

Theory of the Critical Thickness of Rupture of Thin Liquid Films

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On the basis of Navier-Stokes equations, the theory of the spontaneous rupture of thin liquid films is generalized by taking into account the influence of the surfactant on the hydrodynamics of the film. Our measurements of the critical thicknesses of rupture of aniline films, stabilized with $C_{12}H_{25}OH$, confirm the theory at low surfactant concentrations. The discussion of the discrepancy between theory and experiment at higher surfactant concentrations shows that the surfactant influences the properties of the thin liquid films in a specific manner.

1. INTRODUCTION

The resistance to rupture of liquid films is important for the behaviour of foams and emulsions in polymolecular adsorption layers and in the phenomena of wetting and flotation. This problem has been studied theoretically¹⁻³ and experimentally^{2, 4-6}

The comparison of the theoretically calculated critical thicknesses of rupture of free liquid films with the experimental data showed an obvious discrepancy.⁵ This was explained by us for small film radii by taking into account³ the energy of the thicker parts (plateau border) surrounding the film. The discrepancy between theory and experiment for the larger film radii, however, could not be explained. In this paper we attempt to explain the discrepancy. On the basis of the Navier-Stokes equations a new calculation of the critical thicknesses was carried out. The same physical reasons were taken into account as in ref. (3) avoiding as much as possible the approximations. The theory was developed also for the case when the flow of the film surfaces was not entirely hindered by the surfactant adsorption. Finally, the influence of the surfactant concentration on the critical thicknesses was experimentally studied. It was shown that the theoretically predicted values of h_{cr} were reached when decreasing the surfactant concentration.

2. SOME IMPORTANT NOTATIONS

A , wave amplitude ;
 c_0 , detergent concentration ;
 h , mean film thickness ; thickness of the uncorrugated film ;
 h_0 , transition thickness ;
 h_c , critical thickness ;
 K , wave number ;
 K_m , wave number of the critical wave ;
 k , Boltzmann constant ;
 K , van der Waals-Hamaker constant ;
 p , pressure ;
 P_y , capillary pressure in the meniscus ;
 r, θ, z , polar coordinates ;
 R film radius.

t , time ;
 T , absolute temperature ;
 v_r, v_θ, v_z , velocity components ;
 $V = dh/dt$, thinning velocity ;
 $v_\zeta = d\zeta/dt$, curving velocity ;
 γ , interfacial tension ;
 ζ , a half of the deviation of the local film thickness from the mean thickness h ;
 η , dynamic viscosity ;
 ν , kinematic viscosity ;
 Π , disjoining pressure ;
 ψ , harmonic function, solution of eqn. (3.5) ;
 ω , wave frequency.

3. STATIONARY FILM WITH HIGH CONCENTRATION OF SURFACTANT

We examine a circular free film of radius R , formed in the centre of a biconcave meniscus. At first, we confine ourselves to a single surface wave (wave number k). We denote the deviation from the flat surface by ζ . If the two surfaces curve symmetrically, the local thickness is $h+2\zeta$ (fig. 1). Our reason for assuming that this curvature is symmetrical is that if at a given point one of the surfaces curves, so will the other under the influence of the increasing (or decreasing) negative disjoining pressure at the same point. We assume throughout that ζ is much smaller than the wavelength or the thickness of the film, so that the boundary conditions on the surface can be defined for $\zeta = 0$. Later we examine the grounds for this assumptions.

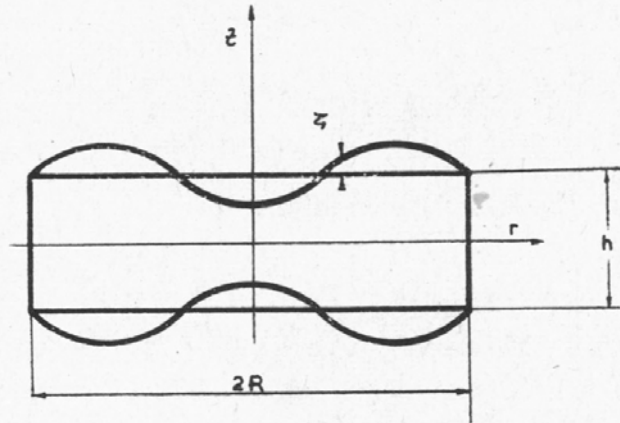


FIG. 1.

We first assume that although $\Pi < 0$, the mean thickness of the film remains constant (stationary film).

The movement of the liquid in the film is then only determined by the surface waves. Since the film is thin* and the flow in it is slow, the latter can be described by the simplified equations of Navier-Stokes; in a cylindrical coordinate system, they are as follows:

$$\frac{\partial v_r}{\partial t} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \frac{\partial^2 v_r}{\partial z^2}, \tag{a}$$

$$\frac{\partial v_\theta}{\partial t} = -\frac{1}{\rho r} \frac{\partial p}{\partial \theta} + \nu \frac{\partial^2 v_\theta}{\partial z^2}, \tag{b}$$

$$\frac{\partial p}{\partial z} = 0, \tag{c} \tag{3.1}$$

$$\frac{1}{r} \frac{\partial}{\partial r}(r v_r) + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z} = 0, \tag{d}$$

in which t is the time; r , θ and z are the cylindrical coordinates; v_r , v_θ and v_z are the velocity components; p is the pressure; ρ is the density; $\nu = \eta/\rho$ is the kinematic viscosity and η is the dynamic viscosity. It was shown in ref. (9) and ref. (11) that at a sufficiently high concentration of surfactant, the adsorption layer of the film does not move tangentially on the surface, and therefore the following boundary conditions are valid:

$$\left. \begin{matrix} v_r = 0 \\ v_\theta = 0 \\ v_z = v_\zeta \\ v_\zeta = \partial \zeta / \partial t \end{matrix} \right\} \text{when } z = \pm h/2 \quad \left. \begin{matrix} \partial v_r / \partial z = 0 \\ \partial v_\theta / \partial z = 0 \\ v_z = 0 \end{matrix} \right\} \text{when } z = 0 \tag{3.2}$$

