

Polydispersity Effect and Coagulation Structures on the Surface Tension of Isotherms for Bentonite Suspensions

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Abstract – The paper presents the results of an experimental study considering the dependence of the surface tension of bentonite aqueous suspensions on the concentration of the solid phase and the time of the surface formation. To conduct experimental studies, a new technique has been developed, which allows leveling the influence of the sedimentation factor on the magnitude of the surface tension. A distinctive feature of the proposed technique is that these methods of measuring surface tension are used for the first time. In this method the process of sedimentation is multidirectional relative to the surface. The results obtained allowed us to determine that the resulting coagulation structures have a significant influence on the nature of changes in the surface tension of bentonite aqueous suspensions. It was established that the polydispersity of the solid phase and

water molecules in the dispersion medium play a key role in the formation of spatial structures and, as a consequence, in the formation of a minimum on the surface tension isotherms of bentonite suspensions.

Keywords – surface tension; bentonite suspension; sedimentation; disperse system; coagulation spatial structures; surface layer.

I. INTRODUCTION

In experimental studies of surface tension isotherms (σ) of multicomponent solutions, any features of this curve (minimum, maximum, inflection point) are usually associated

with the structural features of solutions (chemical compounds, formation of clusters, etc.) [1, 2]. The situation is quite different when studying σ suspensions of bentonite. Unlike solutions, suspensions contain solid particles, and, consequently, the solid-liquid interface, which makes it difficult both to conduct experimental studies and to interpret the data obtained.

The available data indicate that the dependence of the surface properties on the concentration of the solid phase in the dispersion medium is more complex. Thus, according to the data given in [3], with an increase in the concentration of the solid phase, there is not only a smooth change in properties, but with specific values of concentration determined for each system, features that are not characteristic of solutions are observed on σ isotherms. In this regard, the study of the surface properties of a suspension of bentonite lies in the field of scientific and practical interest.

II. THEORETICAL PART

It is known that the main factors affecting the surface and structural-mechanical properties of bentonites are: dispersion, nature of exchange cations, mineralogical composition [4,5]. At the same time, the effect of these factors on the surface properties of bentonite suspensions has not been fully studied until now.

Based on the analysis of the literature devoted to the study of the surface properties of bentonite suspensions, we can distinguish the hypothesis that the features on the σ isotherm are due to the transition of the dispersed system to a new qualitative state — to the appearance of coagulative spatial structures called critical structure formation concentration [6].

The formation of such structures as a result of direct adhesion of particles of dispersed phases or their adhesion through a layer of a liquid medium that is equilibrium in thickness, according to many authors [4, 5, 7], is accompanied by a significant change in the properties of disperse systems, first of all, they affect their rheological and surface properties .

It is known that coagulation structures are formed due to the relatively weak strength of the Van der Waals forces between the particles. Such contacts are made along the hydrophobic areas of the particle surface through the thinnest layers of the aqueous dispersion medium [8].

In addition, the formation of such structures contributes to the mosaic, heterogeneity of the surface, the presence of relatively hydrophobic sites (for polymers - hydrophobic chain sites) on the hydrophilized surface of the particles. At such sites, point contacts appear - the primary links of the structure [6–8].

According to the authors of [5, 8], the emergence of spatial structures is preceded by the formation of weak coagulation contacts with predominant fixation of interacting particles in the position of the far energy minimum (10^{-7} m) and adhesion force in contact (about 10–11 N).

A prerequisite for the formation of coagulation structures is the presence of particles of colloidal size (10^{-9} – 10^{-7} m), which can participate in thermal movement [6]. Real dispersed systems, in addition to particles of colloidal sizes, contain

fractions of coarse particles, the sizes of which may exceed the sizes of colloidal particles. Moreover, the proportion of colloidal particle sizes in such systems may only be a few percent of the total number of particles of the dispersed phase. In the process of Brownian motion of colloidal particles, they are evenly distributed in the total volume of the dispersed system, which, as a result of coagulation interaction with larger particles, form a spatial three-dimensional framework consisting of chains or aggregates. According to the authors of [6, 8], the probability of formation and the rate of formation of such structures, the higher, the greater the dispersion of colloidal particles, i.e. ability to participate in thermal Brownian motion. Another important factor is the presence of a coarse phase, anisometric particles and a hydrophobic-hydrophilic mosaic surface.

III. METHODS AND MATERIALS

The investigated samples of suspensions of bentonites were prepared in distilled water by the weight method. To achieve the optimum degree of dispersion and reduce the measurement error caused by sedimentation, the samples under study were transferred to a dispersion medium after thorough mechanical grinding and were stirred for 1–1.5 hours (magnetic stirrer, with slow heating). After that, the prepared samples are left for some time. As experience shows, to achieve stable values of measurement σ of bentonites, two days of solids in the dispersion medium are sufficient.

