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Abstract

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ON THE JOINT ADSORPTION OF POLYACRYLAMIDE AND A CATION-ACTIVE HYDROPHOBIZING AGENT ON THE SURFACE OF KAOLIN

To elucidate the mechanism of action of additives of a polymeric structure-forming agent—coagulant—using polyacrylamide (PAA) together with a surface-active hydrophobizing agent in the strengthening of clayey soils, their adsorption by the surface of the clay constituent of the soil was investigated. Adsorption was determined by measuring the surface tension (σ) at the air interface by the platinum-ring detachment method for aqueous solutions of the cation-active substance (CAV) (cetyltrimethylammonium bromide) in the presence of PAA before and after adsorption on enriched Prosyanov kaolin with specific surface area $S_{\text{ud}} = 19\ \text{m}^2 \cdot \text{g}^{-1}$ (from methylene-blue adsorption (^{1})). It was found that increasing the PAA concentration in the system decreases the adsorption of CAV (Fig. 1).

[Figure 1 and Figure 2]

Fig. 1. 1 –σ of aqueous CAV solutions in the absence of PAA; 2-7 –σ of aqueous solutions added to kaolin with formation of a 5% suspension, as a function of the concentration of PAA in them: 2 –0.05% PAA; 3 –0.03% PAA; 4 –0.02% PAA; 5 –0.01% PAA; 6 –0.005% PAA; 7 –without PAA

Fig. 2. Volumes of precipitates of Prosyanov kaolin in a 5% suspension as a function of the CAV concentration

The investigations were carried out on a 5% aqueous suspension of kaolin; measurements were made one day after preparation of the systems under study.

The PAA used was synthesized at the Research Institute of Halurgy (Leningrad). The molecular weight of this substance, calculated from the number of amine and carboxyl groups ([2]), is 33000. The concentrations of the aqueous PAA solution were taken in the range 0.005–0.05%. Its maximum adsorption on Prosyanov kaolin, according to measurements on an ITR-2 laboratory interferometer for liquids, is $\sim 2.2\text{–}2.4 \cdot 10^{-3}$ g · g^{-1}, and on Turbov kaolin ($S_{\text{ud}} = 34.6$ m$^2 \cdot$ g^{-1}) $\sim 4 \cdot 10^{-3}$ g · g^{-1}. The minimum concentration of PAA solution corresponding to maximum adsorption on Prosyanov kaolin is $\sim 0.02\%$, and on Turbov kaolin, respectively, $\sim 0.04\%$. According to literature data ([3,4]), hydrogen bonds arise between the adsorbed PAA molecules and kaolinite.

The concentrations of CAA solutions were chosen taking into account the adsorption of CAA by kaolin and the different degrees to which it fills the surface of the clay particles in the interval from 0.005 to 0.1% (5). Thus, concentrations of the CAA solution $< 0.075\%$ corresponded to partial chemisorption filling of the surface of kaolin particles in the absence of PAA. Higher concentrations of the CAA solution corresponded to filling with a second, physically adsorbed layer with the reverse orientation of the molecules, of the micelle-formation type. The degrees of filling of the surface of clay particles are shown on the curve of the dependence of the magnitude of the volumes of precipitates (V) of a 5% kaolin suspension on the concentration of CAA (Fig. 2), where the minimum between two maxima falls precisely at the concentration ($\sim 0.075\%$) at which the surface of the clay particles is completely covered by a chemisorbed layer of CAA molecules.

Table 1

[PAA], %	[CAA], %	σ of mixtures of PAA and CAA solutions, erg/cm^2: before adsorption	σ of mixtures of PAA and CAA solutions, erg/cm^2: after adsorption
0.005–0.1	0	73.0	–
0	0.050	38.0	–
0.020	0.050	38.3*	–
0.050	0.050	38.3*	–
0.075	0.050	39.5*	–
0.050	0.075	37.5*	–
0.0050	0.05	–	48.5
0.0100	0.05	–	39.5
0.0200	0.05	–	38.5
0.0375	0.05	–	39.5
0.0500	0.05	–	38.5
0.0750	0.05	–	38.5
0.005–0.1	0	–	73
0.05	0.030	–	73
0.05	0.050	–	73
0.05	0.075	–	66

[PAA], %	[CAA], %	σ of mixtures of PAA and CAA solutions, erg/cm^2: before adsorption	σ of mixtures of PAA and CAA solutions, erg/cm^2: after adsorption
0.05	0.100	–	58

* The solutions become turbid on mixing.

