PROCESSES OF STRUCTURE FORMATION IN AQUEOUS SUSPENSIONS OF QUARTZ IN CONNECTION WITH THE FEATURES OF FORMATION OF THE ADSORPTION LAYER OF A LONG-CHAIN SURFACE-ACTIVE MODIFIER

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Figure 1

Figure 1: Figure 1

Abstract

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PROCESSES OF STRUCTURE FORMATION IN AQUEOUS SUSPENSIONS OF QUARTZ IN CONNECTION WITH THE FEATURES OF FORMATION OF THE ADSORPTION LAYER OF A LONG-CHAIN SURFACE-ACTIVE MODIFIER

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A number of studies have shown (1–6) that adsorption modification of the surface of filler and pigment particles facilitates the processing of their technological dispersions and improves the quality of the filled and pigmented materials obtained. Therefore the problem of elucidating the regularities of formation of the adsorption layer and their connection with processes of structure formation acquires great significance. Many particular questions of this general problem can be solved by comparing the results of adsorption and structural-mechanical studies (7–9).

In the present work we studied freely sedimenting concentrated suspensions of quartz in aqueous solutions of cetyldimethylbenzylammonium chloride (CDMBAC), $CH_3(CH_2)_{15}C_6H_5CH_2(CH_3)_2NCl$. The adsorption of the surface-active modifier, the specific volume, and the strength (yield shear stress) of the structured quartz sediment were determined. The concentration of the surface-active substance (SAS) was measured with an interferometer; the yield shear stress was measured by the method of tangential displacement of a plate (10).

Fig. 1. Adsorption isotherm (A) of cetyldimethylbenzylammonium chloride (CDMBAC) on quartz from an aqueous medium; C –equilibrium concentration; light points were obtained during adsorption, dark points during desorption.

As can be seen from Fig. 1, the adsorption isotherm of CDMBAC at an equilibrium concentration equal to zero rises vertically upward, which corresponds

Fig. 2

Figure 2: Fig. 2

to chemical, irreversible binding of the entire amount of introduced SAS on the most active areas of the quartz surface. Subsequent uptake of the SAS proves to be reversible, as is evidenced by the good coincidence of the positions of the adsorption and desorption points. At high concentrations ($C > 500$ μmol/l) complete saturation of the surface is observed.

In an aqueous medium, in the presence of chemisorption, the adsorption layer of long-chain SAS in the saturated state consists of two oppositely oriented layers. In the first layer the adsorbed molecules have their polar groups turned toward the surface of the solid particles and their hydrocarbon chains outward, toward the medium; in the second layer, the reverse is true. This is naturally reflected in the conditions of coagulation and in the sedimentation volumes of the sediment V_1 (cm^3/g).

As can be seen from the course of curve 1 in Fig. 2, as A increases the volumes of the sediments increase. This is understandable, since adsorption of the SAS, as a result of hydrophobization of the surface, sharply reduces the aggregative stability of the system; the suspension coagulates more intensely, the aggregates of particles become looser, and flocs are formed. The cessation of growth and the decrease in

sedimentation volumes with a further increase in adsorption is due to the renewed stabilization of the suspension owing to the formation of a second, oppositely oriented adsorption layer with polar groups toward the aqueous medium ([11]). The second layer, which is reversibly adsorbed, is easily washed off. Dilution of such a secondarily stabilized suspension with water, after repeated mixing, leads to a sharp increase in the sedimentation volume (shown by the arrow and the shaded point in Fig. 2). Conversely, at low concentrations of the surfactant, when the second layer has not yet formed on the particle surface, dilution of the suspension has no effect on its volume. This is explained by the fact that the strong chemisorption bonding of the surfactant in the first layer ensures the constancy of the degree of coverage and hydrophobization of the surface achieved during modification, which does not change upon dilution.

Fig. 2. Limiting shear stress (1) and specific sedimentation volume (2) of sediments of concentrated quartz suspensions in water as a function of the degree of modification of its surface—the magnitude of adsorption (A) of CDMBAC.

