HYDRODYNAMICS OF EMULSION FILMS

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The correct interpretation of experimental results on the kinetic behaviour of emulsion films requires the use of an equation for the rate of thinning which accounts for the motion of the liquid in the droplets and the surfactant mass transfer. The problem for emulsion films without surfactant was considered in /1 - 5/. The aim of the present work is to summarise our main theoretical and experimental results about the influence of surfactants on the thinning of plane-parallel emulsion films.

1. Theory – For the sake of simplicity, we are considering the system shown in Fig.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 /6/. 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 << 1. Because of the natural symmetry of the system, we shall use cylindrical coordinates and all calculations will be done only for z > 0. The flow in the film obeys the equations of the lubrication theory. Denoting by an asterisk all quantities refering to the film, we can write these equations in the form /7/,/8/:

Fig. 1.

$$(1a) \quad \frac{\partial^2 v_r^*}{\partial z^2} = \frac{1}{\mu^*}\frac{\partial p^*}{\partial r}$$

$$(1b) \quad \frac{\partial p^*}{\partial z} = 0$$

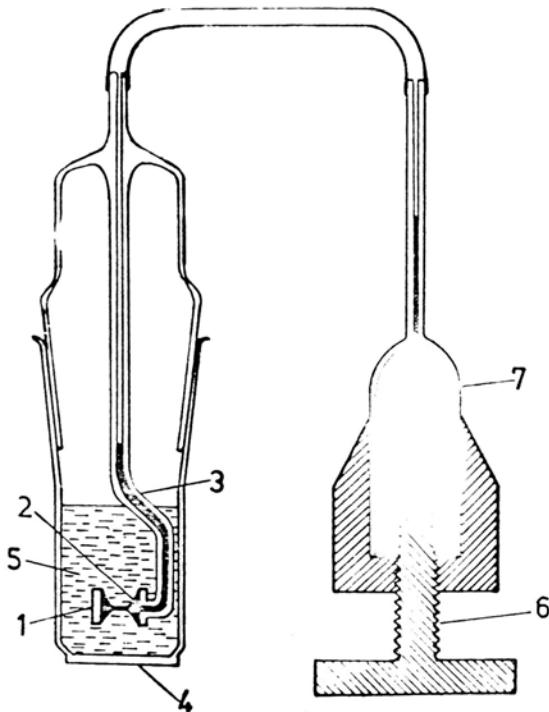$$(1c) \quad \frac{1}{r}\frac{\partial}{\partial r}(r v_r^*) + \frac{\partial v_z^*}{\partial z} = 0$$

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

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

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

$$(2c) \quad \nabla_r v_r + \frac{\partial v_z}{\partial z} = 0 \; ; \quad \nabla_r = \frac{1}{r} \frac{\partial}{\partial r} r$$

where gravity has been disregarded. In (1) and (2), v_r and v_z denote the respective velocity components; t - time; p - pressure; ρ - density; μ 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 in the film obeys the equation /9/

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

(c* is the surfactant concentration) while in the dispersion phase the convective diffusion equation in its approximated form, valid for the diffusion boundary layer must be used:

$$(3b) \quad \frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial r} + v_z \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2}$$

Here D is the bulk diffusion coefficient.

The surface tension σ and the surface and bulk concentration and c (or c*) can be represented as sums of the corresponding equilibrium values σ_0 , Γ_0 and c_0 (or c_0^*) and the small perturbations σ_1 , Γ_1 and c_1 (or c_1^*) caused by the flow ($\sigma = \sigma_0 + \sigma_1$ etc.)

