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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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INVESTIGATION OF THIN LAYERS OF BENZENE ON THE SURFACE OF MERCURY

(Presented by Academician A. N. Frumkin, 3 January 1961)

The method for studying two-sided (free) films with automatic recording of the film thickness as a function of time enabled us, in a number of works (^{1}), to obtain isotherms of the disjoining pressure; moreover, also in the region where it is negative, the film is unstable and, as a result, other static methods (^{2,3}) do not make it possible to determine the magnitude of the disjoining pressure. The present work describes the application of this method to the study of liquid films on a foreign substrate; thus, it is a continuation of the works of B. V. Deryagin and M. M. Kusakov (^{2}) and A. N. Frumkin (^{4}). Mercury was chosen as the substrate because of the homogeneity of its surface. The apparatus used in principle does not differ from the apparatus for studying two-sided films (see (^{1}); the method is described in more detail in (^{5})). The main difference lies in the design of the measuring cell, which makes it possible to obtain wetting films of liquid on the surface of mercury. A microscopic film c on the surface of mercury is formed by suction of the liquid through capillary d (Fig. 1). The entire cell is placed in a closed space saturated with vapors of the liquid under investigation. The thickness of the thin layer is measured interferometrically in reflected monochromatic light. The brightness of the reflected light is recorded as a function of time t, which makes it possible to construct curves $h = h(t)$ (h is the layer thickness). The strong background caused by light reflected from the mercury surface is compensated with the aid of a second photomultiplier illuminated from the same source (a high-pressure mercury lamp), which is necessary for weakening the influence of fluctuations of the light of the latter.

Fig. 1

From the experimentally obtained photocurrent-time curves, it is necessary, as before (^{1}), to calculate the film-thickness-time curves. In the present case, because the reflectivities of the two surfaces are different, more complicated formulas must be used:

Fig. 2

Figure 2: Fig. 2

$$\sin^2\left(\frac{2\pi n_0 h}{\lambda} - \frac{\delta}{2}\right) = -\frac{\Delta}{1 + \dfrac{4\sqrt{RG}}{(1-\sqrt{RG})^2}(1-\Delta)},$$

$$\Delta = \frac{I - I_{\min}}{I_{\max} - I_{\min}}, \qquad \operatorname{tg}\delta = \frac{2n_0 k}{n_0^2 - n^2 - k^2}, \tag{1}$$

$$R = \left(\frac{n_0 - 1}{n_0 + 1}\right)^2, \qquad G = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2}.$$

Here I is the instantaneous value of the brightness of the light reflected from a thin liquid layer; $I_{\max}$ and $I_{\min}$ are the maximum and minimum values of this brightness; h is the film thickness; λ is the wavelength of the monochromatic light; n_0 is the refractive index of the liquid; n and k are the optical constants of mercury; δ is the phase shift upon reflection from the mercury surface; R is the coefficient of reflection of light from the liquid surface, and G is the coefficient of reflection of light from the lower surface of the film at the boundary with mercury. The magnitude of the phase shift δ can be calculated using literature data for n_0, n, and k, or else using the value of I at h tending to zero when the cell is blown through with air. From the agreement of the two values one can check how far the mercury surface under the liquid being investigated has remained unchanged and, consequently, how reliably the thickness values can be calculated from the brightness of the reflected light. We tested ethyl and propyl alcohols, glycerin, aniline, xylene, toluene, benzene, and an aqueous solution of KNO_3 (0.1 mole/l) in this respect. Unfortunately, in all cases except benzene the mercury surface proved to be covered with a layer that changed its reflecting power. This may have been caused in some cases by impurities in the liquids, or by the fact that the work was carried out in air. With benzene, complete agreement was obtained between the values of δ found by both methods, as well as very good reproducibility of the measurements; therefore all the measurements described below were carried out with benzene.

Fig. 2

The photocurrent-time curves were recorded after complete saturation of the measuring cell with benzene vapor (at saturation the mean rate of film thinning is minimal). From these data, using formula (1), the film thickness h was calculated for different instants of time. Figure 2 shows the dependence found in this way

$$\frac{1}{h^2} - \frac{1}{h_0^2} = f(t - t_0),$$

where h_0 is the value of the film thickness at the instant t_0, equal to 1960 Å. The following values of the quantities were used: $\lambda = 4358$ Å, $n_0 = 1.5235$, $n = 0.878$, $k = 3.36$ (the last two values were taken from (^{6})).

