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MECHANICAL BEHAVIOR OF UNSTABLE EMULSIONS

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UDC 532.135:541.18.051.3

Results of experimental studies of the rheologic properties of unstable macroemulsions of the water — oil type are presented. A region of non-Newtonian behavior of the test emulsions is identified.

The rheologic properties of emulsions are far from completely studied, since emulsions are systems difficult to investigate.* This is associated with the fact that the dispersed phase is a deformable fluid. The degree of deformation depends on the globule size and on the shear rate. Special difficulties arise in studies of the rheologic properties of unstable emulsions.

This paper is devoted to a presentation of experimental methods and results for a study of the rheology of unstable macroemulsions of the water — oil type. The emulsions were produced by turbulent mixing of transformer oil and an aqueous solution of 4411 disolvane at a concentration of 0.02 wt. % during their joint flow in a horizontal cylindrical pipe.

Differing degrees of emulsion dispersion were achieved by varying the mean flow velocity ($w = 1.3$ m/sec and $w = 1.7$ m/sec). The content of the dispersed phase varied from 0 to 0.35; stratification of the flow occurred at large Φ with subsequent inversion of emulsion phases.

Since the emulsions studied were unstable, it was not possible to investigate their viscous properties under static conditions. Viscosity measurements of such emulsions were accomplished directly in the flow by means of a capillary method. The essentials of the method developed for this purpose are illustrated by the scheme shown in Fig. 1.

The glass capillary 2 was inserted in the experimental pipe 1 with an internal diameter of 39.4 mm along which the unstable emulsion flowed. The capillary tube was held in position by means of a brass fitting equipped with a packing gland and sealing nut. The capillary was inserted at right angles to the flow so that the upper end of the tube was located on the axis of the pipe. The lower end was inserted in the stopcock 3, which was connected to the calibrated sealed vessel 4 by a flow passage considerably greater than the internal diameter

*The rheology of colloidal systems has been developed in detail.

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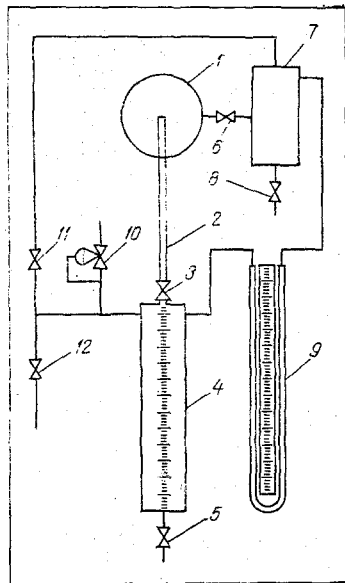


Fig. 1. Arrangement for measurement of the viscosity of unstable emulsions.

of the capillary, as was the case at the fitting; this ensured free discharge of emulsion from the capillary into the vessel 4. From the latter, the emulsion was drained into a cylinder for settling by means of the valve 5.

A pressure takeoff which connected with the transparent separatory vessel 7 was constructed in the same plane as the capillary and at the level of its upper end. The connecting line was horizontal and could be shut off by the valve 6. Emulsion entering the separatory vessel from the pipe was forced back into the pipe by compressed air fed from a compressor through the valves 12 and 11 so that the fluid level in the separatory vessel did not exceed the level of the connecting line and, consequently, the level of the upper end of the capillary. Thus, the air pressure in the separatory vessel was kept equal to the pressure in the pipe. After an experiment, the emulsion was drained from the separatory vessel 7 through the valve 8. The required pressure differential on the capillary was maintained through the establishment of a definite pressure in the measuring vessel 4 by means of the spring-loaded pressure regulator 10 after the valve 11 had been closed. The pressure differential was measured with the U-shaped differential manometer 9 having a mercury or water filling.

