

## HYDRODYNAMICS OF THIN LIQUID FILMS. EFFECT OF SURFACTANTS ON THE VELOCITY OF THINNING OF EMULSION FILMS

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**Abstract**—A hydrodynamic theory of the process of thinning of emulsion films based on the solution of the complete set of Navier–Stokes' equations for the dispersion phase is given. It is shown that the velocity of thinning depends mainly on the viscosity of the dispersion phase. In the presence of a surfactant soluble in the continuous phase, the velocity of thinning differs only slightly from that for foam films, whereas in the case of a surfactant soluble in the dispersed phase, this velocity is the same as in a system without any surfactant. On these grounds a possible explanation of Bancroft's rule for low stability emulsions is put forward.

### 1. INTRODUCTION

In our preceding work (Ivanov & Traykov 1976) a formula was deduced for the velocity of thinning  $V$  of a thin emulsion film, formed when two drops approach each other in the absence of surfactant. Although such films can be formed and investigated (Hartland 1967; Mackay & Mason 1963; Platicanov & Manev 1964; Sheely & Leng 1971), most of the works deal with surfactant stabilised emulsion films (Sonntag 1960; Sonntag & Streng 1970). In practice, the emulsion systems used likewise contain considerable quantities of surfactant (Becher 1965; Shermann 1968). So the present work contains an analysis of the effect of surfactants on the velocity of thinning of plane-parallel emulsion films.

According to Boussinesq (1913), this effect can be accounted for by introducing two surface viscosities—dilational and shear. Levich (1962) has demonstrated that the dilational surface viscosity is equivalent to the Marangoni–Gibbs effect, i.e. it is caused by the disturbance of the surfactant which leads to the appearance of a surface tension gradient and to the interchange of surfactant between the surface and the bulk of the liquid. We shall account for this effect by the method suggested by Levich and used in previous works on the hydrodynamics of foam films (Radoev, Dimitrov & Ivanov 1974; Ivanov & Dimitrov 1974). The shear surface viscosity entails considerable complexities. If it is accounted for, the theory grows more and more complicated, so we shall begin by assuming it to be equal to zero, and in appendix II we shall demonstrate that the velocity of thinning is not dependent on it. We shall account for the effect for the liquid moving within the drops by solving the complete equations of Navier–Stokes, as in Ivanov & Traykov (1976). To simplify the solution, we shall only examine the limiting cases, in which the surfactant is only soluble either in the film or in the drops. In the first instance, it appears that the Marangoni–Gibbs effect has a similar influence as with foam films (Radoev, Dimitrov & Ivanov 1974); in the second instance, it turns out to be zero.

The following section contains the formulation of the problem. The basic equations and the boundary conditions applied now are similar to those used in preceding works on emulsion films (Ivanov & Traykov 1976) and foam films (Radoev, Dimitrov & Ivanov 1974; Ivanov & Dimitrov 1974) where they were discussed in detail. The results obtained are discussed in section 5; their interrelation with Bancroft's rule and the theoretical interpretation of that rule by Davies (1957) are also examined in section 5. The correct formulation of the equations for the diffusion mass-transfer in lubrication approximation is discussed in appendix I.

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## 2. FORMULATION OF THE PROBLEM

For the sake of simplicity, we are considering the system shown in figure 1: the emulsion film of thickness  $h$  and radius  $R$  is formed in a tube of radius  $R_c$  by sucking out the liquid from a biconcave meniscus II. The tube, which is assumed infinitely long, is filled with the liquid I forming the dispersion phase, i.e. the drops. The film is plane-parallel and sufficiently thin, so that  $h/R \ll 1$ . Because of the natural symmetry of the system, we shall use the cylindrical coordinates shown in figure 2, and all calculations will be done only for  $z > 0$ . The flow in the film obeys the equations of the lubrication theory. Denoting all the quantities referring to the film by an asterisk we write these equations in the form (Kochin, Kibel & Roze 1965; Levich 1962)

$$\frac{\partial^2 v_r^*}{\partial z^2} = \frac{1}{\mu^*} \frac{\partial p^*}{\partial r}, \quad [1a]$$

$$\frac{\partial p^*}{\partial z} = 0, \quad [1b]$$

$$\frac{1}{r} \frac{\partial}{\partial r} (r v_r^*) + \frac{\partial v_z^*}{\partial z} = 0. \quad [1c]$$

For the dispersion phase we solve the complete set of Navier–Stokes equations

$$\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left[ \frac{\partial^2 v_r}{\partial r^2} + \frac{\partial}{\partial r} \left( \frac{v_r}{r} \right) + \frac{\partial^2 v_r}{\partial z^2} \right], \quad [2a]$$

$$\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left( \frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2} \right), \quad [2b]$$

$$\nabla_r v_r + \frac{\partial v_z}{\partial z} = 0; \quad \nabla_r = \frac{1}{r} \frac{\partial}{\partial r} r, \quad [2c]$$

where gravity has been disregarded. In [1] and [2]  $v_r$  and  $v_z$  denote the respective velocity components;  $t$ , time;  $p$ , pressure;  $\rho$ , density;  $\mu$  and  $\nu = \mu/\rho$ —the bulk liquid dynamic and kinematic viscosities.