It is known that in suspension of bentonite, which is a polydisperse system, there are coarse particles in addition to particles of colloidal sizes. Consequently, the presence of a sedimentation process and the related dependence of σ on the time of formation of the drop surface can be attributed to the characteristic feature of such systems. Obviously, the instability, disequilibrium suspension and the resulting dependence of σ on the time of formation of the surface, significantly complicate the measurement of σ suspension. The question arises how to minimize the errors due to the time dependence of σ , and find the value of σ at the time of completion of the drop formation process. In our opinion, this problem can be solved if we use two independent methods for measuring σ .

The essence of the proposed method of measuring σ is that the measurement of σ of a suspension of bentonite is carried out on a DSA-100 installation in two independent ways: by the method of hanging and lying drop [9]. It is known that in the proposed methods, the process of sedimentation is multidirectional relative to the formed surface. As in the method of a hanging drop, this process is directed to the surface (surface enrichment with particles of the solid phase occurs), and in the method of a lying drop, on the contrary, from the surface (surface depletion of particles occurs). It is also known that during the transition of bentonite particles from the volume to the surface (the method of a hanging drop) there is a decrease in σ over time, whereas with the reverse process - the transition of particles from the surface into the volume phase, there is an increase in σ over time (lying drop method). Averaging the obtained results of measurements carried out by two methods, in which the time dependences of σ have different directions,

in our opinion, should lead to a significant decrease in the measurement error of σ .

IV. RESULTS

To test the effectiveness of the proposed technique, we studied the concentration dependence σ of a suspension of bentonites using the methods of hanging and lying drops for different time intervals of the formation (exposure) of a drop.

The experimental data obtained show that the values of σ depend significantly on both the measurement method and the time it takes for the drop to hold. In the hanging drop method, a decrease in σ with time is observed. In the method of a lying drop, the picture is opposite, that is, σ increases, and the minimum on the isotherms σ smoothes out, approaching the isotherms σ of the hood.

Since for small time intervals, σ linearly depends on the content of solid particles in the surface, the average value of σ should correspond to σ of the suspension in the initial state.

Therefore, we calculated the average values and constructed isotherms of averaged values of σ . The results are presented on Fig. 1.

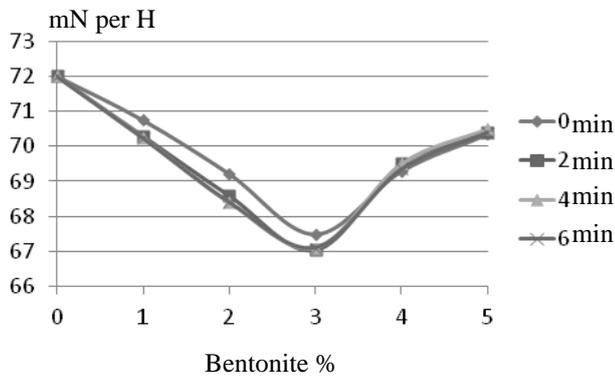


Fig. 1. The averaged values of the surface tension of suspensions of bentonite at 298 K

As can be seen from this figure, measuring σ by two methods (lying and hanging drop), and averaging the obtained values of σ , leads to a decrease in dissonance between the isotherms of σ . The obtained curves within the measurement error coincide. At the same time, the curves obtained at the time of formation of a drop are less than 2 minutes located slightly above the rest. The remaining curves (4 - 6 min.) practically merge.

Consequently, the developed method allows obtaining objective data on the concentration dependence σ of bentonite suspensions.

In addition, it becomes possible to study in more detail the mechanism of formation of spatial structures and the influence of the polydispersity factor of bentonite particles (particles of colloidal size and coarse particles) on the character of the isotherm σ .

For an experimental study of the effect of particle size on the σ value, bentonite suspensions were subjected to ultrasonic

dispersion. It is known that during ultrasonic action on a dispersed system, the main role in the process of grinding the solid phase is played by cavitation processes. Dispersion of solid particles is accompanied by hydromechanical and thermal destruction of their adsorption-solvate structures [1].

The study was subjected to suspensions of bentonites of 10 different concentrations. Ultrasonic impact on these samples was provided for 30 seconds. at a frequency of 35 kHz and power of 350 watts.

The obtained graphs on the particle size distribution [3] made it possible to establish that the ultrasonic treatment led to a significant decrease in the average particle sizes. Thus, for a sample of a suspension of bentonite containing 1% of the solid phase, the average size after ultrasonic dispersion of particles was about 700 nm, while for a sample with 3% of the solid phase, this value is about 300 nm.

Subsequently, in samples subjected to ultrasonic dispersion, σ was measured at various temperatures. The results are presented in Fig. 2.

