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CRITICAL FILM THICKNESS AND COALESCENCE IN EMULSIONS	**154**

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RÉSUMÉ

On met au point une modélisation théorique de l'épaisseur du film critique en présence de surfactant. Durant le processus d'amincissement du film, l'ondulation des surfaces du film provoque de petites fluctuations dans la vitesse, la pression et la concentration de surfactant. La minimisation du temps de rupture du film pour toute la longueur d'onde conduit à une relation explicite pour l'épaisseur du film critique. Cette théorie est appliquée pour la description des données expérimentales sur l'épaisseur critique des films d'aniline stabilises au dodécanol. L'augmentation de l'épaisseur critique allant de pair avec l'accroissement du rayon du film et la diminution de la concentration de surfactant est confirmée par la prévision théorique. L'influence de l'élasticité Gibbs, de la viscosité interfaciale et de la diffusivité sur le temps de rupture du film est démontrée.

Sur la base de la théorie de stabilité de l'émulsion cinétique, une nouvelle explication quantitative de la règle de Bancroft est proposée. L'influence de l'épaisseur du film critique sur la stabilité de l'émulsion est étudiée.

ABSTRACT

The theoretical modelling of the critical emulsion film thickness in the presence of surfactant is developed. During the process of film thinning the corrugation of the film surfaces induces small fluctuations in the velocity, pressure, and surfactant concentration. The minimisation of the film rupture time for all wave length leads to an explicit relation for the critical film thickness. The theory is applied for the description of experimental data for the critical thickness of aniline films stabilised by dodecanol. The increase of the critical thickness with increasing of the film radius and with decreasing of the surfactant concentration is confirmed by the theoretical prediction. The influence of the Gibbs elasticity, interfacial viscosity and diffusivity on the film rupture time is demonstrated.

Theoretical and experimental studies on the stability of emulsion films are described. On the basis of the theory of kinetic emulsion stability, a new quantitative explanation of the Bancroft rule is proposed. The influence of the film critical thickness on the emulsion stability is studied.

CRITICAL FILM THICKNESS AND COALESCENCE IN EMULSIONS

1. Introduction

It is generally recognized that the presence of surfactants plays an important role for the hydrodynamic interactions in thin liquid films and between the droplets in emulsions. The surfactant adsorption monolayers influence not only the disjoining pressure Π (accounting for the molecular interactions across the film), but also reduce the tangential mobility of the fluid interfaces. This affects the flocculation and coalescence rate constants characterizing the coagulation in emulsions (1-3). Depending on the behavior of the film formed between two colliding droplets, two kinds of emulsion stability can be distinguished: *thermodynamic* stability governed by repulsive disjoining pressure, and *kinetic* stability related to the energy dissipation in hydrodynamic and diffusion fluxes throughout the film surfaces and in the adjacent bulk liquid phases. In the case of plane-parallel film these two types of stability are coupled and both of them must be taken into account to interpret of the Bancroft rule (1,4,5). In particular, an emulsion film breaks, or two emulsion droplets coalesce, when the distance between the two fluid interfaces becomes smaller than a certain *critical thickness*, corresponding to the onset of "infinite" growth of the thermally excited fluctuation capillary waves. The determination of the critical thickness is important for the quantitative calculation of the rate constants of flocculation and coalescence.

This article presents a theoretical study of the velocity of approach and the critical thickness for a couple of two emulsion droplets, which slightly deform upon collision. The results are applied to obtain a qualitative explanation of the Bancroft rule.

2. Thinning of Emulsion Films in the Presence of Surfactant
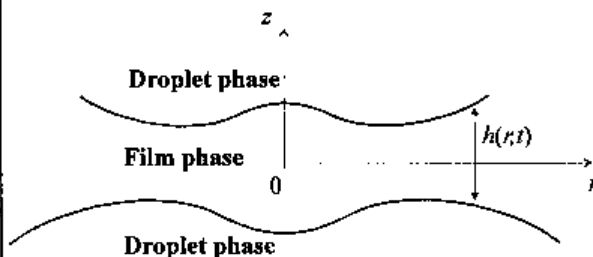

Fig. 1. Schematic picture of a film whose surfaces are subjected to fluctuations.