We are only considering the case of diffusion controlled surfactant transfer. The surfactant repartition obeys the equation of convective diffusion. When the surfactant is only soluble in

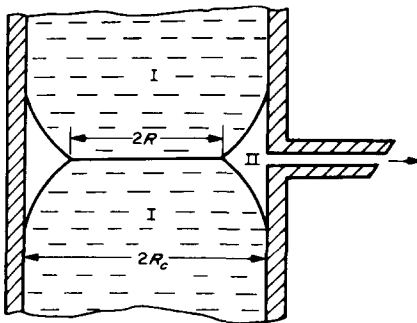


Figure 1.

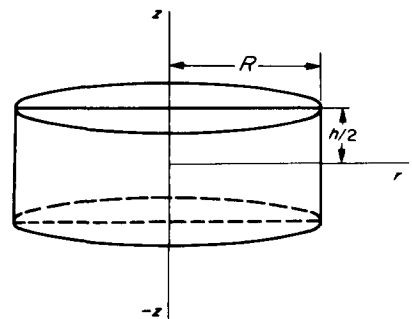


Figure 2.

Figure 1. A model of emulsion film of radius  $R$  formed in a capillary of radius  $R_c$ . I—dispersion phase, II—dispersion medium.

Figure 2. Scheme of a plane-parallel circular film of radius  $R$  and thickness  $h$ .

the film, where the Peclet number  $Pe^*$  is small (Radoev, Dimitrov & Ivanov 1974), this equation acquires the simpler form

$$\Delta_r c^* + \frac{\partial^2 c^*}{\partial z^2} = 0; \quad \Delta_r = \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \tag{3a}$$

where  $c^*$  is the surfactant concentration.

In the dispersion phase the convective and the viscous terms in [2a] are of the same order of magnitude (Ivanov & Traykov 1976), i.e. Reynolds' number  $Re$  is of the order of one. Therefore,  $Pe \gg 1^+$ , and we can use the convective diffusion equation in its approximated form, valid for the diffusion boundary layer (Levich 1962)

$$\frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} + v_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2}, \tag{3b}$$

where  $D$  is the bulk diffusion-coefficient.

The local values of the surface tension  $\sigma$  and surface and bulk concentrations  $\Gamma$  and  $c$  (or  $c^*$ ) for a thinning film, can be represented as sums of the corresponding equilibrium values (at zero flow)  $\sigma_0$ ,  $\Gamma_0$  and  $c_0$  (or  $c_0^*$ ) and the perturbations  $\sigma_1$ ,  $\Gamma_1$  and  $c_1$  (or  $c_1^*$ ) caused by the flow ( $\sigma = \sigma_0 + \sigma_1$  etc.). Since these perturbations are much smaller than the respective equilibrium values, in cases where calculations have to be simplified,  $\sigma$  and  $\Gamma$  are expanded in series with respect to  $c_1$  (or  $c_1^*$ ) and only the linear terms in this series are accounted for (see Levich 1962; Radoev, Dimitrov & Ivanov 1974). Thus, our solution gives, in fact, the linear terms of this perturbation analysis.

When solving [1]–[3], the following boundary conditions are used:

$$\left. \begin{aligned} v_r^* &= v_r = U(r) & [4a] \\ v_z^* &= v_z = -V/2 & [4b] \\ \mu^* \frac{\partial v_r^*}{\partial z} &= \mu \frac{\partial v_r}{\partial z} + \frac{\partial \sigma_0}{\partial c_0^*} \frac{\partial c^*}{\partial r} & \text{at } z = h/2 \text{ [4c]} \\ \nabla_r(\Gamma U) - D_s \Delta_r \Gamma &= -D^* \frac{\partial c^*}{\partial z} & [4d] \end{aligned} \right\}$$

$$\left. \begin{aligned} p^* &= p_0^* \\ c^* &= c_0^* \end{aligned} \right\} \text{at } r = R \tag{4e}$$

$$\left. \begin{aligned} v_r &= 0 \\ p &= p_0 \\ c &= c_0 \end{aligned} \right\} \text{at } z = \infty \tag{4g}$$

$$\tag{4f}$$

$$\tag{4h}$$

$$\tag{4i}$$

where  $V = -dh/dt$  is the rate of thinning of the film,  $U(r)$  is the radial velocity on the interface,  $p_0$  is the pressure in the dispersion phase far from the interface,  $D_s$  is the surface diffusion-coefficient and  $p_0^*$  is the pressure in the hypothetical equilibrium film of the same thickness. This pressure is related to the pressure  $p_m$  in the meniscus through the equation  $p_0^* = p_m + \Pi$ , where  $\Pi$  is the disjoining pressure (see e.g. Toshev & Ivanov 1975). All functions giving the solution of [1]–[3] must obviously be finite at  $r = 0$ . When the surfactant is soluble in the dispersion phase,  $c$  is substituted for  $c^*$  in [4c] and [4d],  $-D$  is substituted for  $D^*$  in [4d] and [4i] is used instead of [4f].