In accordance with this, the largest sedimentation volume of the precipitate, corresponding to the greatest degree of surface hydrophobization, should, it would seem, arise upon saturation of the first monolayer, or at half the adsorption value. However, comparison of the course of the change in the volume of the precipitate with the magnitude of surfactant adsorption (Fig. 2, curve 1) shows that the largest volume corresponds to $A = 0.85$ μmol/g, or 1/4 of the limiting adsorption value $A_m = 3.5$ μmol/g (Fig. 1). When adsorption is increased above 0.85 μmol/g, the volumes decrease and, consequently, the surface becomes hydrophilized rather than hydrophobized, as might have been expected. Thus, the greatest hydrophobicity is observed at half filling of the first monolayer.

This somewhat unexpected result can be explained if, in considering the process of adsorption filling of the surface of quartz particles, one takes into account its macroheterogeneous structure, the existence of which is indicated by the results of a number of studies ([12]-[15]). The significance of such heterogeneities has already been noted earlier ([7]-[9]).

In studying the adsorption modification of quartz with the aid of long-chain amines and the structure formation of its suspensions in oil ([7]-[9]), it was found that the results obtained can be explained only on the assumption of a macromosaic structure of the adsorption layer. Such a structure is due to the dual nature ([15]-[17], [8]) and the nonuniform distribution of active centers on the surface of ground crystalline quartz and, consequently, to the dual nature of the adsorption process ([9], [8]). Amines from solution in xylene, as well as from the gas phase ([18], [19]), are adsorbed on quartz partly by chemisorption and partly through the action of weak physical bonds. Upon saturation of the chemisorption-active regions on the surface, a lyophobic-lyophilic macromosaic arises. Quartz particles with such an optimally modified surface, during structuring of the suspension, interact with one another either through lyophobic or through lyophilic areas. In the first case strong bonds arise between them, and in the second—weak ones. The probability of encounter and adhesion of particles through one or another set of areas, depending on the degree of surface modification and the structure of the adsorption layer, determines the proportion of lyophobic, strong bonds arising per unit volume of the structur—

of the system and, consequently, determines its mechanical properties. The presence of such energetic heterogeneity and of special chemisorption-active regions on the quartz surface must undoubtedly play a definite role in the processes of formation of the adsorption layer and in the processes of structuring of quartz suspensions in an aqueous medium.

In water, just as in xylene, at the initial stage of adsorption modification the chemisorption-active regions of the surface are filled and saturated. The surface becomes increasingly hydrophobic, and the system increasingly less stable. The volumes of the sediments increase. After complete saturation of the most active regions of the surface has occurred (Fig. 3a) and the lyophobic-lyophilic macromosaic has developed (20), further adsorption proceeds not only on free surface areas not yet occupied by tetraalkylammonium ions, but also on modified, hydrophobized areas, and on the latter, probably, more intensively (Fig. 3c). This is indicated by comparison of the critical concentration of micelle formation in the solution, 170 μmol/l, determined from pinacyanol chloride, with the results of adsorption measurements (Fig. 1). Individual regions of the partially formed double adsorption layer may be regarded as a kind of surface micelles. Since the mobility of the molecules adsorbed in the first layer is greatly reduced, such

Fig. 3. Diagram of the formation of the adsorption layer on the macroheterogeneous surface of ground quartz particles in water (a, c, d) and xylene (a, b), and of the formation of a lyophobic-lyophilic macromosaic. The black areas denote chemisorption-active regions of the quartz surface.