When solving eqns. (1)-(3), the following boundary conditions are used:

$$(4a) \qquad v_r^* = v_r = U(r) \qquad\qquad (4b) \qquad v_z^* = v_z = -V/2$$

$$(4c) \qquad \mu^* \frac{\partial v_r^*}{\partial z} = \mu \frac{\partial v_r}{\partial z} + \frac{\partial \sigma_0}{\partial c_0^*} \frac{\partial c^*}{\partial r} \qquad\qquad \text{at } z = h/2$$

$$(4d) \quad \nabla_r (\Gamma U) - D_s \Delta_r \Gamma = -D^* \frac{\partial c^*}{\partial z} \qquad \text{at} \quad z = h/2$$

$$(4e) \quad p^* = p_o^* \quad , \quad (4f) \quad c^* = c_o^* \qquad \text{at} \quad r = R$$

$$(4g) \quad v_r = 0 \quad , \quad (4h) \quad p = p_o \, , \, (4i) \quad c = c_o \quad \text{at} \quad z = \infty$$

where $V = -dh/dt$ is the rate of thinning of the film, $U(r)$ is the radial velocity on the interface, p_o is the pressure in the dispersion phase far from the interface, D_s is the surface diffusion coefficient and p_o^* is the pressure in the hypothetical equilibrium film of the same thickness. This pressure is related to the pressure p_m the meniscus through the equation $p_o^* = p_m + \Pi$, where Π is the disjoining pressure. When the surfactant is soluble in the dispersion phase, c is substituted for c^* in (4c) and (4d) and D is substitut for D^* in (4d).

Since the methods of solution are similar to those, described in /4/,/5/ and /9/, we shall only discuss here some of the more important steps. We shall consider further two limiting cases of surfactant soluble only i) in the dispersion medium and ii) in the dispersion phase.

The particular symmetry of the system suggests the following form of v_r:

$$(5) \qquad v_r = U(r) \, f(\eta)$$

where $\eta = (z - h/2)(U/r\nu)^{\frac{1}{2}}$ is a dimensionless coordinate. Then in the case i) (4c) yields the following algebraic equation for the ratio U/r :

$$(6) \qquad \frac{U}{r} - \frac{V}{2h} \left(+ \frac{U}{r} \left(\varepsilon^c + \varepsilon^f \right) \right) = 0$$

where

$$(7) \qquad \varepsilon^f = \frac{(-\partial \sigma / \partial c_o^*) \Gamma_o}{3 \mu^* D^* \left[1 + \frac{2 D_s (\partial \Gamma_o / \partial c_o^*)}{D^* h} \right]}$$

and

$$(8) \qquad \varepsilon^c = - \left[a_1 \mu h (U/r\nu)^{1/2} \right] / 6 \mu^*$$

and $a_1 = (df/d\eta)_{\eta = 0}$. Eqn.(6) is satisfied by the solution

(9) $\qquad$ $U = Ar$; $\qquad$ $A = V/2h(1 + \xi' + \xi^f)$

The function $f(\eta)$ is obtained by numerical solution of the equation

(10) $\qquad$ $f''''f' - f''^2 + f''f^2 + (2ff'' - 3f'^2)\mathcal{X} = 0$

with

(11) $\qquad$ $\mathcal{X} = (1 - \partial \ln V/\partial \ln h)(1 + \xi' + \xi^J) + h\frac{\partial}{\partial h}(\xi' + \xi^J)$

following from (5),(9),(2a) and (4).This solution shows /5/, that in general case $a_1(\mathcal{X})$ depends slightly on h , while for steady flow $a_1 = -1,19$.

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

(12) $\qquad$ $\int_0^R p_{zz}^* r \, dr = \int_0^R p_{zz} r \, dr$

where p_{zz} and $p_{zz}^* \approx -p^*$ are the normal components of the stress tensor.The problem could be solved without any further approximation /5/, but in order to obtain simpler final results, we assume $p_{zz} = -p_o$. Then we obtain

(13) $\qquad$ $V/V_o = 1 + 1/(\xi^\ell + \xi^J)$

where

(14) $\qquad$ $V_o = 2h^3 \Delta P/3\mu^* R^2$

is Reynolds' velocity of thinning of a film formed between two rigid parallel disks /8/, and $\Delta P = P_c - \Pi$ is the driving force (per unit area) of the process ($P_c = p_o - p_m$ is the capillary pressure).