We consider a thin liquid film (of uneven thickness) formed from a surfactant solution, which is sandwiched between two approaching and deforming emulsion droplets (Fig. 1). It is assumed that the droplets are spherical before the collision, and that a flattening (film) appears in the zone of their contact. We study the stability and thinning of films whose initial thickness is not greater than 100 nm. Therefore one has to take into account the disjoining pressure, which can contain contributions of various physical origin (van der Waals, electrostatic, steric, etc.). It is proven in the literature (1,2,6), both experimentally and theoretically, that if the surfactant is soluble only in the continuous (film) phase and if the bulk viscosities of the two liquid phases have comparable magnitudes, then the *emulsion* film thins like a *foam* film. For such films the flow obeys the lubrication approximation due to Reynolds. The mathematical formulation of the problem is the following.

A cylindrical coordinate system $Orz\varphi$, with origin at the center of the film, is used; r and z are the radial and the vertical coordinates, respectively (see Fig. 1). The drainage of the liquid out of the film is supposed to be axisymmetric. The two film surfaces are described by the equation $z = h_k(r,t)$ ($k=1,2$), and then the film thickness is $h(r,t) = h_2(r,t) - h_1(r,t)$, where t is time. In the framework of the lubrication approximation the pressure in the film is $p = p(r,t)$. After integrating the bulk continuity and momentum balance equations along with the corresponding kinematic boundary conditions, one can derive

$$\frac{\partial h}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}(rhu_a) = 0 \ , \qquad u_a \equiv \frac{u_1 + u_2}{2} - \frac{h^2}{12\eta}\frac{\partial p}{\partial r} \ . \tag{1}$$

Here η is the dynamic viscosity of the continuous phase and u_k (k=1,2) is the radial component of the velocity at the respective film surface. A simple interfacial rheological model is provided by the linear Boussinesq-Scriven constitutive relation. Combining this relation with the lubrication approximation, one obtains two boundary conditions at the film surface stemming from the tangential and normal projections of the interfacial momentum balance:

$$\frac{h}{2}\frac{\partial p}{\partial r} + (-1)^k(u_2 - u_1) = \frac{\partial \sigma_k}{\partial r} + \frac{\partial}{\partial r}\left[\frac{\eta_k}{r}\frac{\partial}{\partial r}(ru_k)\right] \ ,$$

$$p_0 + \frac{2\sigma_k}{a_k} = p + \Pi + (-1)^k\frac{\sigma_k}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h_k}{\partial r}\right) \ , \tag{2}$$

cf. Ref.(6). Here σ_k is the interfacial tension, p_0 is the pressure in the bulk of the continuous phase, and a_k is the radius of the non-deformed (spherical) part of the droplet surface. It turns out that the dilatational, η_k^{dil}, and shear, η_k^{sh}, interfacial viscosities are coupled in Eq. [2] into one surface viscosity, $\eta_k \equiv \eta_k^{dil} + \eta_k^{sh}$.

If the surfactant adsorption monolayer is disturbed, the equilibrium will be restored either by adsorption from the bulk solution, or by surface convection of adsorbed surfactant molecules. In the case of diffusion-controlled adsorption one can combine the bulk and surface diffusion equations to derive the total surfactant mass balance equation:

$$\frac{\partial}{\partial t}(\Gamma_1 + \Gamma_2 + hc) + \frac{1}{r}\frac{\partial}{\partial r}(rj) = 0 \ ,$$

$$j \equiv \Gamma_1 u_1 + \Gamma_2 u_2 + hcu_a - D_1\frac{\partial \Gamma_1}{\partial r} - D_2\frac{\partial \Gamma_2}{\partial r} - hD\frac{\partial c}{\partial r} \ , \tag{3}$$

where D is the bulk diffusion coefficient, Γ_k and D_k (k=1,2) are the adsorption and the surface diffusion coefficient at the respective film surface. Other relation, which holds at the film surfaces, is the adsorption isotherm, which connects the subsurface surfactant concentration, c, with the adsorption Γ_k. In addition, a surface equation of state connects the interfacial tension σ_k with the adsorption Γ_k (k=1,2).

