EFFECT OF THE DIFFUSION RATE OF SURFACTANTS ON THE DEEMULSIFICATION OF PETROLEUM

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The coalescence of droplets of water and surfactant solutions in oil is described and the corresponding diffusion data are presented.

An aqueous solution of surface-active agent (SA) introduced into a hydrophobic oil emulsion is dispersed in the oil. The droplets of SA solution coalesce with droplets of formation water converting them into a dilute solution of SA. The surface-active agents displace the natural emulsifier from the surface of the new droplet and thus facilitate coalescence [1–3].

We have used high-speed motion-picture photography to investigate the mechanism of coalescence of droplets of water in dibutyl phthalate under the conditions of the Plateau experiment.

The photographs on the left of Fig. 1 show the coalescence of a colored and a clear droplet. Despite the fact that coalescence takes hundredths of a second, the contents of the droplets do not mix. The same picture is observed in connection with the coalescence in oil of water droplets with different Laplace pressures due to differences in both the radii (Fig. 1, right) and the surface tension. The absence of mixing is also noted when water droplets of different density coalesce. In the latter case, the heavy part of the droplet is turned downward, which also prevents gravitational mixing in the steady droplet or in a droplet in laminar motion through the emulsion.

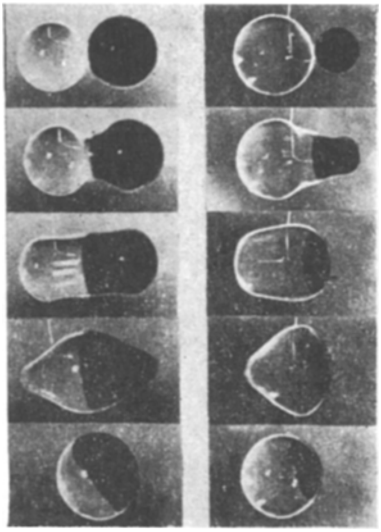
Fig. 1. Coalescence of colored and clear droplets.

When droplets of SA solution coalesce with droplets of formation water, the solution occupies a certain part of the volume of the new droplet. Subsequent mixing of the solution with the water proceeds by diffusion.

The SA molecules diffuse more rapidly over the surface of the droplet than through its interior. However, the surface diffusion eventually slows down, since in the part of the droplet where there is still no internal SA, the SA molecules begin to diffuse back from the surface into the interior of the droplet.

Thus, the rate of attainment of equilibrium adsorption of SA at the surface of the new droplet and displacement of the natural emulsifiers from the phase interface, i. e., the rate of deemulsification of the oil, depends on the rate of diffusion of SA from one part of the droplet (SA solution) to the other (formation water). The effect of this characteristic of SA on the deemulsification of oil (and the destruction of other emulsions) has not been studied, although the difference in diffusion rate explains, for example, the fact that the same reduction of surface tension by different SA corresponds to different rates of deemulsification.

In view of the influence of SA diffusion on the deemulsification process, we investigated the diffusion properties of the nonionogenic SA now used extensively for deemulsification.

To determine the diffusion coefficients, we employed the principle of the Lamm method, which consists in photographing an accurate micrometric scale through the column of liquid in which the diffusion process is taking place [4].

Figure 2 shows the 1800-sec diffusion curve for a 1% solution of Disolvan (4411) under distilled water (curve 1). The curve is asymmetrical with respect to the maximum displacement. This deviation from a normal Gaussian curve is characteristic of all the substances investigated and indicates a diffusion anomaly due to the polydispersity of the medium. In the course of time, the displacement maximum diminishes (Fig. 2, curve 2 after 3600 sec). The asymmetry of the curve, however, does not change. Accordingly, we calculated the diffusion coefficients from the maximum ordinate of the diffusion curve in accordance with the formula [4]

$$D = \frac{G^2a^2b^2(n_1 - n_0)^2}{4\pi t Z^2}. \tag{1}$$

It is clear from expression (1) that, for the diffusion coefficient to be constant with time, it is necessary that the product tZ^2 also be constant. However,

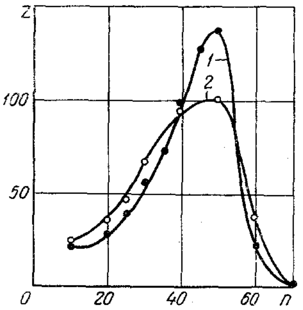

Fig. 2. Diffusion curves for the deemulsifier 4411 (abscissas: scale divisions n, ordinates: relative displacements of the divisions of the principal and ocular scales Z, μ): 1) 1800 sec; 2) 3600 sec.

in the course of time (after about 4500 sec) the value of the product tZ^2 begins to increase, which leads to a decrease in the diffusion coefficient. This indicates a deviation of the SA diffusion from Fick's second law. The physical significance of this is evidently as follows. At the beginning of the experiment, when the SA solution is brought into contact with the distilled water, the rate of diffusion of SA molecules into the pure water is high. After a certain time, primary micelles begin to form in the upper part of the diffusion cell, which slows down the subsequent diffusion. In this case, the higher the concentration, the sooner the diffusion rate begins to slow down.

The concentration dependence of the diffusion coefficient in the range from 0.2 to 1.0% is presented in Fig. 3 for a temperature of 293° ± 0.1° K.

