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Abstract

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STRUCTURE FORMATION IN ADSORPTION INTERFACIAL LAYERS OF SOLUTIONS OF SURFACE-ACTIVE SUBSTANCES AND THE STABILITY OF EMULSIONS AND AQUEOUS DISPERSIONS OF POLYMERS (LATICES)

(Presented by Academician P. A. Rehbinder on 26 IX 1962)

Studies of the dependence of the stability of concentrated emulsions on the structural-mechanical properties of adsorption layers of synthetic soap-like surface-active substances (surfactants) show that sufficiently strong stabilization is often achieved even in those cases when the strength and viscoelastic properties of the emulsifier layers are expressed very weakly. Thus, it was established (^{1}) that the adsorption layers of sodium lauryl sulfate—an effective emulsifier—do not exhibit appreciable surface viscosity. From our measurements it follows, however, that the static limiting shear stress (P_m) of the adsorption layers of a number of surfactants is a small quantity of the order of $P_m \approx 10^{-4}$ dyn/cm, in accordance, obviously, with the fact that, as was established by one of us, condensed monolayers cannot form at the boundary of two liquid phases (^{2}).

In this connection, some investigators (^{3}), as the principal factor in the stabilization of emulsions, accepted the electrostatic interaction of the charged polar groups of adsorbed molecules of ionic surfactants, although this does not make it possible to explain the well-known fact that nonionic soaps possess high stabilizing properties, a fact established, in particular, by these same authors (^{4}), as well as a number of other phenomena (^{5}).

However, the indicated discrepancy between the aggregative stability of emulsions and the strength of adsorption layers is only apparent and can be eliminated if, in measurements of structural-mechanical properties, one takes into account the sharply retarded kinetics of formation of surface stabilizing layers at interfacial boundaries, as was, for example, previously shown by us for solid powder-like emulsifiers (^{6}) and natural "black" emulsifiers of oil (^{7}), as well as for water-soluble nonionic surface-active substances (^{8})—OP-10 (polyoxyethylene ether of alkylphenol) and Pluronic-L64 (a block copolymer of oxyethylene

Fig. 1

Figure 1: Fig. 1

and oxypropylene (9)), with which especially clear evidence was obtained for the large role in emulsion stabilization of the kinetics of formation of the structural-mechanical barrier.

Below are given the data of measurements of the value P_m on the modified instrument SNS-2 (10) for adsorption layers in OP-10 solutions as they form with time under static conditions at the water-xylene interface and, in parallel with this, the results of estimating the stability of concentrated (50%) direct emulsions of xylene in water, as well as polymer dispersions—polystyrene latices stabilized by OP-10 and Pluronics*. The polystyrene latices were synthesized by emulsion polymerization at a phase ratio styrene : water = 1 : 5 at 50°, potassium persulfate being used as the initiator and polymerization was carried out for 10 h. The latexes were tested for stability at low temperatures by a single freezing at $t = -25°$ for 3 and 16 h.

Figure 1 presents the dependence $P_m = f(\tau)$ (where τ is the lifetime of the interface), for OP-10 solutions of different concentrations and for different conditions of introducing the surfactant into the phases to be emulsified.

As can be seen, with increasing concentration of the solutions the rate of increase in the strength of the protective layers of the emulsifier rapidly increases, but even in a 5% solution the limiting value $P_m = 0.25$ dyn/cm (“b” point on curve 4), more than two orders of magnitude higher than the initial value $P_m \approx 5 \cdot 10^{-4}$ dyn/cm, is reached only after 25 h. The strengthening process of the stabilizing layer is even more retarded for Nekal-NB (curve 6). However, if OP-10 is introduced into the emulsion in the same amount, but distributed between both phases (its solubility in xylene is about 30%), then the indicated slow kinetics is practically not observed and high strength arises in the very first minutes of the existence of the interface (curve 5).

Fig. 1. Kinetics of the increase in strength of interfacial protective layers at the interface: 1—4 —aqueous OP-10 solution (xylene), for $C = 0.1$; 2.5 and 5%, respectively; 5 —2.5% aqueous OP-10 / 2.5% xylene OP-10 solution; 6 —5% aqueous Nekal NB solution / xylene; 7 —5.0% aqueous Pluronic-L64 solution / xylene.

It is interesting to note that in a 5% solution of Pluronic-L64, as we established earlier (8), strengthening of the layer occurs practically instantaneously, even if it is present only in the aqueous phase (curve 7). These results determine the principal properties of emulsions—their dispersity and stability. Thus, when

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* N. E. Khokhlova took part in the work.

emulsions are obtained by brief ($\sim$ 10 sec) and very weak shaking in a 5% solution of Pluronic-L64, a highly dispersed stable emulsion is formed with an average droplet size of about 2–3 μ, whereas in an OP-10 solution it is not less than 70–80 μ. With increasing duration of dispersion the droplet size gradually decreases and also reaches 2–3 μ, but this already requires 15–20 min of intensive shaking of the emulsion. In addition, the stability of emulsions sharply increases when they are obtained under conditions in which, to one degree or another, the retarded kinetics of the increase in strength of the stabilizing layers is eliminated; in particular, in a 5% aqueous solution of Pluronic-L64 with pure xylene, as well as in a system consisting of 2.5% aqueous and 2.5% xylene solution of OP-10, the emulsions acquire practically infinite stability.