†  $Pe = Re (\nu/D) \approx 10^3 Re$ .

Equations [4a] and [4b] result from the very formulation of the problem; [4c] is the continuity condition for the tangential component of the stress tensor on the interface; [4d] is the conservation law for the surfactant. Equations [4e] and [4f] follow from the assumption that the liquid in the meniscus is immobile and [4g]–[4i] account for the disappearance of the radial motion of the liquid in the dispersion phase with  $z \rightarrow \infty$ .

### 3. SURFACTANT SOLUBLE IN THE DISPERSION MEDIUM

To simplify matters, we shall first consider the case of a steady flow in the dispersion phase,† i.e. in [2] we shall disregard the derivatives on  $t$ . The case of a non-steady flow will likewise be considered towards the end of this section. Since the method of solving [1] is given in detail in (Radoev, Dimitrov & Ivanov 1974) and (Ivanov & Traykov 1971/72), here we only adduce the final results:

$$v_r^* = \frac{3}{h^3}(2Uh - Vr) \left( z^2 - \frac{h^2}{4} \right) + U, \quad [5a]$$

$$p^* = p_0^* + \frac{3\mu^*V}{h^3}(R^2 - r^2) - \frac{12\mu^*}{h^2} \int_r^R U \, dr. \quad [5b]$$

The concentration repartition  $c^*$  need not be calculated within the lubrication approximation limits; [3a] and [4d] can be replaced by the simpler equation (see appendix I):

$$\Gamma_0 U - \left( D_s \frac{\partial \Gamma_0}{\partial c_0^*} + \frac{D^* h}{2} \right) \frac{\partial c^*}{\partial r} = 0 \quad [6]$$

which affords the determination of  $\partial c^*/\partial r$ .

The particular symmetry of the system suggests the following form of the expression for  $v_r$ :

$$v_r = U(r) f(\eta) \quad [7]$$

where

$$\eta = (z - h/2)(U/r\nu)^{1/2} \quad [8]$$

is a dimensionless coordinate. Thus far unknown, the function  $f(\eta)$  will be determined hereafter. If we express  $\partial v_r/\partial z$  from [7] and  $\partial v_r^*/\partial z$  from [5a], by using [4c] and A.I.5, we obtain the following algebraic equation for the ratio  $U/r$ :

$$\frac{U}{r} - \frac{V}{2h} + \frac{U}{r}(\epsilon^e + \epsilon^f) = 0 \quad [9]$$

where

$$\epsilon^f = - \frac{(\partial \sigma_0 / \partial c_0^*) \Gamma_0}{3\mu^* D^* \left[ 1 + \frac{2D_s(\partial \Gamma_0 / \partial c_0^*)}{D^* h} \right]}, \quad [10]$$

$$\epsilon^e = - [a_1 \mu h (U/r\nu)^{1/2}] / 6\mu^* \quad [11]$$

and

$$a_1 = (df/d\eta)_{\eta=0}. \quad [12]$$

†Because of the very small value of Reynolds' number in the film, the flow there is always steady (see Radoev, Dimitrov & Ivanov 1974).

Equation [9] is satisfied by the solution

$$U = Ar \tag{13}$$

where the constant  $A$  does not depend on  $r$  (see [9]):

$$A = \frac{V}{2h(1 + \epsilon^\epsilon + \epsilon^f)} \tag{14}$$

Any further solution is analogous to that described by Ivanov and Traykov (1976), where the approximations used below are analysed. Integrating [2c] on  $z$ , and with the aid of [4b], [8] and [13], we obtain:

$$v_z = -2(A\nu)^{1/2} \int_0^\eta f(\eta) d\eta - V/2. \tag{15}$$

Taking into account [4h], [7], [13] and [15], we conclude from [2b] that  $p$  does not depend on  $r$ , i.e. that the term  $\partial p/\partial r$  in [2a] disappears. Thus, the following equation for  $f(\eta)$  is obtained from [2a], [7], [8], [13] and [15]:

$$f'' + 2f' \left[ \int_0^\eta f d\eta + V/4(A\nu)^{1/2} \right] - f^2 = 0 \tag{16}$$

which, after differentiation on  $\eta$ , transforms into:

$$f'''f' - f''^2 + f''f^2 = 0. \tag{17}$$

The boundary conditions to be used in solving [17] are:

$$\left. \begin{aligned} f &= 1 \\ f'' &= 1 \end{aligned} \right\} \text{ at } \eta = 0 \tag{18a}$$

$$f = 0 \text{ at } \eta = \infty. \tag{18c}$$

Equations [18a] and [18c] follow from [4a], [4g] and [7]; [18b] follows from [16] and [18a], with  $V/4(A\nu)^{1/2} \ll 1$  (see Ivanov & Traykov 1976). The numerical solution of [17] yields the functions  $f(\eta)$  and  $\int_0^\eta f d\eta$  (see figure 3, curves 1 and 2 respectively), necessary for the calculation of  $v_r$  and  $v_z$  from [7] and [15] and the value of the constant  $a_1 = -1.19$  in [11].