The dimensions of viscometer parts (length and radius of capillary, vessel volume) were selected so that a laminar flow mode was realized in the capillary and the measuring time fell within the range

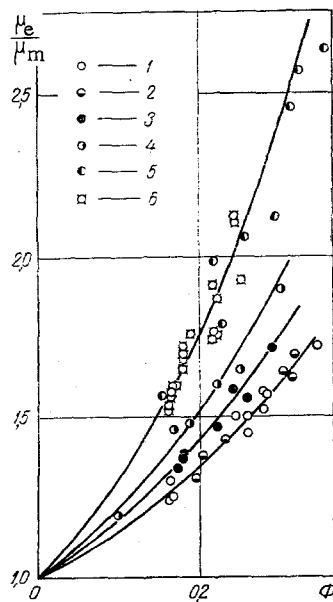


Fig. 2. Dependence of relative viscosity of water — oil emulsion on content of dispersed phase: 1-6) $d_{av} = 0.18$ mm; $P_s = 95.5, 87.15, 56.65, 41.65, 24.15,$ and 16.67 N/m².

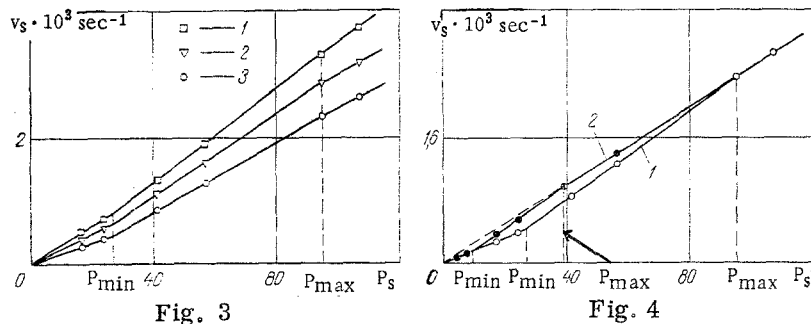


Fig. 3. Flow curves for water — oil emulsions: 1-3) $d_{av} = 0.18$ mm; $\Phi = 0.1, 0.2,$ and 0.3 . P_s , N/m^2 .

Fig. 4. Flow curves for water — oil emulsions: 1, 2) $\Phi = 0.3$; $d_{av} = 0.18$ and 0.306 mm.

100-600 sec. The longer the capillary, the greater the confidence in the accuracy of viscosity measurements; however, stratification of phases can occur in a long capillary in the case of unstable emulsions. It was found experimentally that the most suitable capillary length was 15-20 cm. In the present case, viscosity measurements were made with a capillary 19 cm long having an internal diameter of 2.94 mm.

Viscosity measurements were made in the following way. After establishment of the emulsion flow mode in the pipe and of the pressure differential on the capillary, the stopcock 3 was opened. The emulsion began to flow out of the pipe into the measuring vessel through the capillary. When a stable flow was established, the time taken to fill a given volume of the measuring vessel 4 was determined with a stopwatch and valve 3 was closed. The emulsion was drained into the cylinder and the content of dispersed phase determined after settling.

Calculation of the effective viscosity of the emulsion including losses on entrance and exit was carried out in accordance with the equation derived by Langhaar [1]:

$$\mu_{ef} = \frac{\Pi r^4 \Delta p}{8 l Q} - 0.149 \frac{\rho_e Q}{\Pi l} \quad (1)$$

The emulsion density was calculated from the rule for additivity of the fractions of the two fluids present:

$$\rho_e = \rho_m(1 - \Phi) + \rho_{ph}\Phi \quad (2)$$

The shear rate and shear stress were calculated from the equations

$$v_s = \frac{4Q}{\Pi r^3} \quad (3)$$

$$P_s = \frac{\Delta p r}{2l} \quad (4)$$

The degree of dispersion of the emulsion was estimated by means of numerous observations with a microscope. A sample for study was taken directly from the pipe and quickly deposited in a thin layer on a glass slide, which prevented coalescence of water globules. The emulsions studied were polydisperse systems. Their degree of dispersion was characterized by an average globule diameter which was calculated from a given distribution by the method of the mean volumetric diameter:

$$d_{av} = \sqrt[3]{\frac{\sum_{i=1}^k n_i d_i^3}{\sum_{i=1}^k n_i}} \quad (5)$$

The average diameter of water globules in a water — oil emulsion was 0.306 mm for a flow rate of 1.3 m/sec, and 0.18 mm for a flow rate of 1.7 m/sec.

