STUDY OF THE MECHANICAL PROPERTIES OF THIN LIQUID LAYERS IN CONCENTRATED EMULSIONS BY THE FILTRATION METHOD

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Abstract

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STUDY OF THE MECHANICAL PROPERTIES OF THIN LIQUID LAYERS IN CONCENTRATED EMULSIONS BY THE FILTRATION METHOD

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Previous investigations established that the normal viscosity in low-volatility nonpolar liquids is retained up to the solid surface, and in polar liquids up to the boundary of solvated layers (^{1}).

To study the mechanical properties of volatile liquids (aqueous electrolyte solutions), we used a filtration viscometer; highly concentrated benzene-water emulsions stabilized with saponin served as the narrow-pore filter. In addition, observation of the influence of filtration on the stability of the system can give a direct indication of the role of the mechanical properties of thin layers in emulsion stability. The structure of the emulsion is visible in the microphotograph (Fig. 1). The good visibility of the system under the microscope and the formation of aqueous layers by parallel* boundary surfaces of neighboring drops facilitate the performance of filtration calculations, making it possible to estimate the magnitude of the viscosity and limiting shear stresses in the liquid under investigation.

When the temperature is lowered to 0°, +5.5° C, the benzene drops become solid, while the aqueous layers remain liquid.

The thickness of the layers was determined by dividing the volume of the aqueous medium contained in a unit volume of the system by half of its specific surface area. The latter was found from the microphotograph of the emulsion by the formula (^{4}):

$$\Omega = \frac{4}{\lambda},$$

where λ is the mean value of the segment intercepted on an arbitrary straight line by the walls of the drops.

Calculations carried out for emulsions limiting in concentration, prepared with a 10% aqueous saponin solution, showed that the average thickness of the aqueous layers is of the order of 10^{-5} cm. The small thickness of the layers ensures a low value of the viscous stresses in the liquid during filtration at readily measurable pressure differences, which makes it possible to detect very small plastic shear stresses in liquids that do not strictly obey Newton' s law and follow the well-known Shvedov-Bingham law.

At the same time, at relatively high values of the pressure difference, the true viscosity of the liquid in the thin layer can be determined.

The preparation of emulsions of extremely high concentration was carried out by means of a spiral in a measuring cylinder (^{5}) (97.3-97.6% benzene and 2.4-2.7% aqueous stabilizer solution). Attempts to increase the concentration of benzene in all cases led to the separation of its excess amount on the surface of the system. The emulsion was placed in a special holder with a chamber 5.5 cm in diameter and 0.6 cm thick, to which on one side water was supplied under pressure, and to the other was attached a thin measuring tube placed in a horizontal position.

To determine the magnitude of the true viscosity, filtration was carried out at heads of the order of 100 cm. To determine the limiting shear stresses, the head was reduced to a value corresponding to the initial filtration gradient, at which the motion of the liquid practically ceased. The shear strength of the liquid in the layers was also determined from deviations of filtration from Darcy' s law as the head was lowered.

To determine the order of magnitude of the viscosity and the magnitude of the shear stresses at the boundary surfaces, the following approximate expressions were used, based on the known equations for the motion of a liquid between parallel walls:

$$\eta = \frac{\rho g \chi H^3 I}{R 12 q_{\mathrm{ud}}}; \qquad \tau_0 = \frac{\rho g \Pi}{\Omega} I_0. \tag{1}$$

Here q_{ud} is the specific flow rate per unit cross section of the specimen; R is a coefficient taking into account the tortuosity of the filtration paths; I is the head gradient; I_0 is the initial gradient; Π is the porosity; χ is the specific perimeter of the layers in the filter cross section, determined from the relation $2\chi = \Omega$. For the case of flow around emulsion drops one may put $R = 2$.

To determine the value of τ_0 from the deviation of filtration from Darcy' s law, one may, using the known solutions for viscoplastic flow (6), obtain the following equation, establishing the relation between the initial filtration gradient I_0 and the ratio of the actual flow rate q, at gradient I, to the flow rate q_D that should

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* The parallelism of the boundary surfaces of free films was established experimentally (^{2}) and follows from the theory of equilibrium of such layers (^{3}).

have passed through the filter at this head under strict obedience of filtration to Darcy’ s law:

$$\left(\frac{I_0}{I}\right)^3 - 3\left(\frac{I_0}{I}\right) - 2\left(\frac{q}{q_D} - 1\right) = 0.$$

The main conclusions from the experiments carried out are that the liquid contained in the thin layers separating individual drops has the normal viscosity characteristic of the liquid in bulk; at the same time, traces of plasticity were found in it, manifested in the form of a limiting shear stress τ_0 of the order of $5 \cdot 10^{-3}$ dyne $\cdot$ cm^{-2}, which is overcome during the motion of the liquid.

These conclusions apply both to the layers separating liquid drops and to the layers separating solidified benzene particles.