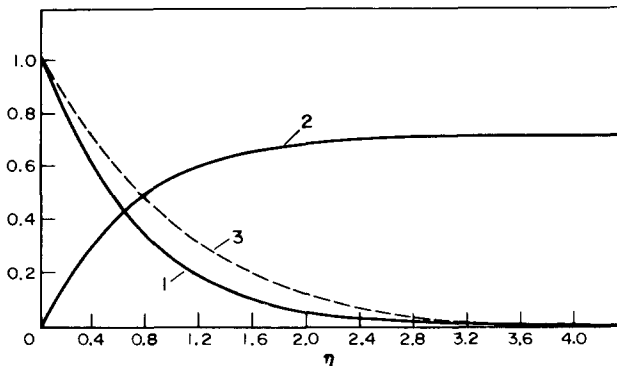


Figure 3. Plots of the solution of [17]: 1—dependence of the function  $f$  on the dimensionless coordinate  $\eta$ ; 2—dependence of the function  $\int_0^\eta f d\eta$  on  $\eta$ ; 3—dependence of the function  $f$  on  $\eta$  obtained in (Ivanov & Traykov 1971–72) by von Karman–Pohlhausen’s method (see also Ivanov & Traykov 1976).

The velocity of thinning is found from the balance of forces acting upon the film surface:

$$\int_0^R p_{zz} r \, dr = \int_0^R p_{zz}^* r \, dr \quad [19]$$

where  $p_{zz}$  and  $p_{zz}^* \approx -p^*$  are the normal components of the stress tensor. The problem could be solved without any further approximations (Ivanov & Traykov 1976), but in order to obtain simpler final results we assume  $p_{zz} = -p_0$ . Then, from [5b], [13], [14] and [19], we obtain:

$$V/V_0 = 1 + 1/(\epsilon^e + \epsilon^f) \quad [20]$$

where

$$V_0 = 2h^3 \Delta P / 3\mu^* R^2 \quad [21]$$

is Reynolds' velocity of thinning of a film formed between two rigid parallel discs (Reynolds 1886), and

$$\Delta P = P_c - \Pi \quad [22]$$

is the driving force (per unit area) of the process ( $P_c = p_0 - p_m$  is the capillary pressure).

When the term  $\partial v_r / \partial t$  in [2a] cannot be disregarded, it can, by using [7], [8], [13] and [14], be transformed, following Ivanov and Traykov (1976), to

$$\frac{\partial v_r}{\partial t} = -V \frac{\partial v_r}{\partial h} = -rA^2(2f + \eta f')\kappa \quad [23]$$

where

$$\chi = \left(1 - \frac{\partial \ln V}{\partial \ln h}\right) (1 + \epsilon^e + \epsilon^f) + h \frac{\partial(\epsilon^e + \epsilon^f)}{\partial h}. \quad [24]$$

Thus, instead of [17], we obtain

$$f'''f' - f''^2 + f''f'^2 + (2ff'' - 3f'^2)\kappa = 0 \quad [25]$$

and the boundary condition [18b] transforms into  $f'' = 1 + 2\chi$  at  $\eta = 0$ . In this case [20] is again obtained, but  $f$ , and therefore  $a_1$  will depend on  $h$ ,  $\epsilon^e$  and  $\epsilon^f$  (through  $\kappa$ ). The values of  $a_1$  for different  $\kappa$  are tabulated in (Ivanov & Traykov 1976).

#### 4. SURFACTANT SOLUBLE IN THE DISPERSION PHASE

We shall now consider only the case of steady flow and surfactant transfer in the dispersion phase. A linear dependence between the surface radial velocity  $U$  and  $r$  [13] was obtained, both for the system without surfactant (Ivanov & Traykov 1976) and for the case of a surfactant soluble in the dispersion medium (section 3 of the present paper). We therefore assume that in the case of a surfactant soluble in the dispersion phase, considered in this section, [13] is still valid, but that the constant  $A$  may be different. This means that the solution and the final results of the preceding section can be used in this case as well, with the exception of the determination of  $A$ .