Eqn. (3.1c) indicates that the pressure p is constant over the entire thickness of the film and is therefore equal to its value on the surface, where it is defined as the

* The concept "thin film" requires a more precise definition, as in this paper it is used in a number of different interpretations. In this instance, it denotes $h \ll R$.

sum of the external pressure p_0 and of the local values of the capillary pressure and the disjoining pressure. With $\zeta \ll h$, the latter can be defined approximately as $\Pi(h+2z) \approx \Pi(h) + 2zd\Pi/dh$. The capillary pressure caused by the local curvature equals $-\gamma\Delta_s\zeta$, in which $\Delta_s = (1/r)[\partial(r\partial/\partial r)/\partial r] + (1/r^2)(\partial^2/\partial\theta^2)$. Since by definition Π is opposed to the capillary pressure, then

$$p = p_0 - \Pi(h) - \gamma\Delta_s\zeta - 2\zeta d\Pi/dh \quad (3.3)$$

For

$$\zeta = A\psi(r, \theta) \exp(\omega t), \quad (3.4)$$

in which ω and A denote the wave frequency and amplitude respectively, the function ψ satisfies the equation¹⁷

$$\Delta_s\psi = -K^2\psi \quad (3.5)$$

with the boundary condition

$$\psi(R, \theta) = 0. \quad (3.6)$$

Substituting (3.3), (3.4) and (3.5) in (3.1a) and (3.1b), and with the boundary conditions (3.2a) and (3.2b), after separating the variables, we obtain

$$\begin{aligned} v_r &= \frac{\gamma K^2 - 2d\Pi/dh}{\rho\omega} \left\{ \frac{\cosh [(\omega/\nu)^{\frac{1}{2}}z]}{\cosh [(\omega/\nu)^{\frac{1}{2}}h/2]} - 1 \right\} \frac{\partial\zeta}{\partial r}, \\ v_\theta &= \frac{\gamma K^2 - 2d\Pi/dh}{\rho\omega} \left\{ \frac{\cosh [(\omega/\nu)^{\frac{1}{2}}z]}{\cosh [(\omega/\nu)^{\frac{1}{2}}h/2]} - 1 \right\} \frac{1}{r} \frac{\partial\zeta}{\partial\theta}. \end{aligned} \quad (3.7)$$

After substituting (3.7) in (3.1d) and integrating with respect to z , with the boundary condition (3.2c), we obtain

$$\begin{aligned} v_z &= K^2 \frac{\gamma K^2 - 2d\Pi/dh}{\rho\omega} \left\{ \frac{\sinh [(\omega/\nu)^{\frac{1}{2}}z]}{(\omega/\nu)^{\frac{1}{2}} \cosh [(\omega/\nu)^{\frac{1}{2}}h/2]} - z \right\} \zeta \quad (a) \\ v_\zeta &= K^2 h \frac{\gamma K^2 - 2d\Pi/dh}{2\rho\omega} \left\{ \frac{\tanh [(\omega/\nu)^{\frac{1}{2}}h/2]}{(\omega/\nu)^{\frac{1}{2}}h/2} - 1 \right\} \zeta. \quad (b) \end{aligned} \quad (3.8)$$

It follows from (3.2d) and (3.4) that

$$v_\zeta = \partial\zeta/\partial t = \omega\zeta: \quad (3.9)$$

therefore, comparing (3.8b) and (3.9), we obtain

$$\omega^2 = K^2 h \frac{\gamma K^2 - 2d\Pi/dh}{2\rho} \left\{ \frac{\tanh [(\omega/\nu)^{\frac{1}{2}}h/2]}{(\omega/\nu)^{\frac{1}{2}}h/2} - 1 \right\}. \quad (3.10)$$

For a sufficiently thick film ($\omega h^2/\nu \gg 1$), and (3.10) gives

$$\omega^2 = -(K^2 h/2\rho)(\gamma K^2 - 2d\Pi/dh),$$

i.e., the viscosity vanishes and the film behaviour is that of a film of ideal liquid. Moreover, if h is sufficiently great, $\gamma K^2 \gg 2d\Pi/dh$ and ω is imaginary. In this instance, we have

$$\omega^2 = \omega_0^2 = -\gamma k^2 h/2\rho \quad (3.11)$$

which, within the factor $\frac{1}{2}$ (relating to the two surfaces of the film), coincides with the frequency of the capillary waves in an ideal liquid in a sufficiently shallow vessel ($Kh \ll 1$).¹⁰ With $\omega h^2/\nu \ll 1$, we obtain

$$\omega = -(K^2 h^3/24\eta)(\gamma K^2 - 2d\Pi/dh). \quad (3.12)$$

A more precise solution of (3.10) indicates that $\omega h^2/\nu \ll 1$ is valid for the aniline films examined experimentally here, for all values of h equal to or smaller than 10^{-5} cm.

For thin films, $d\Pi/dh > \gamma K^2$, $\omega > 0$, and we have an increasing displacement of the curvature. At a definite thickness h_0

$$\gamma K^2 - 2(d\Pi/dh)_{h_0} = 0. \quad (3.13)$$

This equation is equivalent to formula (6) in ref. (2). Vrij³ obtains eqn (3.12) and (3.13) in a different manner.

