L. Ya. Kremnev, L. A. Nikishchekina, A. A. Ravdel

1963

SovietRxiv

Abstract

Full Text

L. Ya. Kremnev, L. A. Nikishchekina, A. A. Ravdel

On the Stability of Emulsions

(Presented by Academician P. A. Rehbinder, May 8, 1963)

Stability, as a kinetic concept, characterizes the properties of any disperse systems, including emulsions. However, in the case of emulsions it is necessary to distinguish the ability of liquid droplets to merge irreversibly into continuous, larger drops (coalescence). Meanwhile, in some works this very essential circumstance has not been given due attention ([1,2]), although it is quite trivial.

One can, of course, find an analogy in the behavior of an emulsion and, for example, a hydrophobic sol. Very small amounts of a neutral electrolyte usually cause coagulation (adhesion) of the particles, and the sol is destroyed. In the presence of liquid interlayers between the coagulated particles, the coagulum separated from the dispersion medium can be peptized. The same conditions promote reversible coagulation of droplets in emulsions on an ionogenic stabilizer, which creates double ion layers at the droplet surface, and the Schulze-Hardy rule may be obeyed. Flocculation accelerates the appearance of a cream layer (sediment), which, upon stirring, is dispersed by the free dispersion medium (a phenomenon analogous to peptization). However, coagulation of droplets does not yet cause destruction of the emulsion and its separation into macrovolumes of the original liquids. An emulsion is destroyed only as a result of irreversible coalescence of the droplets, which occurs when the interdroplet protective layers are destroyed. This is the distinction between emulsions and hydrophobic sols, and the main problem here is the stabilization of droplets against coalescence.

From this point of view, the report by Derjaguin and Titievskaya on the behavior of two gas bubbles stabilized by sodium oleate and pressed against one another in an aqueous solution of the same soap is of particular interest. In this case the thickness δ of the aqueous interlayer separating the drops was measured. When small amounts of NaCl were added to the aqueous solution of sodium oleate, the diffuse layers at the surfaces of the bubbles were compressed and, at the same time, the thickness of the interbubble layers δ decreased. But even with complete overlap of the diffuse layers, the bubbles did not coalesce, and δ assumed a smallest constant value independent of the pressure ([3]). The same results were obtained by van den Tempel with two drops of oil and the addition of small amounts of salt ([4]). Obviously, the coalescence of drops in emulsions and of bubbles in foams is hindered by a factor not associated with the repulsive forces of the double electric layers. True, in van den Tempel' s experiments the drops coalesced at large amounts of salt. There is nothing unexpected in this,

Fig. 1

Figure 1: Fig. 1

since under such conditions, for example, sodium oleate becomes hydrophobized. As is known, soap then loses the ability to stabilize direct emulsions and imparts stability to inverse emulsions ([5,6]).

In connection with the problem of stability against coalescence, we considered it necessary to obtain information on the electrokinetic properties of systems of droplets in the form of highly concentrated emulsions (h.c.e.), containing considerably more than 74–75 vol.% of the dispersed phase, i.e., far above the limit of close packing of undeformed spheres of one size. Such systems consist of a relatively very large volume of droplets, de-

formed into pentagonal dodecahedra and tightly pressed against one another, with a very small volume of the dispersion medium separating them in the form of films.

In its structure, a h.c.e. is a coagulated system: in it all the droplets adhere to one another through continuous layers of the dispersion medium, several hundred angstroms thick (7–9). At the same time, a h.c.e. is a system that is quite stabilized against coalescence and for a very long time does not break down with separation into continuous volumes of liquids.

We measured the streaming potentials for a number of h.c.e.' s, and also studied their behavior during prolonged aging. The emulsions were prepared from benzene and aqueous solutions of stoichiometrically neutral sodium oleate, as well as nonionogenic OP-10, by the reciprocating motion of a flexible spiral (10). Measurements of the streaming potentials were carried out in the usual apparatus (11), using a Teflon cylindrical cell with a perforated base and lid. The perforated surfaces were covered with circles of filter paper having a streaming potential of no more than 0.1 mV. Through the cell, densely filled with emulsion, a sodium oleate solution of equilibrium concentration was forced; this concentration was found from the adsorption isotherm of the soap, constructed on the basis of surface-tension measurements at the liquid–liquid interface.