To calculate the disjoining pressure Π from the dependence

$$\frac{1}{h^2} - \frac{1}{h_0^2} = f(t - t_0)$$

it is necessary to know the theoretical dependence of

$$\frac{d(1/h^2)}{dt}$$

on the total pressure $P = P_0 - \Pi$, which causes thinning of the film, and also the capillary pressure P_0. The Reynolds dependence used by us for two-sided films (^{7}),

$$\frac{d(1/h^2)}{dt} = aP, \qquad a = \frac{4}{3\eta R^2} \tag{2}$$

(η is the viscosity of the liquid, R is the radius of the disk-shaped film, see Fig. 1), is not applicable in the present case, since at the benzene/air boundary no stationary surface-tension gradient is formed that would ensure zero velocity of tangential flow in the adsorption layer (benzene, when an attempt is made to form from it a two-sided foam film, as we established with Ekserova, always gives an instantaneous rupture). Therefore we calculated the dependence of

$$\frac{d(1/h^2)}{dt}$$

on P for the case in which the flow velocity at one surface of the layer (benzene/mercury) is zero, while at the other (benzene/benzene vapor) the boundary condition is satisfied

condition corresponding to a free surface, namely $\left(\frac{\partial v_r}{\partial z}\right)_h = 0$ (v_r is the radial velocity of flow, the z axis is perpendicular to the surface), by the method used for two-sided films (^{8}). As a result, a dependence analogous to (2) was obtained, but with the value of the coefficient before P four times larger:

$$\frac{d(1/h^2)}{dt} = 4aP. \tag{3}$$

Fig. 3

Figure 3: Fig. 3

The capillary pressure P_0 was calculated from the formula derived by B. V. Derjaguin and A. E. Titievskaya (^{3}), which we substantiated additionally (^{5}), namely

$$P_0 = \frac{4\sigma_1}{r} \frac{\sigma_2}{\sigma_1 + \sigma_2}, \tag{4}$$

where σ_1 and σ_2 are the surface tensions at the benzene/vapor and mercury/benzene interfaces, and r is the radius of the tube with a biconcave drop of benzene on mercury, at the center of which the film is formed (Fig. 1). By graphical differentiation of the dependence $\frac{1}{h^2} - \frac{1}{h_0^2} = f(t - t_0)$, the dependence

$$\frac{d(1/h^2)}{dt} = \varphi(h)$$

was obtained, and from it, using formulas (3) and (4), the isotherm of the disjoining pressure $\Pi = \Pi(h)$ (Fig. 3) was calculated for a layer of benzene on mercury. The isotherm ends at the equilibrium film thickness $h_p = 240$ Å, when $\Pi = P_0$. These values of h_p were reproduced with an accuracy of ±30 Å. The thickness values corresponding to the maximum negative disjoining pressure, and this disjoining pressure itself—namely $h_{\text{min}} = 340$ Å and $-\Pi_{\text{min}} = 11\,500$ —were reproduced still better (h_{min} with an accuracy up to ±10 Å). In this isotherm, the part corresponding to positive disjoining pressures at large film thicknesses ($h > 10^{-5}$ cm) is unreliable, since the values of these pressures are small and close to the errors of measurement. The theory of I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii (^{9}) for the case of a nonmetallic liquid on a metallic substrate at large thicknesses, as is easy to calculate, always gives a positive disjoining pressure and thus confirms our results for this range of thicknesses. In the other limiting case of thin layers, this theory for a nonmetallic liquid on a metal also gives positive values of the disjoining pressure. Thus, the experimentally obtained portion of the disjoining-pressure isotherm for a layer of benzene on mercury agrees qualitatively with the theory in the region of small and large thicknesses. The main part of our results, encompassing considerable negative disjoining pressures, apparently corresponds to the transition region between extremely thick and extremely thin layers and at present cannot be compared with the theory, since the latter contains unknown functions $\varepsilon(\xi)$.

Fig. 3

We also carried out qualitative observations on films of other liquids on mercury. In all cases (ethyl and propyl alcohols, glycerin, aniline, xylene, toluene, and benzene), except for water, the films thinned monotonically after their formation until an equilibrium thickness was reached, which, for the reasons noted above, we were unable to meas-

to form. In films from an aqueous solution of KNO_3 (0.1 mole/l), at a certain thickness, round "holes" suddenly appeared, growing at different and irreproducible rates. This phenomenon, apparently representing an elementary act of flotation adhesion, is being studied by us specially in view of its importance.

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