3. Evolution of the Film between Two Colliding Emulsion Droplets

When the driving force F (say the Brownian force) is small compared to the capillary pressure of the droplets, the deformation of two droplets upon collision will be a small perturbation. Then the film thickness and the pressure can be presented as a sum of an non-perturbed part and a small perturbation. Solving the resulting linear problem based on Eqs. [1]-[3] for low interfacial viscosity, an exact formula for the velocity of thinning, $V = -dh_0 / dt$, can be derived

$$\frac{V}{V_{Ta}} = \frac{l}{2h_0}\left[-1 + \frac{d+1}{d}\ln(d+1)\right]^{-1} \ , \qquad V_{Ta} = \frac{h_0}{6\pi\eta a^2}(F - 2\pi af_0) \ , \qquad \Pi = -\frac{df}{dh} \ , \tag{4}$$

where h_0 is the minimal distance between the drops, $a = a_1 a_2 /(a_1 + a_2)$ is the "mean" droplet radius, f is the interaction surface free energy per unit area, $f_0 = f(h_0)$, V_{Ta} is a generalized Taylor velocity of approaching of two non-deformed spherical solid particles, d is a dimensionless parameter inverse proportional to h_0, and l is a characteristic surface diffusion thickness. The parameters d and l are functions of the surface elasticity, diffusivity and the slope of the surfactant adsorption isotherms:

$$b_k = -\frac{3\eta D}{\Gamma_k\left(\frac{\partial\sigma}{\partial c}\right)_k} \quad,\quad l_k = -\frac{6\eta D_k}{\Gamma_k\left(\frac{\partial\sigma}{\partial\Gamma}\right)_k} \qquad (k=1,2),$$

$$b = \frac{4\Gamma_1\Gamma_2 b_1 b_2 - 3(\Gamma_2 - \Gamma_1)(\Gamma_2 b_2 - \Gamma_1 b_1)}{(\Gamma_2 + \Gamma_1)(\Gamma_2 b_2 + \Gamma_1 b_1)} \quad,\quad l = \frac{2\Gamma_1\Gamma_2(l_1 b_2 + l_2 b_1)}{(\Gamma_2 + \Gamma_1)(\Gamma_2 b_2 + \Gamma_1 b_1)} \quad,\quad d = \frac{l}{h_0(1+b)} \cdot \qquad [5]$$

It is important to note that for small deformations and small droplets the contribution of the interaction energy, f, is significant. For large interfacial elasticity the parameter d is very small, $d \ll 1$, and the interfaces are tangentially immobile.

From the solution for the shape perturbation one can obtain the so called *inversion thickness*, h_i, at which the curvature at $r=0$ inverts from negative to positive (the interfacial shape in the zone of contact changes from convex to concave). h_i is a solution of the following transcendental equation

$$h_i = \frac{F}{4\pi\sigma}\phi(d) + \frac{a}{2\sigma}\left[h_i\Pi(h_i) - f(h_i)\phi(d)\right] , \qquad [6]$$

where the dynamic effects due to the presence of surfactant are included in the function $\phi(d)$

$$\phi(d) = \frac{d - \ln(d+1)}{(d+1)\ln(d+1) - d} , \qquad [7]$$

and the mean interfacial tension is $\sigma \equiv \sigma_1\sigma_2 / (\sigma_1 + \sigma_2)$. For large interfacial elasticity $d \ll 1$; then $\phi(d) \approx 1$ and Eq. [6] reduces to the known result $h_i = F / (4\pi\sigma)$, cf. Ref. (6). For small interfacial elasticity the value of ϕ decreases. It is seen that the higher the interfacial mobility the lower the inversion thickness. The attractive surface forces lead to smaller Π and smaller inversion thickness; for large negative (attractive) Π Eq. [6] has no solution for h_i.

