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ON THE MECHANISM OF THE EMULSIFYING ACTION OF SOLID EMULSIFIERS

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According to current ideas on the mechanism of emulsification of liquids by solid emulsifiers (1), the type of emulsion (O/W or W/O) and its stability are determined by the conditions of selective wetting of highly dispersed solid particles by the liquid phases forming the emulsion.

The heterogeneity of individual regions of the solid surface (mosaic character) leads to their different wettability and thereby creates the possibility of particles adhering to the surface of droplets. This presupposes that stable emulsification can be achieved by the formation of a single-particle outer layer armoring the droplets, and that the physicochemical heterogeneity of the particle surface is expressed so sharply that it ensures simultaneous partial wetting of it by both phases.

The results given below for the emulsification of a hydrocarbon oil in aqueous suspensions of bentonite clay—the most widely used solid emulsifier—show that these ideas are insufficient for interpreting the mechanism of the phenomena underlying the formation of highly stable O/W emulsions with the participation of highly dispersed powders.

Bentonite clay activated by additions of electrolytes ($FeCl_3$, $Al_2(SO_4)_3$, etc.) was previously used by us (2) as an accessible and effective emulsifier for cleaning oil-tanker vessels of viscous petroleum products (fuel oils) by converting them into low-viscosity flowing emulsions. The experiments described in the present work also make it possible to explain the essence of such activation of bentonite by electrolytes and to provide a physicochemical substantiation of the method of emulsifying petroleum products with the aid of solid emulsifiers.

We determined the stability of emulsions formed by vigorous mechanical shaking, and the structural-mechanical properties of interfacial layers as a function of the content of solid emulsifier at a constant ratio of the volumes of the liquid phases (water : oil—1 : 1) and of the presence in the system of organic additives (oleic acid in the oil phase) and electrolytes ($AlCl_3$ in the aqueous phase).

The objects of investigation were vaseline (medicinal) oil and carbon tetrachloride, thoroughly purified of traces of polar impurities with the aid of silica gel, and bentonite clay from the Oglandy deposit (Turkmen SSR) (3) in the form of

Figure 1

Figure 1: Figure 1

suspensions of various concentrations (up to 6%), obtained by prolonged aging of the clay in water until complete peptization. Since the pH of these suspensions lies in the range 7.5-9.5, during the formation of emulsions oleic acid, as it was neutralized, passed from the oil phase into the aqueous phase in the form of sodium oleate. The stability of the emulsions was estimated from the time (τ) of partial destruction after formation and the separation of 50% of the oil in the free state. Since, however, along with emulsions that broke down relatively rapidly (τ did not exceed several hours), emulsions with practically infinite stability ($\tau \gg$ 2-3 days) were formed, in what follows as stable

emulsions are those in which no separation of free oil occurred at all over 48 hours (marked in Fig. 1, 2 by the symbol ∞). The structural-mechanical properties of the surface layers were measured with a simple torsion device at the interface CCl_4—water in the presence of a solid phase, which was deposited from the upper aqueous medium in an amount practically corresponding to the thickness of the bentonite layer on the emulsion droplets.

The measurement results show first of all that, with pure vaseline oil, stable emulsions can be obtained only at a comparatively high concentration (4%) of bentonite in the aqueous medium (Fig. 1, curve 1), which already corresponds to the formation of a coagulation structure throughout the entire volume ([4]). When the concentration of the emulsifier is lowered, the stability of the emulsions falls so sharply that, evidently, not only a monolayer directly bound to the surface of the droplets by wetting forces, but also a considerably thicker layer is unable to form any stable emulsion because of the insufficient strength of the spatial structure in the volume of the aqueous medium.

Introduction of oleic acid into the oil sharply changes the emulsification conditions, since the sodium oleate formed on the surface of the droplets, passing into the aqueous phase, hydrophobizes the particles as a result of chemoadsorption (for example, on calcium sites of the surface)*.

Fig. 1. Dependence of the stability of emulsions (τ, min.) on the content in the system of bentonite, oleic acid, and $AlCl_3$. **1** —emulsions of pure oil; **2—5** —oil emulsions containing, respectively, 0.001; 0.01; 0.1 and 1% oleic acid; **6** —emulsions of pure oil in 0.01 N aqueous $AlCl_4$ solution; **7** —emulsions of oil containing 0.1% oleic acid, in 0.01 N aqueous $ClCl_3$ solution.

The effect of such a change in the properties of the solid surface manifests itself differently, depending on the bentonite content. When coagulation structures of bentonite arise in the aqueous medium, at its content $> 4\%$, hydrophobization weakens the strength of the emulsions ([5]), and the more strongly so, the higher the concentration of oleic acid (curves 2—4). As a result, the stability of the emulsions falls so significantly that they either do not form at all, or unstable

Fig. 2

Figure 2: Fig. 2

emulsions of the reverse type (W/O) arise, owing to stabilization of the water droplets by oleophilized bentonite particles that have passed into the oil phase.

