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## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# THE DEMULSIFYING ACTION OF SURFACE-ACTIVE SUBSTANCES AND THE STRUCTURAL-MECHANICAL PROPERTIES OF THEIR ADSORPTION LAYERS

The exceptionally high stability of petroleum emulsions of the "water in oil" type is determined, as is known, by the strong stabilization of them by structural surface layers of natural emulsifiers of complex composition, including both surface-active and inactive components—salts of naphthenic acids, resins, asphaltenes, and particles of solid highly disperse phases. In this connection, the most general physicochemical route for the destruction of such emulsions consists in the action upon them of surface-active substances which, being adsorbed at the droplet-medium interface, displace the adsorption layer either by adsorption or as a result of hydrophilization of the protective film, thereby disturbing the aggregative stability of the emulsion ([1]-[3]).

Thus, in order to manifest its action effectively, a demulsifier must possess, on the one hand, sufficiently high surface activity and, on the other, a considerable wetting capacity in aqueous solutions, i.e., properties which in a number of cases are not combined in one and the same surface-active substance. This circumstance apparently also explains the difficulties arising in the selection of effective demulsifiers even among strongly surface-active substances and in the development of methods for evaluating demulsifying action, as a result of which these methods often have an empirical character.

It is therefore expedient, as the most general method of such evaluation, to use measurements of the structural-mechanical properties of the adsorption layers of emulsifiers that stabilize inverse emulsions, and of their changes under the action of demulsifiers ([4]). The results of such measurements should evidently characterize in aggregate the changes in the properties of the emulsion system that arise in the interaction of the demulsifier both with the surface-active and with the inactive components of the protective films.

At the same time, such measurements make it possible to evaluate the structural-mechanical properties of the adsorption layers of the demulsifiers themselves; and this is important in view of the fact that, if these properties are expressed sufficiently sharply, not only destruction of emulsions may occur, but also their inversion and the formation of emulsions of the direct type.

In the present work, carried out with the aid of a standard SNS-2 instrument specially adapted by us for such measurements (5) (intended for the investigation of the rheological properties of bulk systems—clay suspensions), the strength (two-dimensional limiting shear stress ($P_m$)) was measured for the adsorption layers of one sample of a "black" emulsifier of petroleum emulsions, isolated by the method (6) from a mixture of oils from northeastern fields of the USSR processed at the Gur' ev oil refinery. The oil phase of the emulsions was a 0.1% solution of the emulsifier in a 50% mixture of vaseline oil and xylene; the aqueous phase contained 10% NaCl and various amounts of demulsifier, for which nonionic surface-active substances OP-10 and Samonins of two grades (from the firms Kalbaum and Becker), respectively with very high and low strength of adsorption layers (7), were used. The interfacial surface tension, equal to 45.3 erg/cm$^2$, in the presence of the emulsifier decreased very slightly and amounted to 44.2 erg/cm$^2$.

Measurements of $P_m$ were carried out in the following manner. A glass disk pri-

the device was suspended on a thin elastic thread so that it crossed the interface between the two liquids in the vessel, which, together with the special table, could rotate at a constant speed (0.2 rev/min). In each experiment, rotation was continued until the increasing torque of the thread led to destruction of the interfacial layer at a stress corresponding to its limiting value $P_m$ (^5). After destruction, the structure of the adsorption layers of the systems studied was restored thixotropically so rapidly (the stress relaxation time did not exceed 10-20 sec) that this made it possible to carry out measurements successively, first after 1 min, then after 30-60 min, starting from very small values of the time ($\tau \sim 1$ min.) of existence of the layers up to $\tau \sim 10$ h and more, when the protective coating had formed (see Fig. 1, 1).

In Fig. 1 are presented curves of the dependence $P_m = f(\tau)$ for the adsorption layer of the initial black emulsifier at the interface of a 0.1% solution of it in carbon black oil—10% aqueous NaCl solution (curve 1) and for mixed adsorption layers formed by this same emulsifier and a demulsifier (OP-10 or saponin), added to the aqueous phase at different concentrations (curves 2-7). The course of curve 1 shows that the high strength of the adsorption layers of the "black" emulsifier (maximum value $P_m \sim 1$ dyne/cm) is due to their colloidal structure, forming over a long time and at the same time possessing the ability for rapid thixotropic recovery, as follows from the conditions adopted in the work for measuring $P_m$ (with successive destruction of the adsorption layers being formed). This structure apparently has a complex polymolecular construction, analogous to the structure of protective multilayer coatings of emulsion droplets when they are stabilized by dispersed (not colloidal) solid emulsifiers (^5). It is precisely to such a structure that the exceptionally high strength of the stabilizer layers corresponds, exceeding by at least 3 orders of magnitude the strength of adsorption layers of ordinary surface-active substances at the interface between two liquid phases. As the content of the demulsifier OP-10 in the aqueous phase

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Fig. 1

Figure 1: Fig. 1

is increased from 0.05 to 0.5% (curves 2–5), there occurs not only a sharp (by 2–3 decimal orders of magnitude) successive decrease in the value of $P_m$, but also a regular change in the form of the curves. Owing to the ever-increasing hydrophilization of the demulsifier particles, the protective shell formed by them is gradually destructured and loses its stabilizing ability, as a result of which the stability of the emulsions decreases.