In order to find  $A$ , we must solve the equation of convective diffusion [3b] (with  $\partial c / \partial t = 0$ ). The function  $f(\eta)$  from figure 3 is accurately represented by

$$f = e^{a_1 \eta}. \quad [26]$$

Thus, introducing  $f$  as a new variable (instead of  $\eta$ ), from [3b], [7], [8], [13] and [15] we readily obtain

$$f \frac{\partial^2 c}{\partial f^2} + 2kf \frac{\partial c}{\partial f} - (2k-1) \frac{\partial c}{\partial f} - kr \frac{\partial c}{\partial r} = 0; \quad k = \frac{\nu}{Da_1^2}. \quad [27]$$

Equation [27] allows a solution of the kind  $F_n(f)r^n$ , where  $n$  is a positive number, and  $F_n$  is determined from the equation

$$fF_n'' + 2kfF_n' - (2k-1)F_n' - knF_n = 0. \quad [28]$$

As the solution of [28] is offered through the confluent hypergeometric function  $\phi$  (Janke *et al.* 1960), we can write  $c$  as being

$$c = r^n [B_1 \phi(-n/2, 1-2k, -2kf) + B_2 f^{2k} e^{-2kf} \phi(1+n/2, 2k+1, 2kf)] \quad [29]$$

where  $B_1$  and  $B_2$  are integration constants. This expression will satisfy the boundary conditions [4d] and [4i] only if  $n=0$ . Then, from [4i] we obtain  $B_1 = c_0$ , and [4d], with the aid of the approximation  $\Gamma = \Gamma_0 + (\partial\Gamma_0/\partial c_0)(c - c_0)$  (see Radoev *et al.* 1974), provides

$$B_2 = - \frac{\Gamma_0 e^{2k\beta}}{(\partial\Gamma_0/\partial c_0)\phi(1, 2k+1, 2k)(1+\beta)}. \quad [30]$$

Thus we finally obtain

$$c = c_0 - \frac{\Gamma_0 f^{2k} e^{2k(1-f)} \phi(1, 2k+1, 2kf)}{(\partial\Gamma_0/\partial c_0)\phi(1, 2k+1, 2k)} \cdot \frac{\beta}{1+\beta} \quad [31]$$

where

$$\beta = \frac{(A\nu)^{1/2} (\partial\Gamma_0/\partial c_0)(2k+1)\phi(1, 2k+1, 2k)}{D(-a_1)k\phi(2, 2k+2, 2k)}. \quad [32]$$

Inserting  $f = 1(\eta = 0)$  in [31], we find the concentration  $c(0)$  at the film surface

$$c(\eta = 0) = c_0 - \frac{\Gamma_0}{\partial\Gamma_0/\partial c_0} \frac{\beta}{1+\beta}. \quad [33]$$

The constant  $A$  in [13] is determined, as before, from [4c]. Since the term  $\partial c/\partial r$  disappears for the system under consideration, the surfactant will have no effect at all on the velocity of thinning, and in that respect this system will behave as an emulsion system without surfactant.

## 5. DISCUSSION

In the absence of any surfactant, the parameter  $\epsilon^f$  defined by [10] is zero so that from [20] (see also [21]) we again obtain the results found for this case by Ivanov & Traykov (1976).

When the surfactant is soluble in the dispersion medium and the liquids have comparable viscosities ( $\mu/\mu^* \approx 1$ ), in practice  $\epsilon^e$  in [20] can always be disregarded. Indeed, for surfactants of moderate surface activity  $\Gamma_0 \approx 10^{-5} c_0^*$ ,  $\partial\sigma_0/\partial c_0^* = -10^7 \text{ g cm}^3 \text{ sec}^{-2} \text{ mol}^{-1}$  and  $\epsilon^f \approx 10^9 c_0^*$  (we have taken in [10]  $\mu^* = 10^{-2} P$ ,  $D^* = 10^{-5} \text{ cm}^2/\text{sec}$  and  $D_s = 0$ ). If  $c_0^* = 10^{-9} \text{ mol/cm}^3$   $\epsilon^f \approx 1$ , so that  $V$  is of the order of magnitude of Reynolds' velocity  $V_0$ . With  $A \approx V_0/2h$ ,  $\Delta P = 10^3 \text{ dyn/cm}^2$ ,  $h = 10^{-5} \text{ cm}$ ,  $R = 10^{-2} \text{ cm}$  and  $\mu = \mu^* = 10^{-2} P$ , from [11] and [21] we find  $\epsilon^e =$

$10^{-5}$ . We thus conclude that even negligible contaminations of surfactants that are soluble in the dispersion medium will eliminate the influence of the liquid flow within the droplet and the film will obey the equation of the velocity of thinning of foam films, as derived in Radoev, Dimitrov & Ivanov (1974). The same equation is obtained from [20] by making  $\epsilon' = 0$ . Because of the surfactant diffusion, this velocity is greater than  $V_0$ , although both are of the same order of magnitude (Manev *et al.* 1976).

