimize the influence of sedimentation. Figure 3 shows the ST of bentonite slurry obtained by averaging the results of measuring the ST by the techniques of lying and hanging drop in the indicated time interval. Insignificant deviations of the ST isotherms from the
horizontal line are within the experimental limits (0.1–0.3 mN/m). The constancy of ST (within the measurement accuracy) indicates that the method of superposition of measurement results obtained for hanging and lying drops makes it possible to find ST characterizing a suspension with particles uniformly distributed over the volume.

Figure 3. The time dependence of the ST of bentonite slurry with different solid phase contents (superposition of the results of measuring the surface tension by the methods of lying and hanging drop), at 298 K.

The absence of the influence of substrate on the test liquid (a standard, fluoroplastic plate recommended by the manufacturer of the measuring equipment is used as the substrate) on the ST magnitude can be judged by comparing the measurement results using lying drop that is located on the substrate and hanging drop when there is no substrate.

Figure 4 shows the ST isotherms obtained by two indicated methods, as well as the isotherm calculated by the superposition method at a concentration of 3 % of the mass of solid phase. As one can see from the isotherms 2 and 3, the angle of inclination of both ST isotherms relative to the composition axis is almost symmetric which indicates the absence of significant influence of the substrate on measured ST magnitude.

Figure 4. Time dependence of surface tension of bentonite slurry at 3 mass. % of solid phase: 1 – averaged values; 2 – lying-drop technique; 3 – hanging drop technique, at 298 K.
Figure 5 shows the concentration dependence of the ST of an aqueous slurry of bentonite. The measurements were carried out using the proposed method of superposition (at a confidence level of 0.95, the error in the measurement of ST does not exceed ± 0.6 mN/m).

![Figure 5](image)

**Figure 5.** Dependence of ST on the concentration of solid phase in an aqueous slurry of bentonite at 298 K. (hanging drop technique)

Figure 5 shows the ST isotherm of an aqueous slurry of bentonite at 298 K. In the concentration range of 3 mass. % there is a local minimum. With an increase in the concentration (up to 14–15 %) an increase in ST occurs. A further increase in the concentration of the solid phase (starting from a concentration of 16 %) does not lead to a significant change in ST.

5. **Conclusion**

Since the sedimentation rate with the techniques of hanging and lying drop is the same, but differently directed relative to the surface, the concentration of solid particles has the same influence on the magnitude of ST in time, regardless of the technique applied. Therefore, a superposition of measuring results of the ST of slurry by the indicated methods eliminates the influence of sedimentation on the value of slurry.

In addition, the analysis of the averaged ST isotherms (Figure 3) makes it possible to conclude that it is advisable to measure the concentration dependence of ST by the techniques of lying and hanging drop at a surface age of at least 120 s, since with a shorter drop formation time, there is observed an increased scatter of experimental ST magnitudes. The increased scatter of the measured values or magnitudes in the initial period of droplet formation is explained by the fact that at the beginning (regardless of the measurement method) there are an intense processes of redistribution of solid phase particles between the surface layer and the bulk phase in the droplet due to residual liquid perturbations that occur at the moment of surface formation. After the specified time (120 s), the system approaches a quasi-equilibrium state, which leads to a decrease in the intensity of redistribution of particles, and, as a consequence, to the stability of results.

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