In order to investigate the film stability we introduce small oscillatory perturbations of the derived shape and pressure distributions. We study only the moment at which the instability appears. The corresponding thickness is called here the critical thickness, h_c. We solve the stability problem numerically because of the dependence of the coefficients in the differential equation on time t and radial coordinate r. We proved that the long waves, of length comparable to the minimal film thickness, are the most unstable. In this case an analytical equation for the critical thickness can be obtained: h_c is the solution of the following transcendental equation:

$$\psi\left[F - 2a\pi f(h_c)\right] = \frac{\pi a^2 h_c^3}{16\sigma}\left[\left(\frac{\partial\Pi}{\partial h}\right)_c^2 - \frac{8\sigma}{a}\left(\frac{\partial^2\Pi}{\partial h^2}\right)_c\right] , \qquad [8]$$

where the mobility function ψ depends only on the parameter d and

$$\psi(d) = \frac{(d+2)d^2}{4(d+1)^2\left[(d+1)\ln(d+1) - d\right]} \cdot \qquad [9]$$

For large interfacial elasticity ψ is close to 1, whereas for small interfacial elasticity ψ is proportional to $1/\ln d$. It is seen that the disjoining pressure Π influences the critical thickness in a complicated way. In order to demonstrate the effect of Π we find an approximate solution of Eq. [8] for the case when Π is determined by the van der Waals attraction. Then for large driving forces one obtains $h_c = \left[a^2 A_H^2 / (64\pi\sigma F)\right]^{1/5}$, where A_H is the Hamaker constant. In contrast, for small driving force, F, the critical thickness does not depend on the interfacial tension: $h_c = \left[5aA_H / (6F)\right]^{1/2}$.

To illustrate the predictions of Eqs. [6] and [8] for the case of van der Waals forces, we took values of the parameters for a set of real experimental data about the approaching of oil droplets toward a flat oil-water interface under the action of the buoyancy force. To account for the electromagnetic retardation effect the Hamaker constant A_H is replaced by the effective i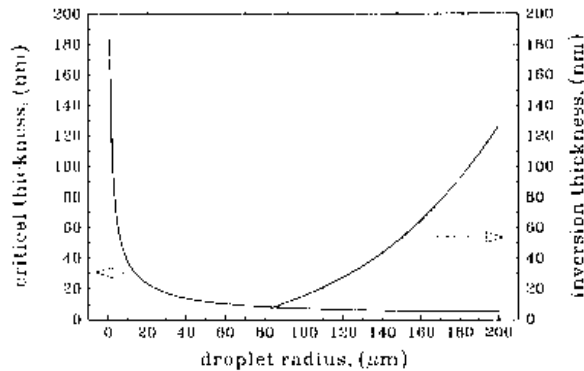nteraction parameter A_{eff}, which for small thicknesses is constant and for large thicknesses is inversely proportional to the thickness h_0, see Ref. 7, p. 155. The electrostatic interactions in this experimental system are strongly suppressed because the aqueous phase contains 0.15 M sodium chloride. The aqueous film is stabilized by Bovine Serum Albumin (BSA) and the droplets are from soybean oil; the respective interfacial tension is $\sigma = 15$ mN/m. The numerical results for the critical

Fig. 2. Dependence of the critical and the inversion thickness on the droplet radius.

and inversion thicknesses, corresponding to this system, are plotted in Fig. 2 vs. the droplet radius a. It is interesting to note that for droplet radii smaller than 83 µm Eq. [6] has no solution, i.e. the droplet surface remains always convex. Because of the high van der Waals attraction the corresponding critical thickness rises up to 180 µm when the droplet radius decreases down to 1 µm. It is interesting to note that for droplet radii greater than 83 µm the critical thickness is smaller than the inversion thickness, i.e. the droplet surfaces will flatten in the zone of contact before the critical thickness is reached; thus a formation of a flat film is initiated.