4. THINNING FILM WITH HIGH CONCENTRATION OF SURFACTANT

In general, the thickness h of the thermodynamically unstable film decreases with time. If the film viscosity and velocity of evaporation are sufficiently low, the thinning is related to the outflow (and not to evaporation) and can also be described by the equations of Navier-Stokes (3.1) with the boundary conditions (3.2), except that the conditions (3.2c) should be replaced by

$$v_z = \pm V/2 + v_\zeta, \quad \text{when } z = \pm h/2 \quad (3.2e)$$

in which $V = -dh/dt$ is the velocity at which the film is thinning.

Since $z \ll h$, it can be assumed that the fluctuations of the film thickness have a negligible effect on its thinning. In this case, the pressure p can be defined as the sum of $p^{(f)}$ the pressure of the outflow from the plane-parallel film and p^* , the perturbation caused by the wave: $p^* = -\gamma\Delta_s\zeta - 2\zeta d\Pi/dh$. Since eqn (3.1) and (3.2) are linear with respect to the velocity components v_i , taking $v_i = v_i^{(f)} + v_i^*$, the system (3.1)-(3.2) can be broken down into two systems.

The solution of the first system (index, f) gives a law analogous to that of Reynolds,^{12, 13}

$$-dh/dt = V = 2(P_y - \Pi)h^3/3R^2\eta, \quad (4.1)$$

in which P_y is the capillary pressure of the biconcave meniscus which stretches the film.

The second system (index, asterisk) takes into account the wave motion of the surface of the thinning film. These equations are of the same kind as (3.1)-(3.2). As we shall be solving only this system, we shall not use the index asterisk. In this case, $h = h(t)$ and it is not possible to obtain a solution by separating the variables. It is therefore necessary to simplify (3.1). We take a characteristic time $\tau \sim \omega^{-1}$. In this case, $\partial v/\partial t \sim v/\tau \sim v\omega$, and $v\partial^2 v/\partial z^2 \sim v\omega/h^2$. At small values of h ($\omega h^2/v \ll 1$), the derivatives with respect to t on the left-hand side of (3.1) can be neglected; hence, instead of (3.1a) and (3.1b) we obtain

$$\eta(\partial^2 v_r/\partial z^2) = \partial p/\partial r; \quad (a) \quad (4.2)$$

$$\eta(\partial^2 v_\theta/\partial z^2) = (1/r)(\partial p/\partial \theta). \quad (b)$$

Since $\omega = \omega[h(t)]$, we again determine ζ with the aid of (3.4). As there are no derivatives with respect to t in (4.2), we apply the method used for the derivation⁹ of (3.7) and obtain

$$v_r = (\frac{1}{2}\eta)(\gamma K^2 - 2d\Pi/dh)(z^2 - h^2/4)(\partial\zeta/\partial r); \quad (a)$$

$$v_\theta = (\frac{1}{2}\eta)(\gamma K^2 - 2d\Pi/dh)(z^2 - h^2/4)(1/r)(\partial\zeta/\partial \theta) \quad (b) \quad (4.3)$$

$$v_\zeta = -(K^2 h^3/24\eta)(\gamma K^2 - 2d\Pi/dh)\zeta. \quad (c)$$

Because of the analogy between (4.3c) and (3.9), we take

$$\omega[h(t)] = -(K^2 h^3/24\eta)(\gamma K^2 - 2d\Pi/dh), \quad (4.4)$$

which is formally identical to (3.12). Here also, $\omega(h_0) = 0$.

We set down (3.2d) in the form $v_z = \partial z / \partial t = (\partial \zeta / \partial h)(\partial h / \partial t)$. With v_z from (4.3c) and dh/dt from (4.1), after integrating with respect to h , we obtain

$$\zeta = \zeta_0 \exp \left\{ -\frac{RK^2}{8} \int_h^{h_0} \frac{\gamma K^2 - 2d\Pi/dh}{P_\gamma - \Pi} dh \right\} \quad (4.5)$$

in which $\zeta_0 = \zeta(h_0) = A\psi(r, \theta)$.

The value of the constant A is dependent on the manner in which the wave is formed. For a fluctuation wave, it can be calculated on the basis of the following considerations. In a thick film, $\omega h^2/\nu \gg 1$, and in eqn (3.1a) and (3.1b), the terms containing the viscosity can be neglected. In this case, it means that the behaviour of the wave is that of a wave on the surface of an ideal liquid, and that its movement does not lead to any dissipation of energy. Therefore, the theorem of Einstein¹⁴ is applicable and gives

$$kT = (\gamma K^2 A^2 / 2) \int \psi^2 dS, \quad (4.6)$$

in which k is Boltzmann's constant and T is the absolute temperature; the integration is carried out over the entire film surface S . Eqn (4.6) determines the amplitude A at greater thicknesses. Since A is not dependent on t or on h , this expression can also be applied to thin films (when $\omega h^2/\nu \ll 1$).

When the film has a square section and an area l^2 , the solution of eqn (3.5) is obtained with trigonometric functions and so for a given K , it follows from (4.6) that

$$A^2 = 8kT/\gamma K^2 l^2.$$

When the film thickness h becomes equal to $2|\zeta(h)|$, it will rupture.* We shall use h_{cr} to denote this thickness. ζ is a function of the wave number k , and so a given wave (let us call it the critical wave) with a wave number k_m will have a corresponding maximum value of h_{cr} which is determined by the condition

$$(d\zeta/dk)_{k_m} = 0. \quad (4.7)$$

Substituting (4.5) into this equation and disregarding the negligible dependence of ζ on K (see (4.6)), we obtain

$$k_m^2 = \left\{ \ln \frac{P_\gamma - \Pi(h_{cr})}{P_\gamma - \Pi(h_0)} \right\} \left\{ \gamma \int_{h_{cr}}^{h_0} \frac{dh}{P_\gamma - \Pi} \right\}^{-1}. \quad (4.8)$$