Emulsion viscosity measurements were made for various values of capillary pressure differential. Figure 2 shows the dependence on dispersed-phase content of the relative viscosity of a water — oil emulsion with $d_{av} = 0.18$ mm obtained for various values of the shear stress. Analysis of the curves shows

that emulsion viscosity increases as the dispersed-phase content increases. In the defined range of shear stresses, emulsion viscosity decreases as P_s increases. There are limiting maximum and minimum values of shear stress at which the viscosity of the test emulsion ceases to depend on the shear stress. The upper curve in Fig. 2 gives the dependence of the maximum viscosity of a water — oil emulsion on dispersed-phase content, and the lowest curve shows how the minimum viscosity of the same emulsion varies with Φ .

The curve for maximum viscosity is described by the Brinkman equation [2],

$$\mu_e = \mu_m(1 - \Phi)^{-2.5}, \quad (6)$$

which is obtained from the Einstein equation [3, 4] for a large number of globules in an emulsion without consideration of deformation. The curve for the minimum viscosity is described by the Leviton and Leighton equation [5],

$$\ln \frac{\mu_e}{\mu_m} = 2.5 \left(\frac{\mu_{ph} + 0.4\mu_m}{\mu_{ph} + \mu_m} \right) (\Phi + \Phi^{5/3} + \Phi^{11/3}), \quad (7)$$

which the authors obtained from the Taylor equation [6] by extending its region of application to more concentrated emulsions with $\Phi \leq 0.4$.

Figure 3 shows the dependence of shear rate on shear stress, or the so-called flow curves, for water — oil emulsions with different dispersed-phase contents. The curves clearly show that one can pick out three straight sections in each of the three flow curves presented.

Drops of a test emulsion having an interphase tension of $14.2 \cdot 10^{-3}$ N/m² underwent deformation in the flow. When $P_s < P_{min}$, the deformation was so small it did not have a significant effect on the viscosity of the emulsion and therefore the initial portions of the curves in Fig. 3 are straight lines starting from the origin. The slopes give the value of the maximum viscosity described by the Brinkman equation.

The effect of drop deformation on the rheologic properties of an emulsion appears in the following manner. Globules of the dispersed phase are elongated with the rise in applied stress as the flow rate increases, changing from spheres to ellipsoids. The deformation of a drop, which is associated with an increase in its surface, requires an additional shear stress. At the same time, drop orientation along the flow occurs which results in a decrease in the expenditure of energy to overcome resistance to the flow of the dispersion medium around a globule and leads to a reduction in the effective viscosity. Deformation and orientation of globules in the flow results in non-Newtonian behavior of an emulsion in the region $P_{min} < P_s < P_{max}$ where the rheologic equation of the emulsion has the form

$$P_s = P_0 + \mu_e v_s. \quad (8)$$

At high shear rates, the drops in an emulsion will be maximally deformed and oriented in the flow, and the emulsion viscosity, having reached a minimum value, will cease to depend on the shear rate. In the flow curves shown in Fig. 3, the minimum value of the viscosity corresponds to the linear portions obtained when $P_s > P_{max}$. These final linear portions once again show a proportionality between shear stress and shear rate.