The situation is quite different for surfactants that are only soluble in the dispersion phase. We have shown in section 4 that in that case the surfactant remains uniformly distributed on the film surface, so that the Marangoni-Gibbs effect disappears. The system will therefore behave as a system without surfactant, and the velocity of thinning can be calculated from [20] by making  $\epsilon' = 0$ . If  $\mu/\mu^* \lesssim 1$ , the velocity of thinning will be many times higher than Reynolds' velocity (Ivanov & Traykov 1976). This conclusion is not compromised by the fact that in section 4 we have disregarded the derivatives of  $v_r$ ,  $v_z$  and  $c$  on  $t$ . We did in fact show in section 3 (see also Ivanov & Traykov 1976) that accounting for the derivatives on  $t$  in [2] leads to an alteration of the values of  $A$  and  $V$ , but does not alter the functionality of  $v_r$  (and  $v_z$ ) on  $r$ . On the other hand the term  $\partial c/\partial t$  could be represented, by analogy with [23] like this:  $\partial c/\partial t = (\partial c/\partial h)/(dh/dt) = -V(\partial c/\partial h)$ . Therefore, the derivative  $\partial c/\partial h$  will appear in [27] and [31]–[33] will naturally be altered, but the conclusion about the independence of  $c$  of  $r$ , and consequently about the independence of the velocity of thinning of the presence of surfactant, will still be valid.

We see therefore that the emulsion system can behave in two wholly different ways, depending on the solubility of the surfactant: first, in the case of a surfactant soluble in the dispersion medium, the velocity of thinning is somewhat higher, but still of the order of Reynolds' velocity, and mainly determined by the properties and concentration of the surfactant; second, in the case of a surfactant soluble in the dispersion phase, the velocity of thinning is much greater than Reynolds' velocity and is wholly independent of the presence of surfactant.† This drastic difference is due to the different way of supplying the surfactant on to the film surface. In the former case, the surfactant is transported from the meniscus at distances which are of the order of the film radius  $R$ . That is why the surfactant flux is small, and incapable wholly to compensate the surface tension gradient caused by the liquid flow. In the latter case the surfactant is transported from the bulk of the dispersion phase on to the surface only through the diffusion boundary layer, and the surfactant flux readily eliminates the surface tension gradient.

This effect is probably related to Bancroft's rule (Bancroft 1913; see also Shermann 1968) and its explanation, as given by Davies (1957). When an emulsion is formed, according to Bancroft, the continuous phase will be the phase in which the surfactant is preferentially soluble. Davies (1957) assumes that the type of the emulsion is determined by the ratio of the rates of coalescence  $v_{0/w}$  and  $v_{w/0}$  of the droplets in the emulsions  $0/W$  and  $W/0$ . He represents these rates by the equation  $v = K_h\psi$ , where  $K_h$  is a hydrodynamic (collision) factor and  $\psi$  is a function of the energetic barrier against coalescence. Assuming that  $K_h$  has the same value for both emulsion types and expressing  $\psi$  through the surfactant properties, he was able to explain Bancroft's rule and the relation between HLB and the type of the emulsion. Our results indicate, however, at least in the case of the droplets' coalescence being preceded by the formation of a thin liquid film, that the hydrodynamic factors for direct and reverse emulsion may differ substantially. This difference may perhaps be immaterial in the case of highly stable emulsions, where the energetic barrier against coalescence is great, but for emulsions of low stability (with  $\psi$  of the order of unity), the ratio of the hydrodynamic factors could play a decisive role. According to the results of the present work, the hydrodynamic factor will be much greater for the droplets formed by the liquid where the surfactant is soluble. This will

†This conclusion was corroborated experimentally in the following work.



lead to a faster coalescence of these droplets and will favour the formation of the emulsion in which the continuous phase is formed by the liquid where the surfactant is soluble. This conclusion is in accordance with Bancroft's rule.

We should point out, however, that the rate of coalescence does not solely depend on the velocity of thinning, but also on the behaviour of the capillary waves on the film surface (Vrij 1966; Sheludko 1962; Ivanov *et al.* 1970). We shall soon be presenting a theory on the rupture of emulsion films, with both effects being taken into account.

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## APPENDIX 1

## DIFFUSION MASS-TRANSFER IN LUBRICATION APPROXIMATION

In investigating the effect of surfactants on the hydrodynamics of thin liquid films, the surfactant transfer is usually calculated with the aid of Fick's second law [3a]. Unlike [1], this equation does not take into account the great difference in the linear dimensions of the film ( $h/R \ll 1$ ). The solution is therefore obtained in the form of series, which requires the additional use of the condition  $h/R \rightarrow 0$  (see, e.g. Ivanov & Dimitrov 1974). This procedure is not wholly self-consistent; it is therefore desirable for the equation describing the surfactant repartition to be so formulated as to be compatible with the lubrication theory [1].

