AN INVESTIGATION OF THE STABILITY OF HYDROCARBON LAYERS
AT THE BOUNDARY WITH AQUEOUS SOLUTIONS OF DE-EMULSIFIERS

A. A. Petrov and S. A. Blatova

One of the main factors which determines the stability of water-petroleum emulsions is the stability of thin hydrocarbon layers which separate water drops when these undergo collision in the volume of the petroleum. Resistance to the thinning out of these layers arises from the viscous resistance of the liquid forced out from the narrow space between two water drops, together with the resistance determined by the fundamental properties of thin liquid layers, and the properties of surface layers at the separating boundary between the petroleum and the water, which possess structural-mechanical properties and interact during the thinning out of the thin hydrocarbon film. The first type of resistance is characterized by the hydrodynamic pressure $P_d$, which depends on the dimensions of the film, the rate of forcing out, and the viscosity of the liquid forced out. The second type of film resistance may be characterized by the magnitude of the additional pressure, above the hydrodynamic pressure, which is needed to bring about the necessary rate of removal of liquid from the film. In addition, if the surface of the film is curved, the capillary pressure must also be taken into account.

Thus, in the squeezing out of a thin hydrocarbon film present between two water drops, the pressure at any moment of time can be represented by the equation:

$$P_g = P_d + P_k + \pi$$

where $P_g$ is the external pressure applied to the drop; $P_d$ is the hydrodynamic pressure; $P_k$ the capillary pressure; and $\pi$ the additional pressure due to the properties of the thin film and restricting its surface layers.

This additional pressure is the cleavage pressure which was discovered by B. V. Deryagin during an investigation together with M. M. Kusakov [1-3], and represents one of the major factors bringing about the stability of petroleum emulsions. The magnitude of the viscous resistance, characterized by the hydrodynamic pressure, depending on the value of the volume viscosity of the petroleum, may retard to some extent the coalescence of a water drop on collision, but will not be able to ensure prolonged independent existence of the drops. It is seen from Eq. (1) that, in the absence of a structure which would create an additional resistance to forcing out ($\pi = 0$), and for sufficiently small curvature ($P_k = 0$), $P_g$ will be equal to $P_d$, that is, pure viscous forcing out occurs, with $\mu$ having a constant value. On the other hand, if a structure exists which opposes the squeezing out forces, the flow may be completely prevented ($P_g = 0$), so that Eq. (1) is converted into $\pi = P_g$. This provides the basis for a static method of measuring the cleaving pressure [2,4]. In the present work, the stability of the water-petroleum emulsion is characterized by the volume of the additional pressure $\pi$ which arises in the hydrocarbon film during thinning out.

Experimental technique. In calculating the additional resistance from Eq. (1), it is necessary to conduct a preliminary determination of $P_d$ and $P_k$ with respect to the kinetics of the thinning out and the shape of the film surface. We have used for this purpose a microinterferometric method developed by Deryagin and Kusakov [2-4], in a dynamic modification of this as used by Sheludko [5]. The construction of the cell is shown schematically in Fig. 1. The cell is made from optical glass and contains water or an aqueous solution of a surface-active agent, above which is placed a layer of a hydrocarbon liquid.

On lowering into this system a plastic plate with an aperture at the end, and a vertical slot, the hydrocarbon liquid wets the plate, and at the site of the aperture forms a biconcave lens surrounded by the aqueous phase. The curvature of the surface is determined by the equilibrium of the forces at each point, in accordance with Eq. (1). Excess of liquid proceeds via the slot into the upper hydrocarbon layer. As the surface approaches the center of the lens, a circular area of low curvature is formed, in which, depending on the properties of the film, an additional positive or additional negative pressure is developed. Experiment has shown that, although at the center the film is more nearly planar, appreciable curvature exists over the entire surface of the film. To measure the thickness of the film among a meridian-section, we have used a photographed process to observe the thinning out, with subsequent photometric representation section by section, after which the data obtained could be evaluated. The photographing
of the interference picture was carried out using the micro-movie-projector MKU-1, by means of which it was possible to scan at a definite rate, or under stationary conditions. The working wavelength chosen was 586 millimicrometers, which corresponded most closely to the maximum value of the light transmission by the petroleum, and the optimum spectroscopic characteristics of the incandescent lamp, and of the sensitivity of the film, type A-2, thereby creating the most favorable conditions for the exposure of the weak light-beam reflected from the film. To obtain a light beam of the necessary wave-length, a light filter OS-12 was employed. The contrast coefficient of the photo-material, measured by a sensitometry method, was $j = 0.6$.

Depending on the experimental conditions, as has already been observed in other publications [2,4,5], equilibrium or nonequilibrium films may be obtained. In the latter case, the films are obtained with a thickening in the central portion, surrounded by an annular “barrier” portion of less thickness than the center. To illustrate the type of films obtained, we give in Fig. 2 a number of frames of a cine-film obtained photographing a system consisting of a solution of sorbitol monooleate in tetralin at the boundary with an aqueous solution of sodium chloride. Visual analysis of these frames shows that initially (frames 1-7) the interference ring is shifted from the center to the edge of the area, with a non-planar film; while subsequently the thickness increases continuously from the center to the edge. Subsequently a thickening is observed at the center of the film (frames 8-16), which is shifted to one side (frames 17-19), after which is distributed over the entire area (frames 21-24), and finally by a discontinuous process a secondary bimolecular black film is formed, which after some time undergoes rupture.

**Determination of film thickness.** An equation has been proposed by M. M. Kusakov [4] to connect the film thickness $h$ with the ratio between the intensity of the incident light $I_m$ and the reflected light $I_r$, under conditions $n_1 < n_2 < n_3$:

$$I = \frac{I_r}{I_m} = c + d \cos \varphi,$$  \hspace{1cm} (2)

where $\varphi$ is the phase difference between the two beams of light reflected from the first and second surfaces of the film, which for normal incident angle is equal to:

$$\varphi = \frac{4\pi}{\lambda} n h.$$  \hspace{1cm} (3)

The coefficients $c$ and $d$ depend on the optical properties of the film and the surrounding medium. Under conditions for which $n_1 = n_3 < n_2$, which corresponds to the systems investigated by us, $d < 0$, and hence Eq. (2) if a simple $d$ is used to denote the absolute value, undergoes conversion to:

$$I = \frac{I_r}{I_m} = c - d \cos \varphi.$$  \hspace{1cm} (4)

At the limiting points $I$ will take up the following values:

$$I_{\text{max}} = c + d \quad \text{when} \cos \varphi = -1 \quad I_{\text{min}} = c - d \quad \text{when} \cos \varphi = +1.$$  \hspace{1cm} (5)

To simplify the calculations we introduce a parameter defining the relative intensity:

$$I_{\text{RF}} = \frac{I - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}} = \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}} - 1.$$  \hspace{1cm} (6)

Then, by inserting Eqs. (4) and (5) in (6), and taking account of (3), we obtain:

$$I_{\text{RF}} = \frac{1}{2} \left( 1 - \cos \frac{4\pi}{\lambda} n h \right),$$  \hspace{1cm} (7)

from which the thickness of the film may be determined in the form:

$$h = \frac{1}{n} \cdot \frac{\lambda}{4\pi} \left[ \arccos \left( 1 - 2I_{\text{RF}} \right) + 2\pi |k| \right].$$  \hspace{1cm} (8)