All this indicates that the occurrence of high strength ($P_m \approx 0.1$ dyn/cm) of the protective layers, which ensures very high stability of emulsions, is associated not with the formation of adsorption layers of emulsifiers as such, which, as we have shown ([11]), requires substantially less time, but with the formation at the interface of two liquid phases of complex supramolecular structures in the form of phase films of multilayer thickness.

The formation of such structures is indeed readily detected visually as a thin, gradually thickening, milky-white layer of an ultramicroemulsion of colloidal dispersity, spontaneously arising from the interface toward the aqueous phase, with droplet diameter $d \ll 1\mu$, and of exceptionally high stability.

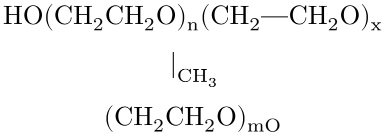
At the same time, a strict similarity is observed in the course of the curves for the increase in the strength of the surface layers of the emulsifier with time and in the appearance and formation of this structure—in a 5% solution of Pluronic-L64 it appeared several minutes after a layer of xylol had been applied to the surface of the aqueous phase, whereas in a 5% OP-10 solution only after 5–6 hours of existence of the interface (on curve 4, point "a" corresponds to this value of τ).

Table 1

No.	Surfactant	Conc. of surfactant, %	Conversion, %	Coagulate, % of dry residue
1	Nekal NB	2.0	100	85
2	Nekal NB	4.0	100	85
3	OP-10	2.5	100	47
4	OP-10	5.0	100	0
5	OP-10 in the aqueous phase; in the xylol phase	2.5; 12.5	100	0*

No.	Surfactant	Conc. of surfactant, %	Conversion, %	Coagulate, % of dry residue
6	Pluronic-L64	4.0	81	0
7	Pluronic-184	7.5	100	0*

Note. The amount of coagulate after freezing at −25°C for 3 hours; the asterisk indicates that the latex withstood freezing for 16 hours. Pluronic-L64 has the formula



$$\mathrm{HO(CH_2CH_2O)_n(CH_2{—}CH_2O)_x}$$
$$|_{\mathrm{CH_3}}$$
$$\mathrm{(CH_2CH_2O)_{mO}}$$

and molecular weight ≈ 3000; Pluronic-184 is an analogue of preparation L64, synthesized in the laboratory of surface-active substances of the Scientific Research Institute of Organic Intermediates and Dyes under the direction of K. G. Mizuch.

The phenomena considered are based on the hydrodynamic effect of spontaneous surface turbulence and convection, causing the one-sided transfer of the hydrocarbon phase into the aqueous phase in the form of an ultramicroemulsion (12). Structured by the adsorption layer of the emulsifier, such a phase film acquires considerable strength and, as a consequence, a high stabilizing capacity. Thus, the discrepancy observed in a number of cases between the high stability of emulsions and the low strength of the adsorption layers of the emulsifiers of these emulsions is only apparent and is due to the fact that these properties are assessed under noncomparable conditions: measurements of P_m are made under static conditions, in which the slow kinetics of formation of supramolecular protective shells manifests itself fully, whereas measurements of emulsion stability are made under conditions of vigorous mixing of the phases, when the influence of this kinetics is eliminated owing to acceleration of the diffusion process and distribution of the emulsifier between the emulsified phases.

In full agreement with the data set forth above are the results of using OP-10 and Pluronic-L64 as emulsifiers for polystyrene latex. The data in Table 1 confirm the decisive role of the strength of protective structures in increasing the resistance of latexes to the action of low temperatures (13).

As is evident from a comparison of the properties of the emulsifiers we used, all of them, while permitting at relatively high concentrations the achievement of practically complete monomer conversion during polymerization, differ very strongly in their stabilizing action.

Latexes obtained with Nekal, upon freezing for 3 hours, coagulate almost completely and irreversibly; latex stabilized with OP-10 coagulates by approximately one half, forming a coagulate partially reversible upon subsequent shaking; whereas latexes emulsified with OP-10 and Pluronics under conditions corresponding to the formation on the surface of globules of strong supramolecular surface structures (systems 4-7) acquire very high stability, not impaired even by prolonged freezing.

Thus it has been established that the principal factor in the strong stabilization of latexes, as well as of concentrated emulsions, is the high strength of the structured stabilizing layers on the surface of droplets or particles of the dispersed phase, which arise under the condition of sufficient solubility of the surface-active emulsifier not only in water, but also in the nonaqueous phase.

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