PHYSICAL CHEMISTRY

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Fig. 1

Figure 1: Fig. 1

Abstract

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RHEOLOGICAL PROPERTIES OF SURFACE LAYERS AT THE OIL-WATER INTERFACE AND THEIR ROLE IN THE STABILITY OF PETROLEUM EMULSIONS

(Presented by Academician A. V. Topchiev, 15 IV 1957)

Petroleum emulsions possess high stability, associated with the formation on the drops of emulsified water of protective surface layers that have enhanced structural-mechanical properties, preventing aggregation and coalescence of the drops ((^1)). To study the rheological properties of surface layers at the oil-water interface, an instrument of the torsion-pendulum type was used. In measurements on such an instrument, the surface layer is inseparable from the bulk phases, and therefore, in determining the rheological characteristics of surface layers, it is necessary to introduce corrections for the viscous resistance of the bulk phases. The results obtained in studying the surface properties of layers at the oil-water interface show that, depending on the composition of the hydrocarbon and aqueous phases, the time of layer formation, temperature, and other factors, three types of motion of the torsion pendulum can be distinguished: (a) damped oscillations, (b) aperiodic motion, and (c) elastic-viscous motion. The most complete information on the nature of the rheological properties of surface layers can be obtained from observation of the elastic-viscous motion of the torsion pendulum.

Fig. 1. Curves of deformation ( ) of the surface layer at the interface between Mukhanovskaya petroleum and a solution of common salt (15% NaCl, pH 6.4) at different values of the applied torque (M_{mean}). Experimental temperature 20-21°, aging time 6.1-7.7 hr.

Typical curves of the development of layer deformation with time for surface layers at the oil-water interface at different magnitudes of the torque are given in Fig. 1. Analysis of these curves shows that the development of deformation of surface layers at the oil-water interface proceeds analogously to the development of deformation in adsorption layers of saponin ((^2)), and also in bulk structured systems ((^{3,4})). Such a form of the deformation-time curves may be caused by the simultaneous development of three types of deformation: instantaneous elastic deformation, deformation of elastic aftereffect, and irreversible flow deformation. -

respectively, the rheological properties of surface layers at the oil-water interface may be characterized by: the viscosity ( ) of irreversible flow, the modulus (E_0) of instantaneous deformation, the modulus (E_p) of elastic aftereffect, the total modulus (E_m) of elastic deformation, defined by the equation (E_m$^{\text{-1}=\text{E\_0}}${-1}+E_p^{-1}), the conditional viscosity (_p) of elastic aftereffect, and the relaxation time (_p) of the elastic aftereffect. For surface layers at the oil-water interface, as a rule, no static elastic limit was observed below which the deformation would be completely reversible; this was also found for adsorption layers at the interface between a saponin solution and air ((^2)).

To investigate the influence of the nature of the oil on the properties of surface layers, the rheological characteristics of surface layers at the interface with a 15% NaCl solution (pH 6.3-7.0) were studied for a number of oils from eastern fields. The results obtained are summarized in Table 1.

Table 1

Physicochemical properties of eastern oils and rheological properties of their surface layers at the interface with NaCl solution (15%) at a temperature of 20°, layer-formation time 16-24 h, and pH of the aqueous solution 6.3-7.0

Oil	Producing horizon	Density (_4^{20}), g/cm^3	Kinematic viscosity (_{20}), cSt	Silica-gel resins, wt. %	Asphaltenes, wt. %	Paraffin, wt. %	Viscosity, irreversible flow ( ), surface poise	Viscosity, elastic aftereffect (_p), surface poise	Instantaneous modulus (E_0), dyn/cm	Elastic-aftereffect modulus (E_p), dyn/cm	Total modulus (E_m), dyn/cm	Relaxation time of elastic aftereffect (_p), sec
Zolninskaya	Devonian	0.7993	3.1	2.16	0.26	4.87	12800	8700	38	65	24	130
Shkapovskaya	Devonian (IV bed)	0.8167	8.2	6.61	1.26	–	980	230	1.1	1.8	0.7	138
Bavlinskaya	Devonian	0.8368	7.9	7.58	1.75	5.62	11100	4200	36	16	11	250
Mukhanovskaya	Carboniferous (I bed)	0.8485	11.8	7.12	1.60	7.5	1020	590	8.3	2.6	2.0	300
Tuimazinskaya	Devonian	0.8493	10.6	7.32	1.56	~7	6700	5700	19	33	12	175

Oil	Producing horizon	Density (_4^{20}), g/cm^3	Kinematic viscosity (_{20}), cSt	Silica-gel resins, wt. %	Asphaltenes, wt. %	Paraffins, wt. %	Viscosity irreversible flow ( ), surface poise	Viscosity, elastic aftereffect (_p), surface poise	Instantaneous modulus (E_0), dyn/cm	Elastic-aftereffect modulus (E_p), dyn/cm	Total modulus (E_m), dyn/cm	Relaxation time of elastic aftereffect (_p), sec
Kalinovskaya	Permian	0.9881	219.5	9.38	2.39	3.54	31	–	–	–	–	–
Radaevskaya	Devonian	0.9043	165	26.0	4.3	4.9	4100	4000	38	21	13.5	190