$\qquad$ In the case ii) we assume that (9) is still valid, but A must be determined by solving (2b).Since f is accurately represented by $f = \exp(a_1\eta)$, we may introduce it as a new variable (instead of η). Then (2b) (with $\partial c/\partial t = 0$) will read

(15) $\qquad$ $f \frac{\partial^2 c}{\partial f^2} + 2\kappa f \frac{\partial c}{\partial f} - (2\kappa - 1)\frac{\partial c}{\partial f} - \kappa r \frac{\partial c}{\partial r} = 0$; $\kappa = \frac{\nu}{Da_1^2}$

The solution of this equation satisfies the boundary conditions (4d) and (4i) only if $c = c(\eta)$:

(16) $\qquad$ $c = c_o - \frac{\Gamma_o f^{2\kappa} e^{2\kappa(1-f)} \Phi(1,2\kappa+1,2\kappa f)}{(\partial\Gamma_o/\partial c_o)\Phi(1,2\kappa+1,2\kappa)} \cdot \frac{\beta}{1 + \beta}$

$$\text{(16a)} \qquad \beta = \frac{(A\nu)^{1/2} \left(\partial \Gamma_o / \partial C_o \right)(2k+1)\, \phi(1, 2k+1, 2k)}{D(-a_1, k\, \phi(2, 2k+2, 2k)}$$

(ϕ - confluent hypergeometric function), i.e., if $\partial c/\partial r = 0$. There-
fore 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. Putting in (13) $\xi^f = 0$, for this case we
have

$$\text{(17)} \qquad V/V_o = 1 + 1/\xi^e$$

The numerical estimate of ξ^f and ξ^e with typical values of
the parameters entering in (7) and (8) shows that for surfactants
of moderate surface activity ($\left(\partial C / \partial C_o \right)_{\to 0} \approx 10^6$) $\xi^f \approx 1$ and $\xi^e \approx$
10^{-5}. 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 effect is probably related to Bancroft's
rule /10/ and its explanation, as given by Davies /11/. Our results
indicate that at least in the case of the droplets' coalescence being
preceded by the formation of a thin liquid film, the hydrodynamic
factors for direct and reverse emulsions in Davies theory may differ
substantially and cannot be equated as Davies did. This difference
may perhaps be immaterial in the case of high stable emulsions, whe-
re the energetic barrier against coalescence is great but for emul-
sions of low stability 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 lead toaa
faster coalescence of those drops 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.

2. Experiment - We have carried out two kinds of experiments. In
the first of them, a certain minimum quantity of surfactant was
added to the dispersion medium in order to reduce the velocity of

thinning to such an extent as to enable us to measure the dependency of the film thickness h on the time t with reasonable precision. At the same time the concentration of surfactant was sufficiently low for the velocity of thinning to be several times higher than Reynolds velocity, which ensures a considerable tangential mobility of the film surfaces, and hence - movement of the liquid in the drops. At such concentration of surfactant in the dispersion phdium, several measurements of the velocity of thinning were carried out at different concentrations of another surfactant in the dispersion phase: one at concentration zero and others at finite concentrations, one of them being sufficiently high to ensure a velocity of thinning close to Reynolds' velocity in the reverse emulsion.

The second kind experiments were carried out at zero concentration of surfactant in the dispersion medium and different concentrations of surfactant in the dispersion phase. In this case as the film thin very fast, the only value to be measured with sufficient precision was the film's lifetime, i.e., the interval of time between the moment of the film's formation and the moment at which it attains its critical thickness of rupture /12/.

The experiments were carried out by the dynamic method of Sheludko and his collaborators /6/. The film thickness was measured interferometrically. In the range $0,8.10^{-5}$ cm $\leq$ h $\leq$ $(1,5 \div 2,0).10^{-5}$ cm it was possible to neglect Π so that $\Delta P = 2\sigma_0/R_c$. The surface tension σ_0 was measured by the stalagmometric method /13/. Benzene and water (triple distilled) used as basic components of the oil and water phases respectively were carefully purified. The electrostatic disjoining pressure in the water films was supressed by $0,3$ mol/dm^3 Na Cl. The surfactants used - lauryl alcohol and sodium octylsulfonate (both p.a. grade) were so chosen as to be mainly soluble in one of the phases.