In reality, the profile of the surface is not determined by a single wave, but the superposition of an infinite number of waves:

$$\zeta(r_1, \theta_1, h) = \sum_K \zeta_K(r_1, \theta_1, h), \quad (4.9)$$

in which ζ_k for small h is obtained from (4.5). The summation in (4.9) is done over all possible K . With $h = h_{cr}$, the function ζ reaches its maximum negative value at a point on the surface with coordinates r_0 and θ_0 . In this case, the condition for the rupture of the film will be

$$h_{cr} = 2|\zeta(r_0, \theta_0, h_{cr})|. \quad (4.10)$$

Though feasible, this method of calculation is very difficult. Accordingly,

* The cavitation mechanism of rupture is energetically unfavourable for thick films; however, it could take place in a highly thinned film, at the point of the maximum approach of the two surfaces. In this case, the film will rupture when its local thickness reaches a definite, sufficiently small value and not when it is reduced to zero. If there is only a negative van der Waals disjoining pressure, the process of the thinning at small local thickness is so rapid that the condition of rupture need not be defined with such precision.

following the example of Vrij,³ we shall assume in calculating ψ from (3.5) that the film has a square section and we shall replace $|\zeta(r_0, \theta_0, h_{cr})|$ in (4.10) by $(\bar{\zeta}^2)^{\frac{1}{2}}$, in which $\bar{\zeta}^2$ is the average square value for the entire surface of the film. We discuss these approximations later.

In (4.5), the function $|\zeta|$ has a sharp maximum when $K = K_m$, and if we replace the sum in (4.9) by an integral, we can use the method of the steepest descent.¹⁵ Accordingly, from (4.5) with (3.13), (4.6) and (4.8), we obtain

$$h_{cr}^2 = \left(\frac{kT}{R}\right) \left[\pi\gamma \left(\frac{d\Pi}{dh}\right)_{h_0} \ln \frac{P_\gamma - \Pi(h_0)}{P_\gamma - \Pi(h_{cr})} \right]^{-\frac{1}{2}} \exp \left[\frac{R^2 (d\Pi/dh)_{h_0}}{4\gamma} \ln \frac{P_\gamma - \Pi(h_{cr})}{P_\gamma - \Pi(h_0)} \right] \quad (4.11)$$

in which h_0 is calculated from (3.13) with K_m from (4.8).

5. CRITICAL THICKNESS WITH LOW CONCENTRATION OF SURFACTANT

As has been demonstrated by Levich,¹¹ and particularly for the thin liquid films in ref. (9), the effect of the surfactant on the flow of the liquid is to reduce the flow on the surface; at a sufficiently high concentration of surfactant, the surface is motionless. With a flowing surface, the conditions (3.2a) and (3.2b) appear as follows:

$$\left. \begin{aligned} \eta \partial v_r / \partial z &= \pm \partial \gamma / \partial r & (a) \\ \eta \partial v_\theta / \partial z &= \pm (1/r) (\partial \gamma / \partial \theta) & (b) \end{aligned} \right\} \text{when } z = \pm h/2. \quad (5.1)$$

The emergence of the surfactant on the film surface takes place in two consecutive stages: first, outward diffusion into the liquid layer situated under the surface itself, and secondly, adsorption of the surfactant from that layer into the surface. The theory is constructed in a different manner, depending on which of the two stages is the rate-determining one. It was demonstrated in ref. (9) that the surfactant ($C_{12}H_{25}OH$) diffused slowly, and that the first stage was therefore the rate-determining one. On the other hand, the results of the theory for the critical thickness are the same for the two mechanisms (slow diffusion and slow adsorption), and we therefore confine attention to the examination of slow diffusion. In this case, the conservation law for the surfactant, with the surface diffusion being negligible, is as follows.¹¹:

$$\text{div}(\Gamma \vec{v}_s) = -D(\partial c / \partial z)_{h/2}, \quad (5.2)$$

in which Γ is the surface excess of the surfactant; c is the bulk concentration of the surfactant; D is the bulk diffusion coefficient of the surfactant; \vec{v}_s is the velocity on the film surface.

We again confine ourselves to small thicknesses ($\omega h^2 / \nu \ll 1$). In this case, eqn (3.1a) and (3.1b) are replaced by (4.2). The distribution of the concentration is given by Fick's law which, in the same approximation, appears as

$$\Delta c = 0 \quad (5.3)$$

(Δ is the Laplace operator) and is solved with the boundary conditions.

$$c = c_0 \quad \text{when } r = R \quad \text{and} \quad \partial c^* / \partial z = 0 \quad \text{when } z = 0, \quad (5.4)$$

in which c_0 is the equilibrium bulk concentration when there is no flow. With a slow flow in the film we can again introduce $p = p^{(f)} + p^*$ and $v_i = v_i^{(f)} + v_i^*$ (cf. §4), respectively $c = c_0 + c^{(f)} + c^*$, $\Gamma = \Gamma_0 + \Gamma^{(f)} + \Gamma^*$ and $\gamma = \gamma_0 + \gamma^{(f)} + \gamma^*$. Here, Γ_0 and γ_0 are the equilibrium values of the surface excess and surface tension, $c^{(f)}$, $\Gamma^{(f)}$ and $\gamma^{(f)}$ are the perturbations caused by the outflow of the plane-parallel film,

and c^* , Γ^* , and γ^* are the perturbations arising from the corrugation of the film surface. Assuming that $\Gamma^{(f)} + \Gamma^* < \Gamma_0$, we can obtain a simpler form than (5.2):

$$\Gamma_0 \operatorname{div} \vec{v}_s = -D(\partial c / \partial z)_{h/2}. \quad (5.2a)$$

All equations are linear and can again be broken down into two systems. The system with index f leads to a generalized law of thinning⁹ (of the same type as that of Reynolds) taking into account the effect of the surfactant*:

$$dh/dt = [2(P_y - \Pi)h^3/3R^2\eta][1 - 3D\eta/\Gamma_0(\partial\gamma/\partial c)]. \quad (5.5)$$

The second system is expressed by the eqn (3.1c), (3.1d), (3.2c), (3.2d), (4.2), (5.1), (5.3) and (5.2a) in which the quantities p , v_s , γ and c are asterisked, and the condition (5.4) is replaced by

$$c^* = 0 \quad \text{when} \quad r = R \quad \text{and} \quad \partial c^*/\partial z = 0 \quad \text{when} \quad z = 0. \quad (5.4a)$$

We shall again abandon the index asterisk.