If there is to be a diffusion flow, the two terms in [3a] should be of the same order. This will be so if we set down  $c^*(r, z)$  in the form of a series in the powers of  $z$  (see also [4d]):

$$c^*(r, z) \approx c_0^* + c_1^*(r) + c_2^*(r) \frac{z^2}{2}, \quad [\text{A.1.1}]$$

with the factors  $c_1^*$  and  $c_2^*$  satisfying the condition (substitute [A.1.1] in [3a]):

$$c_2^* h^2 \approx \frac{h^2}{R^2} c_1^*. \quad [\text{A.1.2}]$$

Accordingly, for the result thus obtained to be compatible with the lubrication approximation, whenever no differentiation is made on  $z$ , the term with  $z^2$  in [A.1.1] should be disregarded. On the basis of [A.1.1] and [3a] we can set down for the concentration gradient

$$-\left(\frac{\partial c^*}{\partial z}\right)_{z=h/2} = -\frac{h}{2} c_2^* = \frac{h}{2} \Delta_r c_1^* \approx \frac{h}{2} \Delta_r c^*. \quad [\text{A.1.3}]$$

Thus, in the case of the surfactant being soluble in the dispersion medium, we shall, instead of [4d], obtain a more simple condition with the aid of the approximation  $\Delta_r \Gamma \approx (\partial \Gamma_0 / \partial c_0^*) \Delta_r c^*$

$$\Gamma_0 \nabla_r U - \left( D_s \frac{\partial \Gamma_0}{\partial c_0^*} + \frac{D^* h}{2} \right) \Delta_r c^* = 0. \quad [\text{A.1.4}]$$

After integration on  $r$ , it yields (the integration constant is to be zero on the requirement for the functions to be finite at  $r = 0$ ):

$$\Gamma_0 U - \left( D_s \frac{\partial \Gamma_0}{\partial c_0^*} + D^* \frac{h}{2} \right) \frac{\partial c^*}{\partial r} = 0. \quad [\text{A.1.5}]$$

## APPENDIX 2

EFFECT OF SURFACE VISCOSITY ON THE VELOCITY  
OF THINNING OF THIN LIQUID FILMS

The effect of the surface shear viscosity  $\mu_s$  on the velocity of thinning of foam films was analysed in Ivanov & Dimitrov (1974); it was demonstrated there that for moderate values of  $\mu_s$  the effect is negligibly small. As, after Plateau's (1869) well-known work, the relation of surface viscosity, velocity of drainage and stability of foams and emulsions has frequently been discussed (see, e.g. Gantz 1967), the conclusion on the independence of  $V$  on  $\mu_s$  ought to be likewise corroborated under some other more general method. To simplify calculations, we shall examine in detail the case of a foam film and demonstrate, towards the end of this appendix that the results are also valid for emulsion films. For a foam with  $\mu_s > 0$  the boundary condition [4c] takes on the form (Ivanov & Dimitrov 1974)

$$\mu^* \frac{\partial v_r^*}{\partial z} = \frac{\partial \sigma_0}{\partial c_0^*} \frac{\partial c^*}{\partial r} + \mu_s \frac{\partial}{\partial r} (\nabla_r U). \quad [\text{A.2.1}]$$

In addition to Marangoni–Gibbs effect, certain authors (Sternling & Scriven 1959) also take into account the surface dilational viscosity  $\mu_d$ . When that is done,  $\mu_s + \mu_d$  should be substituted in [A.2.1] for  $\mu_s$ . After substitution in [A.2.1] of  $v_r^*$  from [5a] and of  $\partial c^*/\partial r$  from [A.1.5] we obtain

$$\alpha L_x U = U - \gamma x, \quad [\text{A.2.2}]$$

where  $x = r/R$ , and

$$L_x = \frac{d}{dx} \left( \frac{1}{x} \frac{d}{dx} x \right), \quad [\text{A.2.3}]$$

$$\alpha = \frac{h\mu_s}{6\mu^* R^2 (1 + \epsilon^f)}, \quad [\text{A.2.4}]$$

With  $\alpha < 1$ , the solution of [A.2.2] can be represented by the series (Vassilieva & Boutuzov 1973; Cole 1968)

$$U = U_0(x) + \tilde{U}_0(\tau) + \alpha [U_1(x) + \tilde{U}_1(\tau)] + \dots, \quad [\text{A.2.5}]$$

where  $\tau = x/\alpha^{1/2}$ ; the functions  $U_i$  and  $\tilde{U}_i$  ( $i = 0, 1, 2, \dots$ ) are determined by substitution of [A.2.5] in [A.2.2] and by equating the coefficients before the identical powers of  $\alpha$ , separately for  $U_i$  and  $\tilde{U}_i$ . We thus obtain the equations

$$U_0 = \gamma x; \quad U_{i+1} = L_x U_i = 0 \quad (i = 0, 1, 2, \dots), \quad [\text{A.2.6}]$$

$$L_x \tilde{U}_i = \tilde{U}_i \quad (i = 0, 1, 2, \dots), \quad [\text{A.2.7}]$$

