PHYSICAL CHEMISTRY

A. B. TAUBMAN and A. F. KORETSKII

1961

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

A. B. TAUBMAN and A. F. KORETSKII

ON THE DISPERSITY AND STABILITY OF EMULSIONS STABILIZED BY SOLID EMULSIFIERS

(Presented by Academician P. A. Rehbinder on 12 V 1961)

The stability of emulsions of the O/W type, stabilized by highly dispersed particles of solids, in many cases proves to be considerably higher than when they are stabilized by adsorption layers of surface-active substances (^1). This is associated with the great mechanical strength of the interfacial protective layers of particles, which are formed as an independent surface phase at the water-oil interface. At the same time, as we have shown, there is a direct correspondence between the strength of these layers and the stability of emulsions ([1],2).

At the same time, the view is generally accepted that a high dispersity of solid emulsifiers is one of the necessary conditions for their effective action, with an optimum particle size on the order of 1-10 μ ([3],4). However, the data obtained by us show that this dependence does not always hold and that, in the stabilizing action of solid emulsifiers, the decisive importance belongs not to their dispersity but to the structural-mechanical properties of the protective interfacial layers formed by them.

To measure the strength of the structure of these layers (the limiting two-dimensional shear stress P_m), we used the standard SNS-2 apparatus intended for the study of clayey solutions (suspensions), which, after modification and improvement carried out by us, can be used as a simple universal instrument suitable for measuring the structural-mechanical properties both of surface layers and of emulsion systems in bulk (^1). In the first case, the coaxial metal cylinders of the apparatus are replaced by a glass disk (30 mm in diameter and 4 mm thick), suspended on an elastic tungsten thread in such a position that its contour intersects the interface between the liquid phases forming the emulsion and contained in a glass crystallizing vessel. At a constant, low deformation rate, produced by rotation of this vessel (at a speed of 0.2 rev/min), the change in torque (M dyn · cm) and, consequently, in the two-dimensional shear stress (P dyn · cm^{-1}) of the undisturbed structure with time (τ_k) was determined, up to its destruction at $P = P_m$, corresponding to the sharply expressed maximum of the P–τ_k curve ([5]-7). The displacement of the disk (the angle of twisting of the thread) was measured optically.

Fig. 1

Figure 1: Fig. 1

The value of P_m was calculated from the formula

$$P_m = \frac{M}{2\pi R^2} = \frac{C_0 \theta_m^0}{360 R^2} = \frac{C_0 S_m}{360 R^2 n} \text{ (dyn} \cdot \text{cm}^{-1}\text{)},$$

where R is the radius of the disk, C_0 is the torsion constant of the thread, θ_m^0 and S_m are the angle of twisting of the thread, expressed respectively in degrees and in centimeters on the reading scale, and n is the conversion factor relating θ_m^0 and S_m. For the threads used by us, 25-30 cm long and 0.05-0.2 mm in diameter, the values of C_0 varied in the range 5-1000 dyn • cm • rad^{-1}.

When the metal cylinders were replaced by glass ones with a ribbed surface,* the apparatus was used to measure the shear stress in the bulk of concentrated, highly stable emulsions stabilized by solid emulsifiers.

Protective layers of solid particles were formed at the water-carbon tetrachloride interface by depositing them from the upper phase—an aqueous suspension—in an amount which, according to calculation, corresponded to the thickness of the emulsifier layer on the emulsion droplets. The emulsions were obtained by shaking cylinders containing both phases (at a volume ratio of $1:1$), the aqueous suspension of the emulsifier, and vaseline oil (or CCl_4), carefully purified from polar impurities. Their stability was assessed from the time (τ) of spontaneous breakdown with separation, in the free state, of half the volume of oil (at values $\tau > 50$ h, the emulsions were conventionally regarded as infinitely stable ($\tau = \tau_\infty$)).

The dispersity of the emulsifier particles ($D = 2r$) was characterized by the content of the main fraction (as a percentage of the total number of particles) corresponding to the maximum of the size-distribution curve. The following mineral powders served as emulsifiers: 1) precipitated calcium carbonate ($D(70\%) < 3\,\mu$); 2) Oglanly bentonite ($D(80\%) \ll 1\,\mu$); 3) aluminum oxide ($D(85\%) \simeq 6$—$40\,\mu$); 4) two samples of crushed glass, differing in dispersity, with particles $D(80\%) < 3\,\mu$ and $D(75\%) \simeq 100\,\mu$.

Confirmation of the above conclusion regarding the ambiguous relationship between emulsion stability and the dispersity of the particles of a solid emulsifier is provided by the data presented in Fig. 1.

Fig. 1. Dependence of the emulsifying ability of solid emulsifiers on their dispersity.
1—precipitated calcium carbonate ($D < 3\,\mu$); 2—Oglanly bentonite ($D \ll 1\,\mu$); 3—aluminum oxide ($D \simeq 6$—$40\,\mu$); 4—crushed glass ($D < 3\,\mu$); 5—the same ($D \simeq 100\,\mu$).

Fig. 2

Figure 2: Fig. 2

As can be seen, in suspensions of calcium carbonate ($D < 3\,\mu$, specific surface $S_0 = 5.1$ m^2/g), stable oil emulsions are formed already at a solid-phase content of 2.5% (curve 1), whereas a bentonite suspension ($D \ll 1\,\mu,\ S_0 \sim 300$ m^2/g) stably stabilizes it only at an emulsifier concentration above 4–5% (curve 2). Aluminum oxide ($D \simeq 6$—$40\,\mu$) gives the same result in a suspension of no less than 10% (curve 3), while with glass powder (as also with any varieties of quartz), irrespective of its dispersity, emulsions cannot be obtained at all (curves 4, 5).