Eqn (3.1d) and (4.2) with the corresponding boundary conditions are solved as before: instead of (4.3), we obtain

$$\begin{aligned} v_r &= (\gamma K^2 - 2d\Pi/dh)\{- (h^2/4 - z^2)(\frac{1}{2}\eta) + B\}\partial z/\partial r; & (a) \\ v_\theta &= (\gamma K^2 - 2d\Pi/dh)\{- (h^2/4 - z^2)(\frac{1}{2}\eta) + B\}(1/r)\partial\zeta/\partial\theta, & (b) \end{aligned} \quad (5.6)$$

in which B is not dependent on z . Substituting (5.6) in (5.2a) with (3.5), we obtain

$$(\gamma K^2 - 2d\Pi/dh)(h^2/8\eta + B)K^2\zeta = (D/\Gamma_0)(\partial c/\partial z)_{h/2}. \quad (5.7)$$

The result of substitution of (5.6) in (5.1) can be written in the form

$$(\gamma K^2 - 2d\Pi/dh)h \operatorname{grad} \zeta = 2(\partial\gamma/\partial c) \operatorname{grad} c,$$

which, after integration with the condition $c = 0$ when $\zeta = 0$ gives

$$(\gamma K^2 - 2d\Pi/dh)h\zeta = 2(\partial\gamma/\partial c)c. \quad (5.8)$$

From (5.3), we obtain

$$c = \psi(r, \theta) \cosh(Kz).$$

Substituting this in (5.7) and (5.8), we obtain (when $Kh \ll 1$)

$$B = -h^2/8\eta + (Dh/2\Gamma_0K) \tanh(Kh/2) \approx -h^2/8\eta + Dh^2/4\Gamma_0.$$

With this value of B , from (3.1d), integrating with respect to z and putting $z = \pm h/2$, we obtain

$$v_\zeta = (K^2h^3/24\eta)(\gamma K^2 - 2d\Pi/dh)[1 - 3D\eta/\Gamma_0(\partial\gamma/\partial c)].$$

Substituting this expression in the equation $v_\zeta = (\partial\zeta/\partial h)(dh/dt)$ and expressing dh/dt by (5.5), then integrating with respect to h , we obtain

$$\gamma = \gamma_0 \exp \left\{ -\frac{R^2K^2}{8} \int_h^{h_0} \frac{\gamma_0 K^2 - 2d\Pi/dh}{P_\gamma - \Pi} dh \right\},$$

which coincides with the value of z at zero velocity of flow on the surface (see eqn (4.5)).

It follows from the above that the critical thickness of rupture within the limits of the stated approximations ought not to be dependent on the concentration of surfactant (providing we disregard the negligible effect due to the change of the equilibrium value of the surface tension γ_0). This is natural, since the increasing velocity of the flow on the surface accelerates both the thinning of the film and its

* Here and hereafter, it is accepted that the concentration is sufficiently low, and that it is therefore possible to use Henry's adsorption isotherm: $\Gamma \sim c$. Hence $\partial\gamma/\partial c = \partial\gamma/\partial c_0 = \text{const}$.

corrugation. The first effect increases the critical thickness, and the second decreases it. At small amplitudes of the waves, the two effects counterbalance each other.

6. EXPERIMENTAL INVESTIGATION OF THE EFFECT OF THE CONCENTRATION OF SURFACTANT ON THE CRITICAL THICKNESS

This investigation was carried out with aniline films, stabilized with $C_{12}H_{25}OH$ since for aniline we have the most reliable data on the isotherm of the disjoining pressure, obtained by the dynamic method for thicknesses up to the critical ones.¹⁶ Moreover, eqn (5.5) for the velocity of thinning was verified for the same system.⁹

The methods, apparatus and processing of the experimental data, which are applied, are described in ref. (5) and (16). The aniline was redistilled before every measurement. The surface tension of the aniline ($\gamma_{20^\circ} = 42.9 \text{ dyn/cm}$) and of the $C_{12}H_{25}OH$ solutions was determined by the ring method. The critical thicknesses of rupture were measured at $C_{12}H_{25}OH$ concentrations c_0 from 0.55×10^{-6} to 5.4×10^{-6} M. As shown in ref. (9), Henry's law for the adsorption of the surfactant is valid throughout this range. The limits of c_0 were so chosen, because solutions with c_0 lower than 0.55×10^{-6} M cannot be prepared with sufficient accuracy, and because with c_0 higher than 5.4×10^{-6} M, the critical thicknesses of rupture are no longer dependent on c_0 .