A further increase in the acid concentration to 1% leads already to another result: the stability of the emulsions increases sharply (curve 5) owing to the stabilizing action of sodium oleate, which is not bound in chemoadsorption layers on the solid surface, is formed in excess in the aqueous phase, and ensures the stability of the emulsions independently of the presence of a solid dispersed phase. This makes it easy to explain why many authors (6) were able to obtain stable emulsions of technical oils, using 1% suspensions of bentonite clay, which, as is clear from what was said above, cannot be obtained with pure or slightly contaminated oils.

In the region of low concentrations of bentonite suspensions (below 1%), in which structuring in the aqueous phase practically does not occur, modification of the surface by adsorption layers has a different effect, since under these conditions the influence of another stabilizing factor may appear—the forces of wetting (adhesion) of the first monomolecular layer of emulsifier particles to the surface of separation. This is seen from the course of curves 1-4 in the left-hand part of Fig. 1. Comparison of curve 1 and curves 2-4, which exhibit sharply expressed maxima, shows that as hydrophobization is intensified and, consequently, as the strength of adhesion of the particles increases, the stability of the emulsions increases, and the optimum of emulsification corresponds to complete coverage of the surface of the droplets by a monomolecular layer. Before the maxima (at bentonite concentrations lower than 0.05-0.1%) there is not enough solid phase for this; above the maxima, "over-wetting" of the particle surface begins to manifest itself, owing to the increase in the concentration of sodium oleate in the aqueous phase due to the rise in pH.

Fig. 2. Surface viscosity of interfacial layers (η_s, surface poises) and stability (τ, min) of emulsions. 1 $-\eta_s$ at the boundary CCl_4 + 0.1% oleic acid—aqueous 0.01 N solution of $AlCl_3$ in the presence of bentonite; 2 $-\tau$ of CCl_4 emulsions containing 0.1% oleic acid in aqueous 0.01 N $AlCl_3$ solution; 3 $-\eta_s$ at the boundary CCl_4—water in the presence of bentonite; 4 $-\tau$ of CCl_4 emulsions in water.

At the same time, the magnitude of the maxima shows that, owing to the increase in the mosaic character of the particle surface as a result of its partial hydrophobization and adhesion of a monomolecular layer to the oil droplets,

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* Hydrophobization of the surface may also occur as a result of its direct adsorption interaction with oleic acid when the particles come into contact with the droplet surface.

obtaining stable emulsions is not possible.

The effect of electrolyte additions on the stability of emulsions manifests itself in a sharply different manner depending on the presence of a fatty acid in the oil. Introduction of $AlCl_3$ into an emulsion of a pure oil, despite the strong coagulation of bentonite particles caused by adsorption of the potential-determining Al^{3+} ion, which increases the mosaic character of their surface, not only does not promote an increase in emulsion stability, as might have been expected, but, on the contrary, greatly lowers it (curve 6). The same addition of electrolyte during emulsification of an oil containing 0.1% oleic acid produces the effect of an exceptionally sharp increase in stability, characterized by curve 7. Similar results are given by the ions Fe, Cu, Co, Zn, Th, and others.

As can be seen, under these conditions a stable emulsion is formed at a bentonite content two orders of magnitude lower than in the absence of electrolyte and fatty acid. This amount of emulsifier corresponds to coverage of the emulsion droplets by a layer approximately one particle thick.

The stabilizing factor in this case is a structural-mechanical barrier—the structuring of the adsorption layers of soaps of polyvalent metals.

It should be noted that this effect of strong stabilization of emulsions arises only in a strictly definite range of pH of the aqueous phase, in which the formation is possible of incompletely substituted metallic soaps of a basic character (7), whose monomolecular adsorption layers possess increased strength.

How strongly the mechanical properties of these layers are expressed is seen from Fig. 2, which presents: curve 1—the viscosity of adsorption layers of aluminum oleate formed at the interface CCl_4 + 0.1% oleic acid—water + 0.01 N $AlCl_3$ in the presence of a bentonite layer, and the corresponding curve 2—the stability in water of CCl_4 emulsions obtained with the same content of the indicated components in them. For comparison, the corresponding data characterizing the behavior of the same systems, but in the absence of oleic acid and $AlCl_3$ (curves 3 and 4), are also given here.

It follows from the foregoing that stable emulsions (O/W) of pure oils can be obtained only on condition that bentonite forms a bulk coagulation structure in the aqueous phase, while a monolayer of a solid emulsifier can stabilize emulsions only in combination with the formation in the surface layer of structured metallic soaps of a basic character. It is important to note here that "hydrophobic" (oleophilic) emulsifiers (metallic soaps), which usually stabilize only emulsions of the reverse type, in the presence of a monolayer of a solid phase of hydrophilic character can, on the contrary, strengthen emulsions of the direct type. This shows that the influence of the mechanical properties of the emulsifier film predominates over the influence of another stabilizing factor—wetting—which, thus, apparently plays a subordinate role and cannot by itself ensure the formation of highly stable emulsions.

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