Let us give an example of the determination of η and τ_0 for an emulsion of concentration 97.5%. By the method described above, the following values of the specific surface and the wetted perimeter were obtained: $\Omega = 5200$ cm^{-1} and $\chi = 2600$ cm^{-1}. Dividing the specific volume of the aqueous medium by half the specific surface, we find that the mean thickness of the layers is $0.96 \cdot 10^{-5}$ cm. At a head of 100 cm and a specimen thickness of 0.5 cm, a flow passed through the filter characterized by the specific flow rate $q_{\text{ud}} = 2.55 \cdot 10^{-6}$ cm/sec. Substituting the above values into the formula for the viscosity η, we find that it has the value $0.734 \cdot 10^{-2}$, which in order of magnitude coincides with the usual value of the viscosity of water at room temperature*.

* The observed deviation is readily explained by the fact that in the calculation we did not take into account the presence of Gibbsian thickenings at the places where boundary surfaces come into contact. As the degree of dispersion of the system increases in the process of emulsification, the layers separating the newly arising boundaries must be formed mainly at the expense of the volumes of liquid contained in these triangles. In the emulsions of limiting concentration investigated, these thickenings, at first clearly visible, disappear from view, and, consequently, their size cannot be more than 0.2–0.3 μ. Knowing this size, it is easy to calculate the part of the flow that can pass through such paths.

Using the formula for flow through triangular capillaries,

$$q = \frac{\sqrt{3}\, a^4 \rho g I}{R 32 l\, \eta},$$

To determine the value of τ_0 in the case under consideration, the results of filtration experiments through one and the same specimen at heads of 1 m and 1.5 cm were compared; from the ratio q/q_D the value of the initial filtration gradient $I_0 = 0.6$ was found, and from formula (1) it was determined that the value of τ_0 is of the order of $3 \cdot 10^{-3}$ dyne $\cdot$ cm^{-2}.

Figure 2

Figure 1: Figure 2

Figure 3

Figure 2: Figure 3

In order to check the influence of the electrolyte content in the aqueous solution on the thickness of the layers and on the course of filtration, a series of experiments was carried out with emulsions prepared on aqueous solutions with different electrolyte (NaCl) contents, namely: $10^{-4}N$, $10^{-3}N$, $10^{-2}N$, and $10^{-1}N$.

Through the emulsions was filtered the same aqueous solution that had been used to prepare the emulsion.

Fig. 2. Course of filtration of aqueous solutions through emulsion specimens: a $-10^{-1}N$, b $-10^{-2}N$, v $-10^{-3}N$, g $-10^{-4}N$

The experimental results show that, with an increase in the electrolyte concentration, the filtration flow decreases (Figs. 2 and 3). From the microphotographs it was also evident that, as the electrolyte concentration increased, the dispersity of the system increased, which corresponds to a decrease in the mean thickness of the aqueous layers.

Fig. 3. Volume of electrolyte solution of different concentration filtered through the viscosimeter over equal intervals of time: 1 –after 10 min., 2 –after 20 min., 3 –after 30 min.

A decrease in the permeability of emulsion specimens is observed only up to a certain value of the electrolyte concentration, of the order of $10^{-2}N$. When the concentration is increased above $10^{-2}N$, the filtration flow increases again (Fig. 3). The following explanation may be given for this fact.

According to the theory, confirmed by direct experiments (3), with increasing electrolyte concentration, along with the decrease in the thickness of the aqueous layers there occurs a decrease in the limiting value of the wedging pressure developed by them. Both these factors worsen the conditions for droplet breakup, since the mobility of the liquid in the layers decreases as they become thinner, which worsens the possibility of rapid formation of new layers separating the drops, while the decreasing force barrier that prevents coalescence of the drops limits the degree of dispersity, since an increase in the latter entails an increase in capillary

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where a is the size of the side of the triangle; R is the coefficient of tortuosity of the paths, which we must here take as equal to $R = \frac{\pi}{2}$. Taking the viscosity as normal and finding the number of thickenings per 1 cm^2 from the microphotograph ($4.25 \cdot 10^6$ thickenings), we find that in our case the flow passing through these paths is $2.3 \cdot 10^{-7}$ cm • sec^{-1}, i.e., about 10% of the total flow.

of the Laplace pressure on the layer from the side of the drops, arising from their dome-shaped form at the boundary of the filter.

A worsening of the emulsification conditions should lead to retention of the aqueous solution in the Gibbs thickenings and to an increase in the share of their participation in filtration, which is what determines the increase in the permeability of the system.

The preservation of the stability of the emulsion under consideration in the presence of filtration through layers, when the limiting resistance to shear has been overcome, and the change in filtration and dispersity at different electrolyte contents in one medium indicate the thermodynamic character of the equilibrium of the layers, governed in the case considered mainly by the ionic-electrostatic component of the disjoining pressure.

It is also of interest to note that here the gelatinization process of the system is based on forces of molecular and ionic-electrostatic interaction. Indeed, the components of the system possess practically normal fluidity, whereas the system as a whole is a gel possessing a considerable modulus of shear elasticity. The nature of such elasticity has already been considered in earlier works ([7],[8]).

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