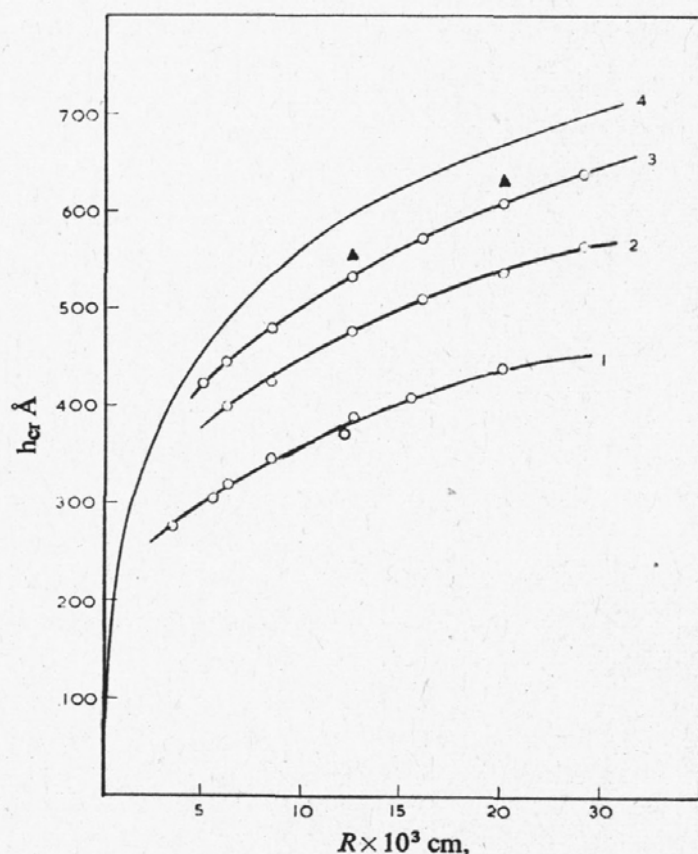


FIG. 2.—Dependence of the critical thickness of rupture h_{cr} on the film radius R for aniline films stabilized with $C_{12}H_{25}OH$.

The results of the measurements are shown in fig. 2, 3 and 4. Every point on these curves was obtained by the statistic processing of some 100 different measurements. Fig. 2 shows the dependence of h_{cr} on R at four different values of c_0 : curve, 1, 5.4×10^{-6} M $C_{12}H_{25}OH$; curve 2, 1.6×10^{-6} M; curve 3, 0.8×10^{-6} M;

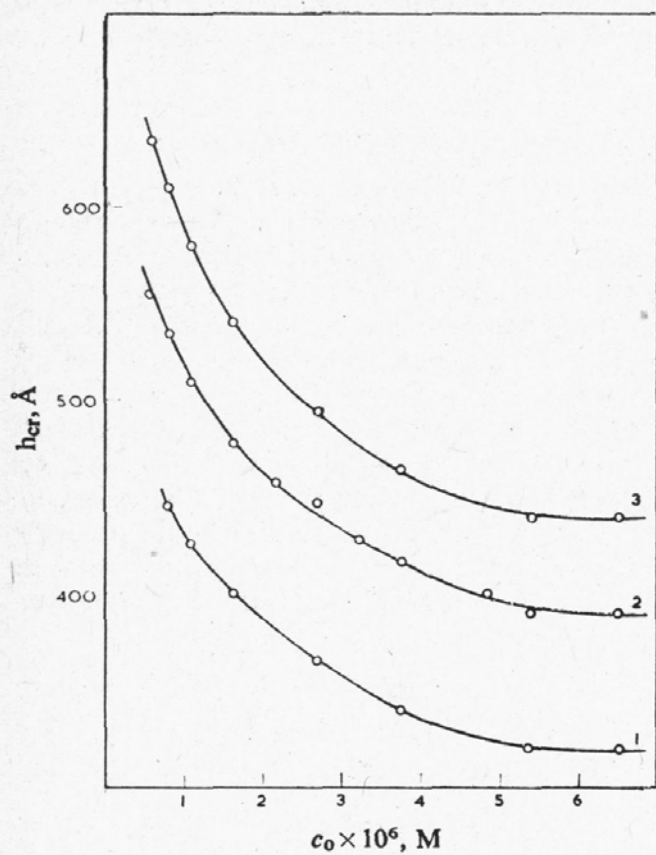
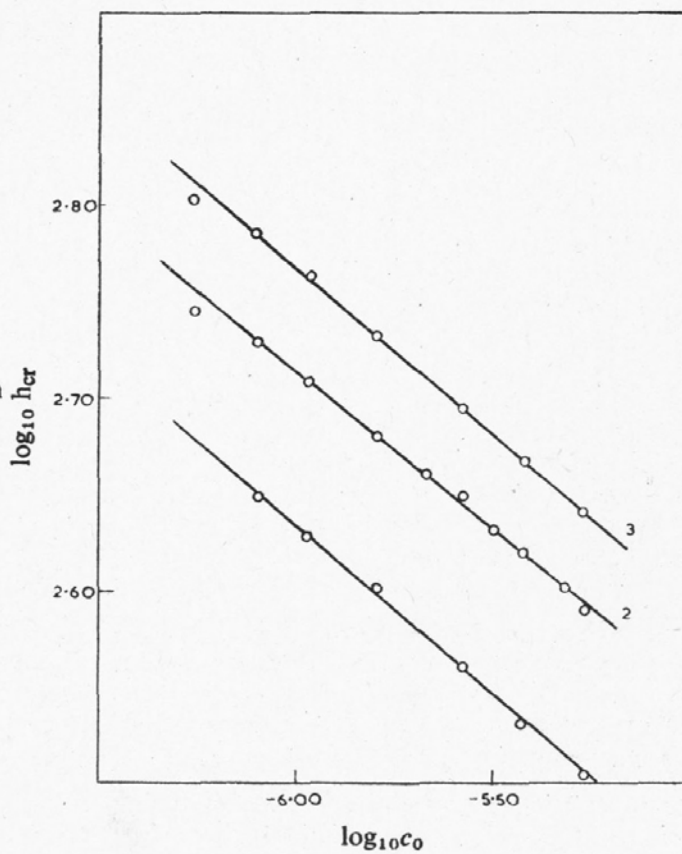


FIG. 3.—Dependence of the critical thickness of rupture h_{cr} of aniline films on the concentration c_0 of the surfactant ($C_{12}H_{25}OH$).