Fig. 1

Figure 1 shows the change in the magnitude of the electrokinetic potential ζ as a function of the volume concentration of the h.c.e. With increasing concentration of emulsions on sodium oleate, the ζ-potential decreases and takes its smallest value in the limiting (99%) emulsion: $\zeta = 51.5$ mV. Apparently, in the limiting emulsion on soap, in which the thickness of the protective aqueous layers between droplets is $\delta = 100$ Å (7), the diffuse layers are sufficiently close together and overlap. With decreasing h.c.e. concentration, the distance between droplets increases, the diffuse layers expand, and the ζ-potential rises.

It might have been assumed that the comparatively high values of the ζ-potential indicate the presence of an energetic barrier of electrostatic nature, preventing coalescence of the h.c.e. droplets. However, even very small amounts of NaCl sharply reduce the magnitude of the electrokinetic potential: for example, in a 97% emulsion made from a $9 \cdot 10^{-4}$ N salt solution, the ζ-potential decreases from 103 to 5.2 mV. At the same time, this is not reflected in the stability of the emulsion against coalescence, since visible separation of a continuous volume of benzene always begins only after 7 days of aging, irrespective of the presence of salt.

The properties of h.c.e.' s on the nonionogenic emulsifier OP-10 are very interesting: as was to be expected, they have a very small ζ-potential. When OP contaminated with electrolytes is used, $\zeta = 3.5$ mV, and for emulsions with purified stabilizer, $\zeta = 0.2$ mV. The stability of emulsions both on contaminated and on purified OP-10 greatly exceeds the stability of h.c.e.' s on sodium oleate: even after 280 days of aging they did not separate benzene.

Thus, the stability of emulsions against coalescence, and consequently against destruction, is not determined by the presence of an electrical double layer at the droplet surface, as, for example, Wojucki (2) insists, proceeding from experiments on coagulation of emulsions but not on their coalescence. As is known, according to Rebinder (12, 13), the principal factor in the stability of emulsions is the structural-mechanical barrier at the interphase surface.

New convincing confirmation of this view was recently obtained by Taubman and Nikitina, who established that a structural-mechanical barrier in the form of phase films imparts high stability to emulsions (14).

Leningrad Technological Institute
named after Lensovet

Received
22 IV 1963

CITED LITERATURE

[1] S. S. Voyutskii, *Koll. zhurn.*, **33**, 353 (1961).
[2] S. S. Voyutskii, *Usp. khim.*, **30**, 1237 (1961).
[3] B. V. Deryagin, A. S. Titievskaya, *Koll. zhurn.*, **15**, 416 (1953).
[4] M. van den Tempel, *J. Coll. Sci.*, **13**, 125 (1958).
[5] L. Ya. Kremnev, N. I. Kuibina, *Koll. zhurn.*, **16**, 358 (1954).
[6] L. Ya. Kremnev, ibid., **20**, 546 (1958).
[7] L. Ya. Kremnev, S. A. Soskin, ibid., **9**, 269 (1947).
[8] L. Ya. Kremnev, R. N. Kagan, ibid., **10**, 436 (1948).
[9] L. Ya. Kremnev, N. I. Kuibina, ibid., **16**, 447 (1954).
[10] L. Ya. Kremnev, *DAN*, **79**, No. 4, 655 (1951).
[11] O. N. Grigorov, Z. P. Kozmina et al., *Electrokinetic Properties of Capillary Systems*, Publishing House of the Academy of Sciences of the USSR, ed. Acad. P. A. Rebinder, Moscow—Leningrad, 1956.

[12] P. A. Rebinder, *Koll. zhurn.*, **20**, 527 (1958).
[13] P. A. Rebinder, A. B. Taubman, ibid., **30**, 359 (1961).
[14] A. B. Taubman, S. A. Nikitina, ibid., **33**, 633 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.