The equations [A.2.7] have the solution (Korn & Korn 1961)

$$\tilde{U}_i = C_i I_1(\tau) + C_i^* K_1(\tau) \quad [\text{A.2.8}]$$

where  $I_1$  and  $K_1$  are modified Bessel's functions of the first order, respectively of first and second kind. For  $U$  to be finite at  $r = 0$ , all the constants  $C_i^*$  have to be equal to zero. We thus obtain from [A.2.5]–[A.2.8]

$$U = \gamma x + C I_1(x/\alpha^{1/2}), \quad [\text{A.2.9}]$$

where

$$C = \sum_{i=0}^{\infty} C_i \alpha^i. \quad [\text{A.2.10}]$$

Equation [A.2.9] can also be obtained directly from [A.2.2] but we applied the above more complicated method so as to demonstrate that  $C$  allows an expansion in a series of Taylor with respect to  $\alpha$ . With  $\alpha \rightarrow 0$  (i.e.  $\mu_s \rightarrow 0$ ), [A.2.9] should turn into the expression (see [13] and [14] with  $\epsilon^e = 0$ )

$$U = Vr/2h(1 + \epsilon^f) = \gamma x. \quad [\text{A.2.11}]$$

That is possible if  $C_0 = 0$ . In order to determine the remaining constants  $C_i$  ( $i = 1, 2, 3, \dots$ ), we shall expand  $I_1$  into a series of Taylor. Then [A.2.9] yields (see Janke *et al.* 1960)

$$U - U_0 = \sum_{i=1}^{\infty} C_i \alpha^i \sum_{j=0}^{\infty} \frac{(x/2\alpha^{1/2})^{2j+1}}{j!(j+1)!} = \sum_{i=1}^{\infty} C_i \alpha^{i-1} \sum_{j=0}^{\infty} \frac{(x/2)^{2j+1} \alpha^{1/2-j}}{j!(j+1)!}. \quad [\text{A.2.12}]$$

With  $\alpha \rightarrow 0$ , only  $C_1$  remains in the first sum. Since at this  $U$  should tend to  $U_0$ , we have

$$\lim_{\alpha \rightarrow 0} (U - U_0) = C_1 \lim_{\alpha \rightarrow 0} \sum_{j=0}^{\infty} \frac{(x/2)^{2j+1} \alpha^{1/2-j}}{j!(j+1)!} = 0. \quad [\text{A.2.13}]$$

That is only possible if  $C_1 = 0$ . By following the same procedure over again, it can be shown that  $C_2 = 0$ , and so on. As all constants  $C_i$  are equal to zero, it follows from [A.2.9] that with  $\alpha > 0$ , [A.2.11] will also be valid, and that therefore  $\mu_s$  will have no effect on the velocity of thinning  $V$ . This conclusion will be justified for those values of  $\alpha$  at which the expansion [A.2.5] may be used. If we assume that for that it is necessary to have  $\alpha \leq 0, 1$ , we obtain from [A.2.3]

$$\mu_s \leq \frac{0,6\mu^*R^2(1 + \epsilon^f)}{h} = 6 \cdot 10^{-2}(1 + \epsilon^f). \quad [\text{A.2.14}]$$

Here we have used the values  $\mu^* = 10^{-2}$  P,  $h = 10^{-5}$  cm and  $R = 10^{-2}$  cm, which are typical for the experiments with microscopic thin films (Sheludko 1966; Sonntag & Strenge 1970; Manev, Vassiliev & Ivanov 1976). Even at low concentrations of surfactant  $\epsilon^f \approx 1$  (Radoev, Dimitrov & Ivanov 1974; Vassiliev, Manev & Ivanov 1976). Then the condition [A.2.14] will be valid with  $\mu_s \leq 0.1$  s.P. Such high values of  $\mu_s$  are hardly possible at low surfactant concentrations.  $\mu_s$  increases with the rise of surfactant concentration, but so does  $\epsilon^f$ , so that the effect of  $\mu_s$  on the velocity of thinning may prove to be substantial only in certain cases of abnormally high surface viscosity.

With emulsion films the term  $\mu(\partial v_t / \partial z)$  (see [4c]) should be inserted into the R.H.S. of [A.2.1]. Expressing this term through [7] and [8], in the case of the surfactant being soluble in the dispersion medium, instead of [A.2.2] we shall obtain

$$\alpha L_x U = \left(1 + \frac{\epsilon^e}{1 + \epsilon^f}\right) U - \gamma x. \quad [\text{A.2.15}]$$

The correction term  $\epsilon^e/(1 + \epsilon^f)$  greatly increases at  $c_s^* \rightarrow 0$ , since then  $\epsilon^f \rightarrow 0$ , whereas  $\epsilon^e$  increases. However, even with  $c_s^* = 0$ ,  $\epsilon^e$  does not usually exceed  $10^{-2}$  (Ivanov & Traykov 1976), so that this term may practically always be disregarded. This means that the conclusion on the independence of  $V$  on  $\mu_s$ , which we reached on the basis of [A.2.2], will also be valid for

emulsion films. One can proceed to a more rigorous analysis of [A.2.15] by applying a further expansion of  $U$  and  $\gamma$  in a series over the powers of the small parameter  $\epsilon^e/(1 + \epsilon^e)$ . As this approach conduces to the same results, we shall not adduce here the long calculations associated with it.

In the case of surfactant being soluble in the dispersion phase, the above analysis cannot be carried out as owing to the assumption that [13] is still valid (see section 4), the term with  $\mu_s$  in [A.2.1] is identically annulled.

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