We have previously shown (^{8}) that the presence in the oil phase of even traces of surface-active substances capable of chemoadsorptive interaction with emulsifier particles sharply increases the stability of the emulsions formed, especially in cases where electrolyte ions are simultaneously present in the aqueous phase, forming insoluble soaps with the surface-active substance (^{2}). Evidently, the protective surface structures of even one and the same emulsifier, depending on their strength, must ensure the formation of emulsions of different dispersity.

Figure 2 presents a microphotograph of emulsions of vaseline oil stabilized by one and the same emulsifier–aluminum oxide ($D \approx 6$–$40\,\mu$) in a 10% aqueous suspension: a) in the absence of additives; b) in the presence in the oil of 0.001% oleic acid; and c) containing the same amount of acid in the oil and aluminum chloride in the aqueous phase at a concentration of 0.01 N.

As can be seen, the average droplet size of the emulsions does indeed decrease successively and sharply from 1.5–2.0 mm to 0.5–1.0 mm and then to 0.05–0.1 mm. Measurements of the strength of the interfacial layers showed that the corresponding values of P_m for these three cases of stabilization are 0.008; 0.015; and 9.8 dyn/cm, respectively; in the last case a very large excess reserve of strength ensures practically infinite stability of the emulsions–in a number of cases they remained without noticeable changes over a two-year observation period.

Fig. 2. Structure of protective coatings and dispersity of emulsions of vaseline oil in water stabilized by Al_2O_3 (10×): *a*–pure oil–water; *b*–oil + 0.001% $C_{17}H_{33}COOH$–water; *c*–oil + 0.001% $C_{17}H_{33}COOH$–0.01 N aqueous solution of $AlCl_3$

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* Selective wetting of the walls of glass cylinders (unlike metal ones) by the external aqueous phase of M/W-type emulsions and their special ribbing (with very small curvature of the projections) eliminates partial destruction of the emulsions and separation, in free form, of the lubricating oil film that usually causes wall slip of the liquid (^{1}).

The thickness of the protective coatings in this case decreased from 6–8 layers of loosely packed particles (*a*) to a single, strongly structured layer (*c*), as a result of which, to obtain maximally stable emulsions, it was possible to use not a 10% suspension, but only a 1% suspension of Al_2O_3. It follows from this that not only the stability of emulsions but also their dispersity are directly determined by the mechanical properties of the protective shells arising in the form of coagulation structures at the phase boundary ([9]), and depend only to a very slight degree on the dispersity of the emulsifier particles.

The essence of this influence comes down to the fact that the coalescence of droplets of the oil phase occurring after dispersion has been completed (leading to an increase in their size) is arrested at different stages depending on how sharply expressed the "armoring" ability of the emulsifier is, this ability being determined by the strength of the structure of the stabilizing shell. System 2c is evidently characterized by the primary, maximally high dispersity of droplets arising during dispersion. It goes without saying that highly dispersed emulsions with droplet sizes of another order (1 μ, or below) can be obtained only by using, as emulsifiers, surface-active substances that strongly lower the surface tension (the work of formation) of the interface of the phases forming the emulsions.

The results presented make it possible to interpret a number of features of the process of emulsifying residues of viscous petroleum products in the technology of the mechanized method, developed by us earlier, for washing the surface of the walls of oil-storage tanks and oil-tanker vessels free of them. In this method a solid emulsifier—bentonite clay ([10])—was used,

and subsequently water-soluble surface-active substances (SAS) with additions of electrolytes[1], for example in the form of the following composition: sodium dodecylbenzenesulfonate + Na_2CO_3 + Na_2SiO_3, etc. It was established that the emulsifying capacity of SAS under washing conditions is so weakly expressed that the required technological effect was achieved only in solutions of high concentration (4-5%). However, upon introducing polyvalent ions of hardness salts into these solutions—for example, Mg^{2+} ions—or when using seawater, the required concentration could be reduced to 0.5% and below.

The reason for such a sharp enhancement of the emulsifying capacity of SAS, as it turned out, lies in their formation of a highly dispersed (colloidal) solid phase—precipitates of $MgCO_3$ and $MgSiO_3$—which essentially assume the function of stabilizing the emulsions. The presence of the solid phase is detected nephelometrically and is confirmed by the fact that, after the solution is passed through a filter, it completely loses its emulsifying capacity.

In this case the carbonate particles, whose surface is readily modified (hydrophobized), interact chemisorptively with the acidic components of the petroleum product (naphthenic acids, etc.) and acquire the ability to form structured, mechanically strong protective surface coatings which, depending on the degree of

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[1] A. F. Koretskii, A. B. Taubman, in: *Mechanization of the Cleaning of the Oil-Loading Fleet*, Astrakhan, 1959, p. 87.

modification, can stably stabilize emulsions of both the direct and the reverse type[2]. The chemically inert particles of magnesium silicate, while retaining their original hydrophilicity, are capable of forming only unstable emulsions of the first kind and, thus, are antagonists both of the natural "black" emulsifiers contained in petroleum products and of magnesium carbonate in the case when it is hydrophobized more strongly than necessary.

By using these features in the properties of solid emulsifiers and in the process of structuring protective emulsion coatings, it is possible to regulate, within broad limits and in a sensitive manner, both the stability and type of emulsions and their dispersity; this was used by us to obtain the optimal technological effect.

In conclusion, we express our deep gratitude to P. A. Rebinder for his interest in the work and for valuable advice.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
5 V 1961

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

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[2] A. B. Taubman, A. F. Koretskii, *DAN*, **124**, no. 2, 358 (1959).