The basic results, obtained from the measurements of the velocity of thinning, are presented in Table 1. The concentration of sodium octylsulfonate c_o^w in water and of lauryl alcohol c_o^o in benzene used for the different kinds of emulsion (column 2) are given in columns 3 and 4 respectively. Reynolds' velocity V_o and the corresponding slope $(dh^{-2}/dt)_{V=V_o}$ (see colums 7 and 8) of the dependency h^{-2} vs. t are calculated on the basis of equation (14). The mean slope $\Delta h^{-2}/\Delta t$ in column 6 and the velocity of thinning V in column 8 are calculated from the experimental data for h(t).

Table 1

No.	Type	c_o^w mol/dm³	c_o^o mol/dm³	σ_o dyn/cm	$\Delta h^{-2}/\Delta t \cdot 10^{-9}$ cm^{-2}sec^{-1}	$(dh^{-2}/dt) \cdot 10^{-9}$ cm^{-2}sec^{-1}	V/V_o
1	W/O	0	10^{-1}	28,0	0,9	0,85	1,06
2	W/O	0	5.10^{-7}	35,0	4,0	1,06	8,8
3	W/O	2.10^{-3}	5.10^{-7}	34,0	4,0	1,03	3,9
4	O/W	2.10^{-3}	0	34,0	1,1	0,63	1,7
5	O/W	10^{-7}	0	35,0	5,4	0,65	8,3
6	O/W	10^{-7}	10^{-3}	34,8	5,3	0,64	8,3
7	O/W	10^{-7}	10^{-1}	28,0	4,7	0,53	8,8

The data in Table 1 indicate that at a sufficiently high concentration c_o^* of surfactant in the dispersion medium, the film surfaces are practically immobile tangentially - for systems 1 and 4, the ratio V/V_o is 1,06 and 1,7 respectively. The rise of V/V_o when c_o^* fall by several orders of magnitude (see systems 2 and 5) can be explained by the reduction of ξ^{it}. In this case the behaviour of emulsion films is wholly similar to that of foam films.

System 3 differs from system 2 and system 6 and 7 differ from system 5 in having a surfactant added to the dispersion phase; in systems 3 and 7 the concentration of surfactant is so high that in the corresponding reverse emulsion (systems 4 and 1 respectively) it would ensure a velocity equal or close to Reynolds' V_o. It turned out that the presence of surfactant in the dispersion phase had no practical effect on the mean slope $\Delta h^{-2}/\Delta t$ and on the ratio V/V_o.