Figure 3: Fig. 3. Diagram of the formation of the adsorption layer on the macroheterogeneous surface of ground quartz particles in water (a, c, d) and xylene (a, b), and of the formation of a lyophobic-lyophilic macromosaic. The black areas denote chemisorption-active regions of the quartz surface.

surface micelle formation (local formation of a double layer) should begin at concentrations much lower than 170 μmol/l. At an equilibrium concentration of 170 μmol/l, in accordance with the adsorption isotherm (Fig. 1), approximately half of the amount of CDMBAC that is ultimately adsorbed in the form of a bimolecular layer at concentrations above 500 μmol/l is retained on the quartz surface. This means that at concentrations much lower than 170 μmol/l, i.e., the concentrations necessary for surface micelle formation, the amount of adsorbed substance will be substantially less than that required to fill the surface with a monolayer. Thus, adsorption on already modified regions and, consequently, the formation of the second layer actually begins before formation of the first monolayer has ended (Fig. 3c). Hence, in the present case, in the adsorption process, owing to surface micelle formation, there is no separate isolated stage of complete saturation only of the monomolecular layer, as occurs in xylene (Fig. 3b). This sequence of adsorption is connected with the fact that, in water, the interaction between the hydrocarbon chains of the molecules and already hydrophobized regions is far more favorable than the weak interaction of the hydrophilic groups of the surfactant with the weakly active regions of the quartz surface. This also explains why, after the chemisorption-active regions have been filled (at $A \approx 0.85$ μmol/g), hydrophobization is not observed, but rather hydrophilization of the surface; the system becomes increasingly stabilized, and the sedimentation volume decreases. Upon complete saturation of the surface with formation of a double adsorption layer (Fig. 3d), the particles are again extremely hydrophilized and stabilized, and the sediment volume is the smallest (Fig. 2, curve 1).

Fig. 3. Diagram of the formation of the adsorption layer on the macroheterogeneous surface of particles of ground quartz in water (a, c, d) and xylene (a, b) and the formation of a lyophobic-lyophilic macromosaic. The black areas denote chemisorption-active regions of the quartz surface.

The greatest development of the lyophobic-lyophilic macromosaic, both upon adsorption of an ammonium-base salt from water and upon adsorption of alkylamines from xylene, corresponds to one and the same half coverage of the surface, which indicates a certain commonality in the nature of adsorption in the two systems.

In considering the proposed mechanism of surface filling, it should be noted that it allows for different sequences in the formation of a complete double adsorption layer. After the appearance on the surface of a lyophobic-lyophilic macromosaic, under conditions of simultaneous adsorption of surfactant on hydrophobized regions of the surface and on regions that still remain hydrophilic, the process of hydrophilization (Fig. 3b) may be replaced by a process of surface hydrophobization as a result of a slowing of the process of surface micelle formation and a sufficiently high intensity of adsorption on the free surface. This will be reflected in the curve of volumes $V_1(A)$, on which a second maximum may appear. In the present case it was not observed; however, recently (21) such an effect was recorded in the study of suspensions of kaolin and bentonite.

In a nonpolar hydrocarbon medium, double adsorption layers of the type considered are not formed; a continuously increasing lyophilization of the surface is observed (Fig. 3b).

The results of measuring the strength (limiting shear stress) of quartz sediments are given in Fig. 2 in the form of the curve ($P_m(A)$), which is strictly opposite to the curve $V_1(A)$. The opposite character of these curves indicates the strong influence on the strength of the system of its structural density (22); it masks the influence on the strength of the change in the distances between the surfaces of solid particles at their points of contact. Nevertheless, the influence of modifying the quartz surface and changing its nature on the strength of individual contacts and of the entire system as a whole is clearly manifested here as well. Thus, despite the fact that the volumes of sediments formed by unmodified and maximally modified quartz are practically equal, the strength in the first case is 20 times higher than in the second. This directly indicates a sharp weakening of the bonds at contacts between particles with a maximally modified surface. Such weakening is apparently due to an increase in the distances between the contacting particles and is associated with significant solvation of the polar groups of the modifier molecules facing the medium, which are located in the second layer.

At the same time, the position of the minimum on the curve $P_m(A)$ corresponds to an adsorption value of 0.85 μmol/g, which confirms the features of the volume measurements and their connection with the structure of the adsorption layer.

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Note: Figure translations are in progress. See original paper for figures.