Figure 3 indicates that the values of μ_e and P_0 appearing in Eq. (8) are functions of the dispersed-phase content. For μ_e , this functional relation takes the form of a quadratic function:

$$\frac{\mu_e}{\mu_m} = 1 + 0.25\Phi + 4\Phi^2. \quad (9)$$

Measurements of the viscosity of water — oil emulsions of a low degree of dispersion ($d_{av} = 0.306$ mm) performed over a wide range of shear stresses (from 3.79 to 56.65 N/m²) also revealed the existence of maximum and minimum viscosities which are described by the same equations (6) and (7). The presence of water globules of larger size in the emulsion changes the shape of the rheologic curve somewhat. Figure 4 compares flow curves for water — oil emulsions differing in degree of dispersion. Drops of larger size are subject to deformation at lower values of shear stress. For a water — oil emulsion with $d_{av} = 0.18$ mm, $P_{min} = 27$ N/m²; for a water — oil emulsion with $d_{av} = 0.306$ mm, $P_{min} = 10$ N/m². The linear portion of curve 2 (Fig. 4) from P_{min} to P_{max} has the same slope as the corresponding portion of curve 1 [the slope gives the value of μ_e in Eq. (8)], but it is shorter and intersects the abscissa at a lower value of P_0 . The additional shear stress has a higher value for the more disperse emulsions. Thus, P_0 is a function of dispersed-phase content and of the degree of dispersion of an emulsion.

NOTATION

$\rho_m, \rho_{ph}, \rho_e$, densities of dispersion medium, dispersed phase, and emulsion, respectively; kg/m^3 ;
 μ_m, μ_{ph}, μ_e , viscosities of dispersion medium, dispersed phase, and emulsion, respectively, $\text{N}\cdot\text{sec/m}^2$;
 μ_{ef} , effective viscosity of emulsion, $\text{N}\cdot\text{sec/m}^2$; Φ , volumetric concentration of dispersed phase; d_{av} , average volumetric diameter of globule, mm; n_i , number of globules with diameter d_i ; k , number of globule sizes; w , average velocity of emulsion in a tube, m/sec; Q , volumetric emulsion flow rate in a capillary, m^3/sec ; r, l , radius and length of capillary, m; Δp , pressure differential on capillary, N/m^2 ; v_s , shear rate, sec^{-1} ; P_s , shear stress, N/m^2 ; P_{min}, P_{max} , limiting minimum and maximum shear stresses, N/m^2 ; P_0 , additional shear stress, N/m^2 .

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IMPROVEMENTS IN THE DYNAMIC THERMOCOUPLE TECHNIQUE

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UDC 537.562.083

The paper describes an improved method for measuring the temperature of a low-temperature plasma. The method has been verified experimentally. An electronic method for inserting the thermocouple into the plasma is described. An error analysis is given.

Reiser and Olsen [1] describe a method of measuring the temperature of a low-temperature plasma using a periodically heated thermocouple. The essence of the method is that a thermocouple is inserted into the plasma for a time t_1 , and then cools for a time t_2 . The process is repeated a number of times, and then the experiment is changed so that the time spent in the plasma is t_3 and in cooling, t_4 . For this situation the energy-balance equation is

$$\int_0^{t_1} Q_1 dt = \int_0^{t_2} Q_2 dt, \quad \int_0^{t_3} Q_3 dt = \int_0^{t_4} Q_4 dt. \quad (1)$$

The heat flux values in Eq. (1) are replaced by the expressions

$$\begin{aligned} Q_1 &= \alpha_1 S (T_c - \bar{T}_1), \quad Q_2 = \alpha_2 S (\bar{T}_1 - T_0), \\ Q_3 &= \alpha_1 S (T_c - \bar{T}_2), \quad Q_4 = \alpha_2 S (\bar{T}_2 - T_0). \end{aligned} \quad (2)$$

From Eqs. (1) and (2), using the fact that T_0 is known, we finally obtain

$$T_c = \bar{T}_2 + \frac{T_1 - T_2}{1 - \frac{\bar{T}_1 t_1 t_4}{\bar{T}_2 t_2 t_3}}. \quad (3)$$

To implement the technique we developed a device for periodically exposing the thermocouple to the test plasma. The periodicity is generated by a light beam, interrupted by a synchronous rotating shutter and a photodetector, which controls the periodic insertion of the thermocouple.

Artem Dnepropetrovsk Mining Institute. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 30, No. 3, pp. 473-477, March, 1976. Original article submitted August 14, 1975.

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