The dependence of the rheological properties of surface layers on the content of the polar part of the oil and of other components entering into the composition of the layers was studied for layers of Romashkino oil at the interface with distilled water. To reduce the concentration of polar substances, the oil was diluted with a low-viscosity mixture of vaseline oil and nonpolar kerosene. Figure 2 gives (in logarithmic coordinates) the isotherm of surface viscosity over a concentration interval from 0 to 100%. In accordance with the maximum values of surface viscosity, the surface layers in the concentration interval from 0.5 to 10% possess elastic properties; their isotherms, as well as the isotherms of the viscosity of irreversible flow for different torques, are shown in Fig. 3.

The surface layers of individual oils at the oil–water interface possess high elastic-viscous properties: the magnitude of the surface viscosity reaches values on the order of (10^4) surface poise. Comparison of the general physicochemical properties of the oils (density, viscosity, content of resins and asphaltenes) and the rheological properties of the surface layers at the interface with water shows that, although with increasing density and viscosity of oils there is an increase in the content of asphalt-resin substances, which are among the main components of surface layers, the change in the elastic-viscous properties of the layers does not follow parallel to the change

content of asphaltenes and resins. The absence of such a dependence is evidently connected with the fact that the strength characteristic of the layers is determined primarily not by the absolute content in the oil of the components entering into the composition of the layer, but by their physicochemical nature. Therefore, the more “heavy”oils (Kalinovskaya, Radaevskaya) form a less viscous and strong layer,

Fig. 2. Isotherm of surface viscosity η for solutions of Romashkino oil at the interface with water. Experimental temperature 20°, aging time 4.0–4.5 h.

than the more “light” oils (Zolninskaya, Bavlinskaya, Tuymazinskaya). The

Fig. 2. Isotherm of surface viscosity η for solutions of Romashkino oil at the interface with water. Experimental temperature 20°, aging time 4.0–4.5 h.

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isotherms of the viscoelastic properties of surface layers of Romashkino-oil solutions at the interface with water (Figs. 2 and 3) have a sharply pronounced maximum at an oil concentration of 1-2%.

The occurrence of a maximum in the strength of surface layers at the interface with water in the region of dilute oil solutions is evidently connected with more intense gel formation of asphaltic-resinous substances in the surface layer, caused by dilution of the oil with a nonpolar solvent containing little aromatics, since it is known (1) that hydrocarbons of the paraffin and naphthene series are coagulants of asphaltic-resinous substances, whereas aromatic hydrocarbons serve as their peptizers. In addition, dilution of oil with a nonpolar solvent lowers the concentration of asphaltenes and resins in the mixture, which apparently facilitates the formation of paraffin microcrystals, since asphaltic-resinous substances retard its crystallization. At the same time, dilution decreases the content in the solution of substances entering into the composition of the layer, which should lead to a decrease in strength. As a result, at the beginning of dilution of the oil with a nonpolar solvent, the strength of the layer increases, reaches a maximum, and then rapidly falls. This decrease in the values of the parameters of the viscoelastic properties of the surface layer should correspond to a decrease at the oil–water interface in the content of surface-active substances (acids, resins, asphaltenes, etc.) and other components (paraffin microcrystals, mineral particles, etc.) that provide the strength properties of the layer. This should occur in the region far from saturation concentrations of the layer components, which is also observed for solutions of Romashkino oil, for which the decrease in viscosity and strength of the layer occurs at concentrations from 0 to 1%, while saturation of the layer with surface-active substances corresponds to a concentration of about 8%.

Investigation of the influence of the composition of the oil and aqueous phases, temperature, time of formation of the layer, and other factors on the rheological properties of surface layers will make it possible to substantiate the choice of a method for dehydrating and desalting this oil, to characterize its parameters, and to evaluate the effectiveness of demulsifiers.

Fig. 3. Isotherms of the stress relaxation time (_m= /E_m) and of the elastic aftereffect (_p= _p/E_p), of the surface viscosity of irreversible flow ( ) and of the elastic aftereffect (_p), and of the moduli of elasticity of the total (E_m) and elastic aftereffect (E_p), for the surface properties of solutions of Romashkino oil at the interface with water for various values of the twisting moment (M). Experimental temperature (20^{ }), holding time 4.0–4.5 h.

Fig. 3. Isotherms of stress relaxation time (_m= /E_m) and elastic aftereffect (_p= _p/E_p), surface viscosity of irreversible flow ( ) and elastic aftereffect (_p), elastic moduli of the total (E_m) and elastic aftereffect (E_p) for the surface properties of solutions of Romashkino oil at the interface with water at various values of the twisting moment (M). Experimental temperature (20^{ }), holding time 4.0-4.5 h.

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