FIG. 4.—The same dependence from fig. 3 on a log-log scale.



for $c_0 = 0.55 \times 10^{-6}$ M, the values of h_{cr} are denoted with small triangles, and the curve 4 was calculated theoretically on the basis of (4.11), using the isotherm $\Pi(h)$ for aniline from ref. (16).

In fig. 3, some of these results are given in coordinates h_{cr} against c_0 ; in fig. 4, in coordinates $\log_{10} h_{cr}$ against $\log_{10} c_0$. Curves 1, 2 and 3 correspond to film radii of 6.2×10^{-3} , 1.25×10^{-2} and 2×10^{-2} cm respectively. The slopes of the straight lines in fig. 4 are practically the same and close to $-\frac{1}{6}$, and the rise of the critical thicknesses with the concentration of surfactant starts at approximately the same value of the concentration $c_0^* = 5.4 \times 10^{-6}$ M. Taking $h_{cr}^*(R)$ to denote the value of the critical thickness for $c_0 \geq c_0^*$, we obtain (with $c_0 < c_0^*$):

$$h_{cr}(R_1 c_0) = h_{cr}^*(R)(c_0/c_0^*)^{-1/6}. \quad (6.1)$$

When $c_0 = 0$, this dependence no longer has any significance.

7. DISCUSSION

It is difficult to compare the calculation of this paper with the calculation of Vrij,³ as his calculated results are not presented in an explicit form. In both calculations, the curves h_{cr} against R for the same $\Pi(h)$ and P_γ of the aniline were nearly coincident (curve 1 in fig. 5); it does not follow, however, that these curves would be similarly coincident if the initial data for $\Pi(h)$ and P_γ were different.

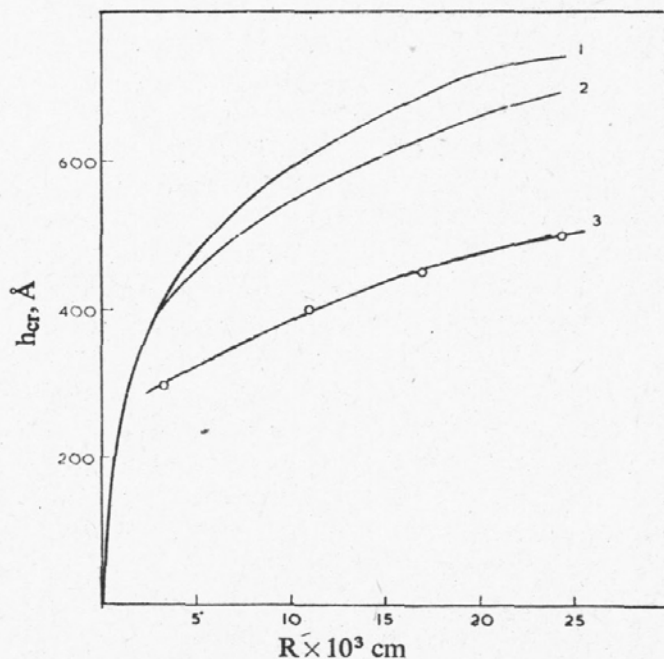


FIG. 5.—Critical thickness of rupture h_{cr} of aniline films as a function of the film radius. Curve 1, theoretical dependence with consideration of the wave superposition; curve 2, theoretical dependence without wave superposition; curve 3, experimental results at a high surfactant concentration.

We now assess the assumptions made in deducing (4.11), viz., the replacement of the condition (4.10) by the condition $h_{cr} = 2(\zeta^2)^{\frac{1}{2}}$, and (b) the representation of the circular film as a square one. To avoid the difficulties associated with the consideration of wave superposition, we replace the sum in (4.9) by the maximum term ζ_{km} . The results of this calculation (when approximations (a) and (b) are retained) are shown by curve 2 on fig. 5. If only the greatest term is taken into account, approximations (a) and (b) can be dispensed with. The differences between the values of h_{cr} calculated

in this manner and the corresponding values from curve 2 are less than 1 %. Wave superposition would hardly affect this estimate.

In the deduction of (4.11), the only important approximation that cannot be assessed is that ζ is much smaller than h . It will affect the result, but (see later) its effect cannot be a determining one. If we disregard it for the present, it appears that the error in (4.11), within the limits of the model we have used, will be only a few per cent. At the same time, however, the experimental data for high concentration of surfactant ($c_0 > c_0^*$) are about 30 % lower than the theoretical ones. According to our theory, moreover, h_{cr} should not depend on the concentration of surfactant (see §5), whereas the experiment shows a pronounced increase of h_{cr} with the decrease of c_0 .

The agreement of the values of h_{cr} calculated by Vrij³ with those obtained in the way shown here for aniline, as well as the analyses of the approximations which have been done in this paper, showed that the discrepancy between theory and experiment can hardly be due to the approximations in the theory.

An analysis of the preconditions of the theory indicates that these discrepancies between the theoretical and experimental data may be due to some obstacle to the thinning at the point of maximum approach of the two film surfaces. If there is such an impediment to the inward bending process, it could well bring about a further decrease of the mean thickness of the film, i.e., to smaller values of h_{cr} . There seem to be two important factors for this reduction of the velocity of the thinning: an increased viscosity and the appearance of a new positive component of the disjoining pressure at very small thicknesses. The analysis of the results of the investigation of thin liquid films, in ref. (18), indicates that such a component of the disjoining pressure is likely to appear in very thin films. It is probably caused by the adsorbed layer of surfactant, and should decrease with the decrease of the concentration of the surfactant. If this additional disjoining pressure is sufficiently great, it can lead to the formation of second black films; we have therefore denoted it by Π_{b1} . If it is small (as for aniline films stabilized with $C_{12}H_{25}OH$), it cannot counterbalance the negative disjoining pressure and bring about the formation of a second black film; nevertheless, it hinders the rupture and consequently leads to a decrease of the critical thicknesses.