4. Critical Thickness of Plane-Parallel Films Formed between Larger Drops

When the drops are larger (say, $a > 100$ µm), an almost plane-parallel film of radius R is formed in the zone of their contact (1,2). The stability of the film in the process of its thinning is governed again by Eqs. [1]-[3]. The leading terms in the expressions for the interfacial shape, h_e, and the pressure distribution were reported in Ref. (2). The expression for h_e reads

$$h_e = h_0 + \frac{r^2}{2a} - L\ln\left(1 + \frac{r^2}{2aL}\right) - \frac{r^2}{4a\left(1 + \frac{r^2}{4aL}\right)} ,$$ [10]

where the thickness L is defined by $L = F/(4\pi\sigma)$. We performed a fluctuation analysis of this solution, and obtained the following equation for determining the critical thickness, h_c:

$$\frac{2+d}{1+d} = \frac{h_c R^2}{16\sigma[p_c - \Pi(h_c)]}\left(\frac{\partial\Pi}{\partial h}\right)_c^2 , \qquad p_c = \frac{2\sigma}{a} .$$ [11]

Here R is the film radius and p_c is the capillary pressure. The numerical investigations confirm that the instability is triggered by the long waves, of length comparable to the minimal film thickness. Eq. [11] shows that the disjoining pressure significantly influences the critical thickness. The influence of the surfactant enters the theory through the parameter d, the disjoining pressure Π, and the surface tension σ. Eq. [11] is valid for the case when the disjoining pressure is smaller than the capillary pressure, $\Pi < p_c$, i.e. the film thins and ruptures before reaching its equilibrium thickness.
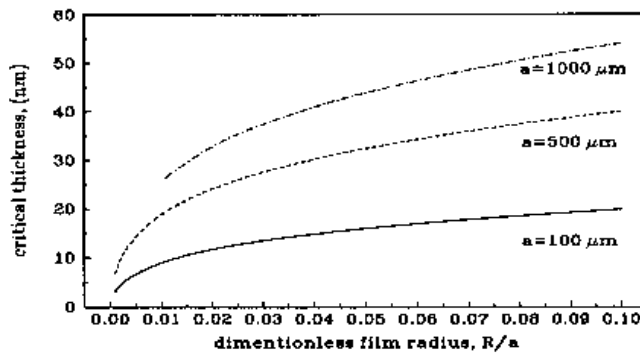
Fig. 3. Dependence of the critical thickness h_c on the dimensionless film radius R/a.
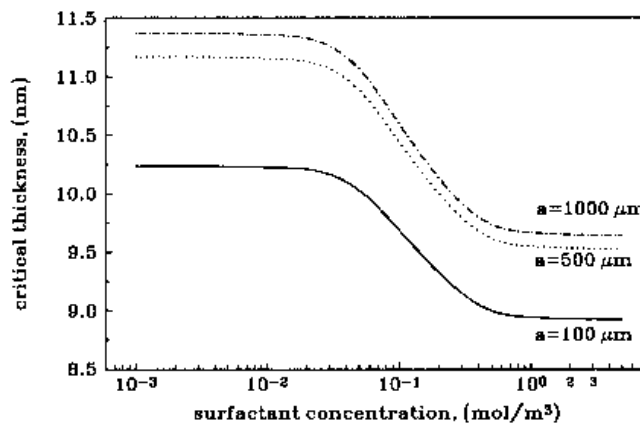

Fig. 4. Dependence of the critical thickness h_c on the surfactant (SDS) concentration.

The numerical solution of Eq. [11] for an emulsion film stabilized by sodium dodecyl sulfate (SDS), below the critical micellization concentration are illustrated in Figs. 3 and 4. The van der Waals and electrostatic interactions are taken into account in the calculation of the disjoining pressure Π. It is seen that for a given surfactant concentration and droplet radius the critical thickness increases with the rise of the film radius, R. This effect was observed experimentally for free aniline films (2). The influence of the surfactant concentration on h_c is illustrated in Fig. 4. The radius of the film is taken to be $R = 1$ μm and the calculations are performed for three different values of the droplet radius a. The effect of increase of the film stability with the rise of the surfactant concentration is well pronounced for all values of a. The experimental data for the dependence of h_c on the surfactant concentration (the dodecanol concentration for the aniline films in Ref. 2) shows the same qualitative behavior. For all surfactant concentrations the increase of the droplet radius, a, leads to larger critical thickness, h_c, and lower stability of the corresponding film.

