ON CERTAIN FEATURES OF THE EMULSIFICATION OF STRUCTURED LIQUIDS

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Abstract

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ON CERTAIN FEATURES OF THE EMULSIFICATION OF STRUCTURED LIQUIDS

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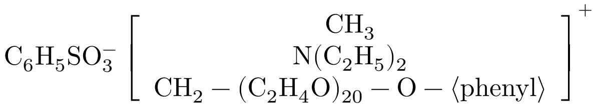
As is known, the type of aggregatively stable concentrated emulsion formed from two model liquids with low Newtonian viscosity (for example, water and benzene) is determined mainly by the molecular-surface properties of the emulsifier used, which forms a structural-mechanical barrier on the surface of the droplets and prevents their coalescence (^{1}). In this case hydrophilic emulsifiers promote the formation of direct emulsions (of the O/W type), while oleophilic ones stabilize inverse emulsions (of the W/O type).

However, spatially structured liquids possessing a high effective (structural) viscosity exhibit specific behavior during emulsification. These include, for example, bitumens and tars of viscous grades at temperatures above 40° (^{2}), and less viscous grades at ordinary temperature. In the presence of a hydrophilic surface-active emulsifier, in concentrations that considerably structure water, they are capable of forming with water not only direct but also inverse emulsions.

When gradually added bitumen (tar) is mixed with an aqueous solution of a hydrophilic emulsifier of concentration C, as should be expected, a direct emulsion arises, and the concentration of bitumen in it can be brought to high values, up to the formation of an extremely concentrated (limiting) emulsion (Fig. 1, 1). In the reverse case—when bitumen (tar) is mixed with a gradually introduced aqueous solution of the same hydrophilic emulsifier—an inverse emulsion (of the W/O type) is always formed, the concentration of which can be increased to a certain limit Q, corresponding to the content C of emulsifier in the water (Fig. 1, 2). Q denotes the weight concentration of the disperse phase in the limiting emulsion.

As an example, Fig. 1 gives emulsification isotherms obtained with bitumen of grade B-5, which at ordinary temperature is a highly structured system, and with aqueous solutions of the cation-active emulsifier (leveler A-20) benzolsulfonate—methyldiethyl-2,5-dioctylphenoxypolyethyleneoxidemethylammonium



$$C_6H_5SO_3^- \left[\begin{array}{c} CH_3 \\ N(C_2H_5)_2 \\ CH_2 - (C_2H_4O)_{20} - O - \langle\text{phenyl}\rangle \end{array} \right]^+ ,$$

Fig. 1

Figure 1: Fig. 1

where $R = \mathrm{C_8H_{17}}$.

The results of emulsification are determined, of course, not only by the selected hydrophilic emulsifier and its concentration, but also by the content of oleophilic surface-active substances in bitumens and tars, and also

the thixotropically structured state of these systems. Along the curves, three regions of concentration of the hydrophilic emulsifier C are distinguished, which affect emulsification in different ways.

In region I only inverse emulsions (of the W/O type) are stabilized. It is characteristic that, when pure water is emulsified, the weight concentration of the emulsion Q is maximal; with an increase in the concentration of the emulsifier in water, however, Q decreases sharply from 77.8 to 20%. This effect is caused by the antagonistic interaction between the oleophilic emulsifiers of the bitumen and the hydrophilic emulsifier in the aqueous solution; each of them tends to emulsify, respectively, the aqueous solution and the bitumen, as a result of which mutually neutralizing amounts of both stabilizers are excluded from the emulsification process (^{3}).

Fig. 1

In region I there is no excess of hydrophilic emulsifier and, naturally, stabilization of direct emulsions (of the O/W type) is impossible.

In region II direct emulsions of bitumen in water (of the O/W type) arise; at first they are coarse, since the excess of hydrophilic emulsifier is still insufficient for stabilizing highly dispersed emulsions, but with increasing concentration of the hydrophilic emulsifier the dispersion of the emulsions increases. In the same region a certain decrease of Q continues in the inverse emulsions, which may be caused by a change in the structural-mechanical properties of the bitumen under the influence of VA-20.

In region III, highly dispersed emulsions of both types are obtained equally easily, with the corresponding order of introducing the liquid to be emulsified. A certain decrease of Q for direct emulsions is determined by the continuing increase in the dispersion of the bitumen droplets. As for inverse emulsions, in this interval of hydrophilic-emulsifier concentrations the emulsification results, as in region II, are determined entirely by the structural-mechanical properties of the bitumen. Stabilization of water droplets and aqueous solutions in region I is accomplished both by the oleophilic emulsifiers of the bitumen and, to a considerable extent, through incorporation of the droplets into the spatial network of the bitumen, which is thixotropically restored after its partial destruction during dispersion. But in regions II and III the emulsifying properties of the oleophilic emulsifiers of the bitumen are suppressed by their antagonistic interaction with the hydrophilic emulsifier. Consequently, the sole factor of aggregate stability of the inverse emulsions obtained here is the structural-mechanical properties of the bitumen.

In full accordance with the ideas of P. A. Rehbinder (^{1}), the universal structural-mechanical factor of stability of disperse systems under our conditions strikingly predominates over the hydrophilic properties of the emulsifier and, even at very high concentrations of it in the aqueous solution, ensures the production of aggregatively stable emulsions of the W/O type.

An analogous effect of strong stabilization of direct emulsions by hydrophobic metallic soaps, as a result of the formation of a structural-mechanical barrier, was earlier found by A. B. Taubman and A. F. Koretskii (^{4}) in obtaining oil emulsions with the aid of solid emulsifiers.

The same results as with bitumen of grade B-5 were obtained by us also with anion-active hydrophilic emulsifiers, both with tars and with bitumens of viscous grades possessing, at ordinary temperature, solid-like—

properties (^{2}). In these cases the bitumen was heated to 60–70°, i.e., to the state of a highly structured liquid, and was then subjected to emulsification.

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References Cited

[1] P. A. Rebinder, *Koll. zhurn.*, **20**, 527 (1958); ibid., **8**, 157 (1946). N. V. Mikhailov, S. Ya. Shalyt, *Koll. zhurn.*, **18**, 609 (1956). [3] L. Ya. Kremnev, *Koll. zhurn.*, **20**, 546 (1958). [4] A. B. Taubman, A. F. Koretskii, *DAN*, **120**, No. 1, 126 (1958); *Koll. zhurn.*, **20**, 676 (1958).

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