Disolvan (4411) has the greatest diffusion coefficient. As will be shown below, at low concentrations the agent 4422 has about the same diffusion rate as 4411. At high concentrations, however, its diffusion coefficient is much smaller than that of 4411. This is evidently the reason for its relative ineffectiveness as a deemulsifier, even though it is highly active.

The curves for OP-10 and OP-7 almost coincide.

The deemulsifier OZhK has the lowest diffusion coefficient of all the SA studied.

Since it was not possible to determine the diffusion coefficients at low concentrations, we conducted experiments to register the mean translational velocity of the SA molecules.

Into a cylinder filled with a 0.5% solution of SA, we lowered a capillary $1.3 \cdot 10^{-3}$ m in diameter containing distilled water, so that its tip was in contact with the surface of the solution. The height of the column in the capillary was measured with a microscope from the bottom of the meniscus. During the experiments, the temperature was maintained at 293° ± 0.1° K.

When the capillary is brought into contact with the surface, the SA molecules diffuse into the water and, after a certain time, reach the meniscus. The SA molecules move at different velocities, and those possessing the highest velocities reach the surface of the meniscus first.

When the SA molecules appear at the surface, the level of the water column in the capillary begins to fall. This fall becomes noticeable at very low concentrations of SA at the surface, since, for many SA, concentrations of not more than 0.001% will halve the surface tension of the water at the air boundary. In the experiments, the reduction in level was measured at certain intervals with a measuring microscope accurate to $2 \cdot 10^{-6}$ m. The results of the experiments with the deemulsifiers 4422, 4411, OP-10, and OZhK are presented graphically in Fig. 4.

Until the SA molecules reach the surface of the water column, the curves are characterized by a straight-line segment. Then the level falls at a rate determined by the diffusion rate and the activity of the agent. Finally, when the surface becomes saturated with SA molecules, the water level reaches a minimum and thereafter remains constant. It is clear from the initial linear segments of the curves that the 4411 molecules have a somewhat greater diffusion rate than the 4422 molecules. The OP-10 and OZhK molecules have approximately the same rate which, however, is much less than that of 4411 and 4422.

As a result of the large size of the macromolecules, the investigated SA resemble typical colloidal systems with respect to their diffusion properties. The diffusion coefficient D_0 for a spherical particle (equal in

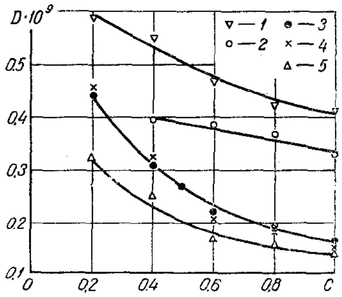

Fig. 3. Diffusion coefficient D (m^2/sec) as a function of concentration C (%): 1) 4411; 2) 4422; 3) OP-10; 4) OP-7; 5) OZhK.

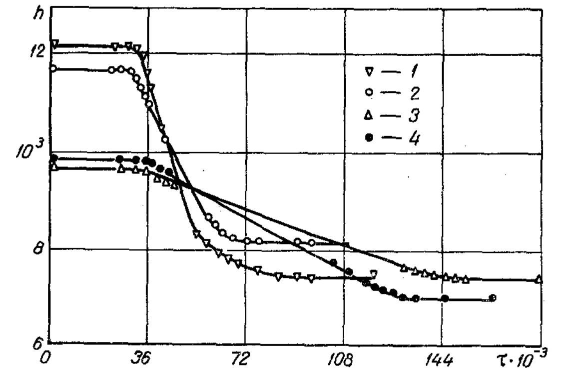

Fig. 4. Fall in the height h (m) of the water column in a capillary as a function of time t (sec): 1) 4411; 2) 4422; 3) OP-10; 4) OZhK.

mass to a particle of arbitrary shape) is related to the diffusion coefficient D by the expression

$$D_0 = D \frac{B}{B_0}.$$

The quantity B/B_0 is called the coefficient of dissymmetry and is equal to 1 for spherical particles. For asymmetrical particles, $B/B_0 > 1$. The value of B/B_0 is related to the ratio l/d of the semimajor and semiminor axes of a prolate ellipsoid, the form in which an asymmetrical particle in solution is usually represented.

Since the physichochemical properties of the SA investigated can be regulated by varying the number of ethylene oxide groups on the molecule, if we wish to increase the diffusion coefficient, it is necessary to try and make the coefficient of dissymmetry B/B_0 as close as possible to unity.

It should be noted that in this case the surface activity may be reduced. Accordingly, it is necessary to establish the conditions under which the diffusion coefficient of the SA and its surface activity are optimum.

However, an increase in the rate of molecular diffusion of the SA may still fail to ensure the sufficiently rapid mixing of the contents of the droplets.

To accelerate mixing, it is possible to resort to turbulent agitation of the emulsion at reasonably large Reynolds numbers. In this regime, the spatial orientation of the droplets continuously changes, as a result of which gravitational forces play a more important part in the mixing of the SA solution with the formation water.

NOTATION

D is the diffusion coefficient; n_1 and n_0 are the refractive indices of the solution and the solvent, respectively; G is the photographic magnification of the scale; a is the thickness of the cell, i.e., the geometric thickness of the layer of liquid in which the diffusion takes place; b is the optical distance from the scale to the center of the cell; Z is the maximum displacement of the scale divisions; t is the time from the initial instant of contact between the solution and the solvent.

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