The values of h_c, calculated from Eq. [11], can be used in a quantitative explanation of the Bancroft rule for the emulsion stability. The rate constant of coalescence is inverse proportional to the film life-time. The film life-time, τ, depends strongly on the inversion and critical film thicknesses (1).

5. Theoretical Interpretation of the Bancroft Rule

Let us consider an oil-water system in which the surfactant is soluble only in the aqueous phase. In the highly dynamic process of emulsion formation by stirring (homogenization) both oil-in-water emulsion (System I) and water-in-oil emulsion (System II) appear. The emulsion with lower coalescence rate will be the one which will survive. Note, that System I contains the surfactant in the continuous phase, whereas System II contains the surfactant in the disperse (droplet) phase. In Refs. (1,4-6,8) the Bancroft rule is discussed for the case of large driving forces, when plane-parallel films are formed between the droplets. We combine Eq. [4] with the theoretical expression from Ref. (8) for the ratio of the coalescence rates in Systems I and II:

$$\frac{\text{Rate II}}{\text{Rate I}} \approx \frac{V_{II}}{V_I} = 0.811\sqrt{\frac{a}{h}}\frac{2h}{l}\left[\frac{d+1}{d}\ln(d+1)-1\right]\frac{(F-2\pi a f)_{II}}{(F-2\pi a f)_I} , \qquad [12]$$

$$l = \frac{6\eta D_s}{E_G} , \quad b = \frac{3\eta D}{E_G}\left(\frac{\partial c}{\partial \Gamma}\right) , \quad d = \frac{l}{h(1+b)}$$

where V_1 and V_{II} are the respective velocities of film thinning, $E_G = -(\partial\sigma/\partial\ln\Gamma)$ is the Gibbs elasticity and D_s is the surface diffusion coefficient. In the case of System II the surfactant does not influence the flow inside the two droplets and they approach each other like droplets from pure liquid phases (without surfactant). Therefore, for the velocity of approach of such two aqueous droplets one can use the approximate expression $V/V_{Ta} = 0.811\eta\sqrt{a}/(\eta_d\sqrt{h})$ from Ref. (9), where η_d is the dynamic bulk viscosity of the oil phase. For the most types of surfactants the surface elasticity is high enough, $d \ll 1$, and the ratio of the two coalescence rates is simplified to read

$$\text{Rate II}/\text{Rate I} \approx 0.811\sqrt{a}(f\text{-}2\pi af)_{II}/\left[(1+b)(f\text{-}2\pi af)_{I}\sqrt{h}\right].$$

For typical emulsion systems this ratio is large, Rate II / Rate I $\gg$ 1; therefore System I will survive. For larger droplets (larger a) the critical thickness is smaller and the difference between the coalescence rates in Systems I and II becomes larger. On the other hand, the difference between the coalescence rates in Systems I and II decreases with the reduction of the droplet size, which is accompanied with an increase of the critical thickness (see Fig. 2). The interaction energy per unit area, f, for both systems can be rather different due to the different types of surface forces operative in water and oil films.

6. Conclusions

First we theoretically investigate the velocity of film thinning and the critical film thickness for relatively small emulsion drops, for which the interfacial deformation in the zone of droplet collision is also small. We establish a significant influence of surfactant concentration and surface forces on the hydrodynamic interactions between such droplets. The surface dynamic parameters (elasticity and viscosity) turn out to be more important for the film stability than the surface tension. The van der Waals forces lead to surprisingly high critical thickness when the droplets are small.

Second, we investigate the hydrodynamic interactions between larger emulsion droplets, which exhibit a well pronounced flattening (film) in the zone of their contact upon collision. The theoretical predictions (Figs. 3 and 4) are consonant with the experimental findings about the effect of surfactant concentration and film radius on the critical thickness of film rupture. On the basis of the theory of kinetic stability of emulsions, we propose a qualitative explanation of the Bancroft rule, see Eq. [12]. The difference between the coalescence rate in O/W and W/O emulsions is found to decrease with the reduction of the droplet size.

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