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Abstract

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SPONTANEOUS THINNING OF THIN DOUBLE-SIDED LIQUID FILMS

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As is known, double-sided liquid films usually thin spontaneously under the action of the suction pressure of their thickened and concave ends. An investigation we carried out (^{1,2}) for comparatively thick films with thickness greater than $0.2\,\mu$ showed that, when the film is plane-parallel, the outflow of solution from it occurs as from a slit and obeys the Reynolds relation

$$\frac{d(1/h^2)}{dt} = \frac{2}{3\eta}\,\frac{b^2+c^2}{b^2c^2}\,P_0, \tag{1}$$

where η is the viscosity of the solution, b and c are the semiaxes of the elliptical film, h is its thickness, t is the thinning time, and P_0 is the capillary pressure causing the thinning. The solutions studied contained 0.1 mole KCl per liter in order to suppress diffuse Gouy electrical layers. In the absence of electrolyte or at its low content, the thinning slowed down to the point of stopping, apparently because of electrostatic repulsion between the Gouy layers (^{3}).

In the present work we investigated the spontaneous thinning of thinner double-sided liquid films for the range of thicknesses between 0.2 and $0.03\,\mu$. The film thickness as a function of time was recorded automatically by means of an interference microphotometer specially constructed by us (^{2}). The investigations were carried out with microscopic $\sim 2\cdot 10^{-2}$ cm double-sided liquid films of aniline with the foam stabilizer 0.5% $C_{12}H_{25}OH$, and with aqueous films containing KCl 0.1 mol/l and the stabilizer OP10 0.01% or sodium oleate 0.0056 mol/l. The concentrations of the stabilizers were chosen to be minimal (film rupture at a thickness of about $0.03\,\mu$) so as, as far as possible, to exclude the influence of adsorption layers on the properties of the film and to avoid rheological changes during their thinning.

Figure 1 gives the dependence of film thickness on time in the coordinates $\frac{1}{h^2} - \frac{1}{h_0^2}$, $t - t_0$ (where h_0 is the thickness at the time t_0), respectively for aniline and water (OP10 and sodium oleate). The dashed straight lines correspond to formula (1). These results show that, beginning approximately with a thickness of $0.1\,\mu$, the thinning rate increases in comparison with the rate corresponding

Fig. 1

Figure 1: Fig. 1

to expression (1), and that this difference increases smoothly as the film becomes thinner.

We see no reason to suppose that the nature of the regime of solution outflow from the film, expressed by relation (1), changes for thicknesses smaller than $0.1\,\mu$. An estimate of the thinning of the film due to its evaporation, caused by the difference in pressure and the corresponding difference in vapor pressure of the film and its thickened ends, shows that this

the correction plays no role for aniline and is minimal for aqueous films. An estimate of the influence of diffusion of the surface-active stabilizer from the bulk of the film to its surfaces on the rate of sliding of the adsorption layer shows that this factor is also minimal and likewise cannot explain the deviations of the thinning rate from the values corresponding to expression (1). Finally, the circumstance that in thin films we observe an **increase** in the rate of drainage evidently excludes the influence on this increase of changes in the rheological properties of the film, for example an increase in its viscosity, in comparison with the properties of the bulk liquid.

Fig. 1

All these considerations lead us to the idea that the accelerated thinning of thin double-sided films, as compared with (1), is caused by the appearance of an additional pressure due in origin to long-range intermolecular forces, i.e., according to Derjaguin, a disjoining pressure, in the present case negative. According to Frenkel' (4), an approximate, estimated calculation of this pressure π for a double-sided liquid film leads to the formula

$$\pi = -\frac{4\sigma\delta^2}{h^3}, \tag{2}$$

where σ is the surface tension of the liquid, and $\delta = \sqrt[3]{\frac{v}{N_A}}$ (v is the molecular volume, N_A is Avogadro' s number) is its molecular diameter. Expression (2), more precisely, the power 3 of h, corresponds to London intermolecular interaction. Such a law is applicable in our case, since the films investigated have a thickness of the same order as λ, and in them, especially in approximate calculations, there is as yet no need to take electromagnetic retardation into account. As is seen from (2), Frenkel' s calculation agrees in sign with our observations.

If an additional negative pressure $-\pi$ appears in the film, then in formula (1) P_0 should be replaced by $P_0 - (-\pi)$, whence for $-\pi$ we obtain

Fig. 2

Figure 2: Fig. 2

$$-\pi = \frac{3\eta}{2}\,\frac{b^2c^2}{b^2+c^2}\,\frac{d(1/h^2)}{dt} - P_0, \tag{3}$$

where $\frac{d(1/h^2)}{dt}$ for various values of h can be calculated by graphical differentiation of the experimentally obtained curves of Fig. 1, and P_0 is determined as $2\sigma/R$ (where R is the radius of curvature of the concave ends of the film, in our case the radius of the tube (0.2 cm) in which the microscopic film is formed). The curves obtained in this way, $-\pi = f(h)$, are presented in Fig. 2 in the coordinates $-\pi$, $1/h^3$, respectively for aniline

and aqueous films (OP-10 and sodium oleate). As can be seen, for aniline (Fig. 2a) good agreement is obtained with the dependence $-\pi \sim 1/h^3$. The slope of these straight lines varied within 10% for different measurements around the mean value $3.7\cdot10^{-13}$, close to that theoretically calculated by Frenkel from equation (2): $4\sigma\delta^2 = 4.8\cdot10^{-13}$ ($\sigma = 43$ and $\delta = 5.3\cdot10^{-8}$ for aniline). For water (Fig. 2b, c), the curves $-\pi = f(h)$* do not coincide with the theoretical curves (dotted straight lines in Fig. 2, I, II –OP-10 and sodium oleate). The obtained values of $-\pi$ are lower than the theoretical ones and, as the film becomes thinner, apparently increase more slowly than $-\pi \sim 1/h^3$.

Fig. 2

All measurements were carried out at room temperature (20°). The values of surface tension and viscosity used in this work were determined by conventional methods. The dimensions of the films (semiaxes b and c) were determined from photographs of the films.

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* Because of the large scatter, curves **b** and **c** for aqueous films were plotted on the basis of several measurements.

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