The experiments of the second kind involved investigation of the dependency of the film lifetime $\tilde{t}$ on the concentration of surfactant in the dispersion phase, with the dispersion medium being a pure liquid. Since the critical thicknesses of rupture of the different systems investigated do not differ considerably, the film lifetime can provide information on the kinetics of film thinning. Fig.2 shows the distribution curves for pure benzene films with concentration of surfactant in the dispersion phase c_o^w - 0; 10^{-4} mol/dm³ and 2.10^{-3} mol/dm³ (curves 1, 2 and 3); Fig.3 shows the distribution curves of pure water films with concentration of surfactant in the dispersion phase c_o^o - 0; 2.10^{-3} mol/dm³ and 0,1 mol/dm³
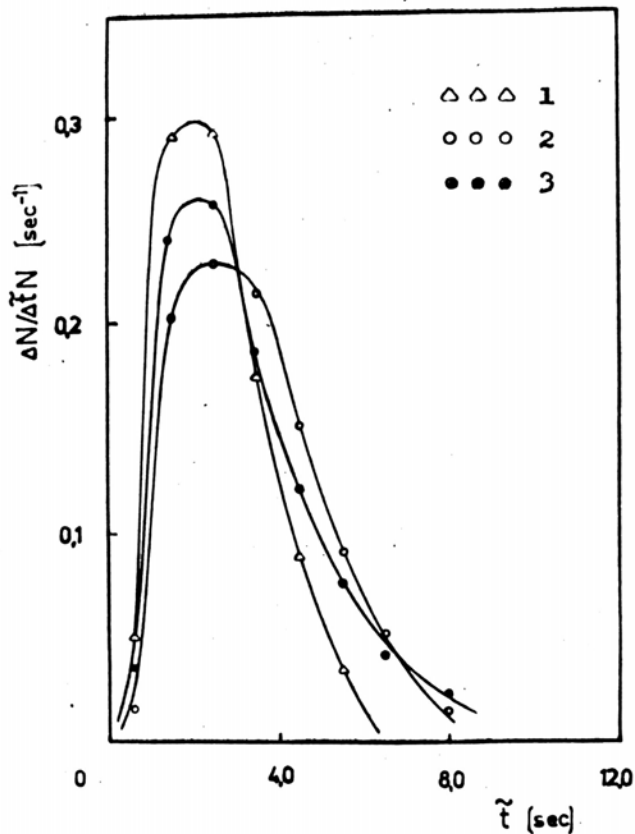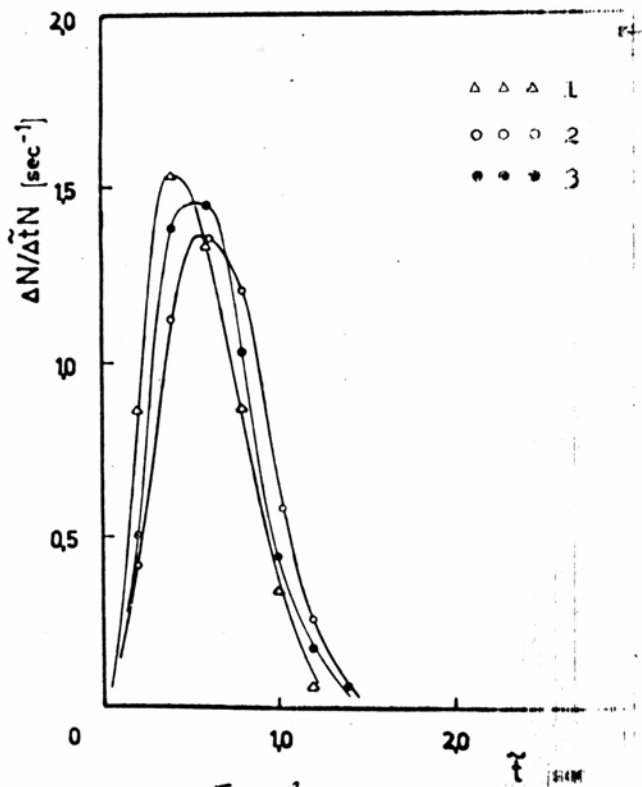
Fig. 2.

Fig. 3.

(curves 1, 2 and 3). In these plots, N is the number of investigated films for each curve, ΔN is the number of films with lifetime within the range $(\tilde{t} - \Delta\tilde{t}/2,\ \tilde{t} + \Delta\tilde{t}/2)$. Results were prosessed as described in /12/, with $\Delta\tilde{t} = 0,2$ s in Fig.2 and $\Delta\tilde{t} = 0,5$ sec in Fig.3; the total number of investigated films for each curve is $N \approx 150$. The mean benzene films lifetime for all three curves is about 0,5 sec; the mean water film lifetime – 2÷3 sec. There is obviously a great difference between the lifetimes of these films and those of films with tangentially immobile surfaces (on which data were adduced above). The independence of the mean lifetime of the concentration of surfactant in the dispersion phase is unquestionable, as well. The relatively higher value of the lifetime of surfactant-free benzene films, is probably due to the much more difficult elimination of surfactant concentration from water than from nonpolar liquids, which inevitably leads to the presence of slight, undefined quantities of surface active agents in the film.

Although it was not possible to proceed to a quan-

titative comparison of the results of these experiments with the theory, these experiments, as well as the experiments on the velocity of thinning examined above, clearly point to the conclusion that a surfactant soluble in the dispersion phase has much less effect on the velocity of thinning than a surfactant soluble in the dispersion medium. This corroborates the main conclusions reached in our theory on the velocity of thinning and on the effect of surfactants on it, and on the need to take account of the hydrodynamic factor in the theoretical interpretation of Bancroft's rule /10/ as given by Davies /11/.

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