At the same time, we cannot rule out the possibility that the increased viscosity in the very thin films may also contribute to the observed decrease of h_{cr} from the theoretical values. It was indeed established¹⁹ that the activation energy of ionic mobility in the second black films is considerably greater than that in the bulk liquid; this may result from the higher viscosity in the very thin film. Nevertheless, in as much as the equilibrium black films can only be explained by thermodynamic factors, the effect of Π_{C1} seems to be the predominant one, and the increase of the viscosity ought to be taken as a secondary complicating phenomenon.

We finally examine the validity of the approximation $\zeta \ll h$. With $\zeta \lesssim h/2$, it is invalid; however, if there is only a negative van der Waals disjoining pressure ($\Pi_{C1} = 0$) in the film, the velocity v_c of the critical wave at $\zeta \lesssim h/2$ is so great ($v_c \gg V$) that this fact is not important. Naturally, with $\Pi_{b1} > 0$, this assumption leads to an additional discrepancy between the theory and the experimental data.

It is clear that the effect of all the additional factors leading to a divergence of the experimental data from the theoretical results (viz., the existence of Π_{b1} , the increase of the viscosity and the violation of the condition $\zeta \ll h$) ought to disappear at very low (not equal to zero) concentrations of surfactant. This inference is in accordance with the experimental results (e.g., see fig. 2,) which, with c_0 decreasing, approach more closely the corresponding theoretical values calculated by using the isotherm

$\Pi(h)$, obtained for thick films in which Π_{b1} does not exist. It can therefore be assumed that the theory for the critical thicknesses is corroborated for films stabilized with a minimum of surfactant; however, at higher values of c_0 , the divergences from this theory have not yet been explained.

In conclusion, this theory contains two other simplifications which are also present in Vrij's theory, and which have not been examined in this paper:⁵ (a) with regard to the fluctuating parameters, the averaging is done in the process of the calculations; therefore, the final result for h_{cr} contains no probability factor. Hence we do not observe the scattering of results which is so typical of these processes and which is both a source of further information and a means for the verification of the theory. However, in so far as the fluctuating parameters show little divergence from the mean values, it can scarcely lead to any significant inaccuracies in the mean or most probable values of h_{cr} that we have obtained. Actually, the scattering of h_{cr} experimentally obtained is slight, and symmetrically disposed around the most probable value.⁵

(b) Of greater importance is the disregard of the transitional sections of the thin film towards the meniscus. If the film radius R is sufficiently large, this assumption leads to correct results, but it precludes the extrapolation of the theory to $R = 0$, as the theory requires h_{cr} to tend towards zero with $R \rightarrow 0$, whereas the experimental data⁵ show that with $R \rightarrow 0$, there is a limiting value $h_{cr}^{(0)}$.

¹ A. De Vries, *Rec. trav. chim.*, 1958, **77**, 383; *Rubber Chem. Tech.*, 1958, **31**, 1142; A. Frumkin, *Zhur. Fiz. Khim.*, 1938, **12**, 1; B. Derjaguin and V. Gutop, *Kolloid. Zhur.*, 1962, **24**, 431.; B. Derjaguin and V. Gutop, *Compt. rend. U.R.S.S.*, 1963, **153**, 809.

² A. Scheludko, *Proc. K. Akad. Wetensch. B*, 1962, **65**, 87.

³ A. Vrij, *Disc. Faraday Soc.*, 1966, **42**, 23.

⁴ D. Exerowa and T. Kolarov, *Annuaire Univ. Sofia, Fac. Chim.*, 1964/65, **59**, 207.

⁵ A. Scheludko and E. Manev, *Trans. Faraday Soc.*, 1968, **64**, 1123.

⁶ D. Platikanov and E. Manev, *Proc. 4th Int. Congr. Surface Activity*, Brussel, 1964, (Gordon & Breach, London), p. 1189.

⁷ M. v. Smoluchowsky, *Ann. Physik.*, 1908, **25**, 225.

⁸ L. Mandelstamm, *Ann. Physik.*, 1913, **41**, 609.

⁹ B. Radoev, E. Manev and I. Ivanov, *Kolloid-Z.*, 1969, **234**, 1037.

¹⁰ N. Kochin, I. Kibel and N. Rosé, *Teoreticheskaya gidromekhanika, Fizmatgiz* (Moscow, 1963), vol. 1, p. 445.

¹¹ V. Levich, *Physicochemical Hydrodynamics*, (Prentice-Hall, Engelwood Cliffs, 1962), chap. 7 and 8.

¹² O. Reynolds, *Phil. Trans.*, 1886, **177**, 157.

¹³ A. Scheludko, G. Dessimirov and K. Nikolov, *Annuaire Univ. Sofia, Fac. Chim.*, 1954/55, **49**, 2.

¹⁴ A. Einstein, *Ann. Physik.*, 1910, **33**, 1275.

¹⁵ A. Sveshtnikov, *Teoria funktsij kompl. perem., Naouka*, (Moscow, 1967), p. 257.

¹⁶ E. Manev and M. Bouleva, *Abhandlungen Deutsch. Akad. Wiss., Berlin*, 1966, **6b**, 557.

¹⁷ N. Koshlyakov, E. Gliner and M. Smirnov, *Osn. difer. uravn mat. fiz. Fizmatgiz*, (Moscow, 1962,) p. 250.

¹⁸ A. Scheludko, *Annuaire Univ. Sofia, Fac. Chim.*, 1976/78, **62**, in press.

¹⁹ D. Platikanov and N. Rangelova, *Comp. rend. Acad. Bulgare Sci.*, 1968, **21**, 913.