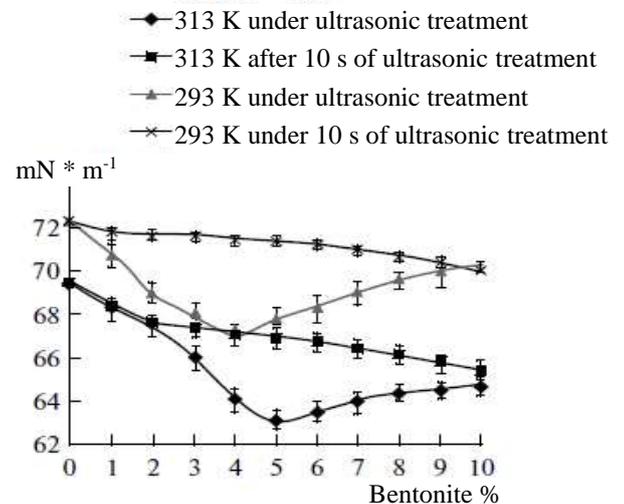


Fig. 2. Concentration dependence of the surface tension of bentonite suspensions before and after ultrasonic treatment (10 s)

As can be seen from Fig. 2, the minima on the isotherms of σ suspensions of bentonite, after ultrasonic treatment, practically disappear, which indicates that the particle sizes affect the character of the isotherms σ of suspensions of bentonite.

Based on the analysis of experimental data on the concentration and time dependence of σ suspensions of bentonites (Fig. 1.2) of varying degrees of dispersion, we can make an assumption about the possible influence of coagulation structures and their spatial orientation relative to the surface on the nature of isotherms σ of bentonite suspensions.

Consider the essence of this assumption. It is known that during the formation of an aqueous suspension of bentonite, in the process of spontaneous dispersion particles with a wide range of size distribution are formed - from coarse dispersed (10^{-4} - 10^{-6} m) to colloid (10^{-7} - 10^{-9} m) [10].

Since particles of colloidal sizes can participate in thermal motion, accumulate at the phase boundaries and possess kinetic stability, from the system's desire to minimize free energy, some of the colloidal particles can transfer from the volume to the surface layer. Experimental confirmation of this process can be considered as a decrease in σ up to a concentration of up to 3-4% of the mass of the solid phase of bentonite observed on the isotherms of the surface tension [3].

In our opinion, with an increase in the concentration of the solid phase in suspensions of bentonites, there is an increase in the fraction of the area occupied by particles and at a certain concentration (3-5%) the surface is saturated with them. This saturation of the surface layer corresponds to a minimum on the surface tension isotherm.

With a further increase in the concentration of the solid phase in a suspension of bentonite, colloidal particles, due to weak coagulation contacts made through a layer of water, begin to form with larger particles a spatial framework consisting of aggregates. A further increase in the number and strength of such contacts in the surface leads to the formation of increasingly large aggregates and their coagulation. This leads to partial or complete loss of the kinetic stability of the largest aggregates and their transition from surface to volume.

Such a structural rearrangement leads to an increase in the anisotropy of the surface of the suspension, its mosaicity, which is accompanied by an increase in the proportion of water molecules in the surface layer and an increase in σ of the suspension of bentonite. On the isotherms σ , the beginning of this process corresponds to a section of 3-4% of the mass of the solid phase of a suspension of bentonite, where an increase in σ with an increase in the content of the solid phase is observed [3].

The proposed hypothesis is confirmed by numerous experimental data indicating that with a decrease in the number of coarse phase in a dispersed system, as a result of ultrasonic or thermal dispersion, there is a decrease in the minimum depth up to complete disappearance.

The presence of coagulation contacts in the dispersion and their influence on the formation of these structures is also confirmed by our studies of the dependence of σ on the concentration of the solid phase of bentonite in binary dispersion media (water - ethanol; water - glycerin). It has been established that even an insignificant increase in the fraction of the organic component in the dispersion medium (ethanol, glycerin) leads to an almost complete disappearance of the minimum on the σ isotherms. These data show that a decrease in the proportion of water that is a conductor of electrostatic interactions between two contacting particles (unlike organic substances) leads to a decrease in the strength and number of weak coagulation contacts and, as a result, to the attenuation of structure formation processes in a dispersed system.

V. CONCLUSION

The results obtained by averaging the value of σ measured by two independent methods (Fig. 2) indicate a decrease in dissonance between the isotherms of σ obtained at different

times of surface formation, which confirms the effectiveness of the proposed technique.

The observed decrease or complete smoothing of the minimum on the σ isotherms after dispersion of the particles of the solid phase suggests that coarse particles play an important role in the formation of spatial structures in the suspension of bentonite. More precisely, during the formation of spatial structures, coarse particles play the role of "structure formation centers", around which, due to weak coagulation contacts, particles of colloidal sizes can form spatial structures through a layer of water.

The presence of coagulation contacts in the dispersion and their influence on the formation of these structures is confirmed by our studies of the dependence of σ on the concentration of the solid phase of bentonite in binary dispersion media (water – ethanol; water – glycerin). Studies have shown that even a slight increase in the proportion of the organic component in the dispersion medium (ethanol, glycerin) leads to the almost complete disappearance of the minimum on the σ isotherms.

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