In Fig. 1 are given the dependences of the surface tension on the concentration (C), $\sigma = f(C_{\text{CAA}})$, before adsorption (curve 1) and after adsorption (curve 7) on kaolin. At $C_{\text{CAA}} > 0.075\%$, a sharp drop begins in curve 7, $\sigma = f(C_{\text{CAA}})$, which corresponds to the beginning of filling of the kaolin surface by a physically adsorbed second layer of CAA molecules; and in Fig. 2 this phenomenon is accompanied by the appearance of a second maximum on the curve $V = f(C_{\text{CAA}})$.

In determining σ of PAA solutions before and after adsorption, it was confirmed that PAA does not change the magnitude of the surface tension of the solutions.

When σ of mixtures of PAA and CAA solutions before adsorption was measured, it was shown that the presence of PAA does not affect the value of σ (Table 1), but the mixture of solutions becomes turbid, apparently as a result of the formation of a PAA coacervate. The introduction of PAA solutions of various concentrations into a kaolin suspension 1 day before introducing the CAA solution prevents adsorption of CAA, and σ of the solutions (when their PAA content is $\gtrsim 0.02\%$), after their interaction with clay, proves to be very close to σ of the initial CAA solutions (curve 1, Fig. 1). In the case of small amounts of PAA, when part of the surface of the clay particles still remains unoccupied, adsorption of CAA takes place, and σ of the solutions correspondingly becomes higher (Table 1).

Conversely, if CAA is first introduced into the kaolin suspension, at a concentration that will correspond to the first, chemisorbed layer ($C \lesssim 0.075\%$) (Fig. 1, curve 7 and Fig. 2), and then (after 1 day) PAA solutions at any concentrations are introduced, then σ of the solutions after their interaction with the clay proves to be very close to σ of water, i.e., the CAA remains adsorbed on the surface of the clay particles. If, however, the initial CAA concentration is above 0.075%, then σ of the solutions in the presence of PAA proves to be approximately equal to σ of CAA solutions of the corresponding concentration after its adsorption in the absence of PAA (Table 1). Thus, it has been shown experimentally that addition of PAA to a suspension of previously hydrophobized kaolin does not displace the adsorbed CAA.

With simultaneous treatment of kaolin with PAA and CAA solutions at various concentrations, filling of the surface of the kaolin particles depends on the initial concentrations of PAA and CAA. The principal role in this, apparently, is played by the kinetics of adsorption. The greater rate of physical adthe sorption of PAA, as compared with the slower process of chemisorption of the CAS, determines predominantly the adsorption of PAA. From a comparison of the curves in Fig. 1, one can calculate the amount of CAS adsorbed simultaneously with PAA. The adsorption at point A of curve 2 in Fig. 1, for example, is 0.0016 $\text{g} \cdot \text{g}^{-1}$, at point B of curve 3 it is 0.002 $\text{g} \cdot \text{g}^{-1}$, and at point C of curve 6 it is 0.005 $\text{g} \cdot \text{g}^{-1}$; i.e., with a decrease in the PAA concentration in the system the amount of adsorbed CAS increases. At $C_{\text{PAA}} \approx 0.02\%$, the entire free surface of the kaolin particles could be completely occupied by adsorbed PAA molecules, but, despite this, adsorption of CAS molecules takes place (Fig. 1, curves 2, 3, 4). This is explained by the fact that the large PAA molecules, which are a coagulant, when adsorbed on the surface of clay particles, form loose aggregates whose pore sizes may hinder the penetration of PAA molecules, but do not prevent the adsorption of the comparatively small CAS molecules on the remaining unoccupied surface of the clay particles. Therefore, in PAA solutions whose initial concentration is $\approx 0.02\%$, CAS adsorption still occurs during simultaneous treatment of kaolin with PAA and CAS. If, however, preliminary treatment with PAA was carried out with additional stirring or drying, CAS adsorption practically did not occur during the period studied (1 day).

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