**Fig. 1.** Curves of the dependence $P_m = f(\tau)$ of adsorption layers of the "black" emulsifier in a 0.1% solution in a 50% mixture of Vaseline oil and xylene at the interface with a 10% aqueous NaCl solution, in the absence and in the presence of a demulsifier.
1-5 –OP-10 at concentrations of 0; 0.05%; 0.1%; 0.25% and 0.5%, respectively; 6 – "Beker" saponin 0.5%; 7 – "Calbaum" saponin 0.5%; 8 – "Calbaum" saponin 0.5%, solution without emulsifier.

The following results of measurements of the stability of emulsions (at 70°), formed by shaking a solution of the "black" emulsifier in the oil phase with 3% by volume of an aqueous phase containing 10% NaCl, as well as the demulsifier OP-10, are in good agreement with these data on the strength of interfacial layers (stability was characterized by the time ($t$) for separation from them, in free form, of half the amount of emulsified water):

| Concentration of "black" emulsifier in the oil phase, % | 0.1 | 0.1 | 0.1 |
|---|---|---|---|
| Concentration of OP-10 in the aqueous phase, % | 0 | 0.25 | 0.5 |
| Duration of separation ($t$), min. | $2 \cdot 10^3$ | $2 \cdot 10^2$ | $6 \cdot 10$ |

It is important to note that the process of destruction of the protective film of the emulsifier proceeds as it interacts with the molecules of the demulsifier-wetting agent and, consequently, has a time-dependent character. Therefore, under nonequilibrium conditions, when the system is shaken, the gradually separating water, if there is enough of it, can form the external phase of a direct-type emulsion, o/w, and then a multiple (mixed) emulsion ([8]) arises, with different volume ratios in it of emulsions of both types (depending on the intensity and duration of mixing and on the water content). In this, however, the stabilizing ability of the demulsifier is of decisive importance.

If the structural-mechanical (strength or structural-viscous) properties of its adsorption layers are very weakly expressed, as in the case of the strongly surface-active demulsifier OP-10 (the surface viscosity of the saturated layer in a 0.5% solution is of the order of $\sim 10^{-3}$ surface poise, while the surface tension of this solution is $\sigma \approx 30$ erg/cm$^2$), then hydrophilization of the particles of the "black" emulsifier causes a decrease in $P_m$ to its lowest value, and destruction of the initial emulsion proceeds without formation of an o/w emulsion (see curves 4–5).

When saponins are used—substances much less surface-active (their 0.5% solutions have practically the same limiting reduced $\sigma \approx 40$ erg/cm$^2$)—their action manifests itself differently depending on the structural-mechanical properties of their adsorption layers. According to data ($^7$), the surface viscosity of 0.5% saponin solutions differs by seven orders of magnitude, amounting to $10^{-3}$ and $10^4$ surface poise.

In accordance with this, as can be seen from the figure, the first of them has a relatively weak effect on the behavior of the initial emulsion (curve 6), slightly lowering $P_m$, but not changing the S-shaped form of the dependence curve $P_m = f(\tau)$, characteristic of the "black" emulsifier, which thus largely retains its emulsifying properties. As a result, in this case the reverse-type emulsion, obtained from equal volumes of the aqueous and oil phases, was destroyed only partially, and a multiple emulsion was formed.

The saponin "Kalbaum" behaves quite differently, in accordance with its high strength properties. As is seen (curve 7), it completely changes the shape of the curve $P_m = f(\tau)$: the rectilinear dependence, analogous to curves 4 and 5 for OP-10, indicates complete displacement from the interface of the colloidal structure of the "black" emulsifier by a monomolecular layer of saponin. At the same time, the values of $P_m$, practically identical to the value characteristic of the adsorption layer of pure saponin ($P_m \sim 1$ dyn/cm) in the absence of the "black" emulsifier (cf. curves 7 and 8), give grounds to conclude that in this case saponin causes phase inversion and formation of a highly stable direct-type emulsion.

Thus, measurements of the structural-mechanical properties of interfacial layers do indeed make it possible, in a visually clear form, to characterize changes in the aggregate stability of reverse-type petroleum emulsions when they interact with demulsifiers.

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