

HYDRODYNAMICS OF THIN LIQUID FILMS. EXPERIMENTAL INVESTIGATION OF THE EFFECT OF SURFACTANTS ON THE DRAINAGE OF EMULSION FILMS

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Abstract—In our previous theoretical work on the velocity of thinning of emulsion films we reached the conclusion that this velocity differs only slightly from that for foam films when the surfactant is soluble in the dispersion medium and is equal to that for a system without any surfactant when the surfactant is soluble in the dispersion phase. In the present work these results are checked experimentally by investigating the effect of different concentrations of surfactant in the dispersed phase (a) on the velocity of thinning of films, containing very low concentrations of surfactant soluble in the dispersion medium and (b) on the life time of films from pure liquids. The experiments show that within the precision limits of the experimental methods used, the presence of surfactant in the dispersed phase has no effect on the velocity of thinning and life time of emulsion films in accord with the theoretical conclusions.

1. INTRODUCTION

The theory of thinning of emulsion films with plane-parallel surfaces advanced in Ivanov & Traykov (1976) has been generalized (Traykov & Ivanov 1977) (the previous work) to take into account the effect of surfactants. Two limiting cases were examined therein: (i) surfactant soluble only in the film (dispersion medium) and (ii) surfactant soluble in the drops (dispersed phase). The main conclusion reached in the previous work was the drastic difference between these two cases—in the first case the effect of the surfactant on the flow in the drops is insignificant and the film virtually behaves like a foam film, whereas in the second case the presence of surfactant does not at all alter the velocity of thinning V which has the same value as in emulsion films formed of pure liquids. Expressions were also derived for the velocities of thinning V' and V'' for the two respective cases (i) and (ii):

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

$$V''/V_0 = 1 + 1/\epsilon^e. \quad [2]$$

Here

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

is Reynolds' velocity (Reynolds 1886), with which a film of thickness h , radius R and dynamic viscosity μ^* would thin under the effect of a driving pressure $\Delta P = P_c - \Pi$ (P_c is the capillary pressure of the meniscus, Π is the disjoining pressure), provided its surfaces do not perform tangential motion; the quantity

$$\epsilon^e = \frac{2}{3B^{3/2}\mu^*} [\rho\mu h(V - V_0)]^{1/2} \quad [4]$$

accounts for the flow in the drops, and

$$\epsilon^f = - \frac{(\partial\sigma_0/\partial c_0^*)\Gamma_0}{3\mu^*D^* \left[1 + \frac{2D_s(\partial\Gamma_0/\partial c_0^*)}{D^*h} \right]} \quad [5]$$

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accounts for the effect of the surfactant (i.e. for the Marangoni-Gibbs effect). In the above formulae ρ and μ are the density and viscosity of the dispersion phase; D^* and D_s are the coefficients of bulk (for the film's liquid) and surface diffusion of the surfactant; Γ_0 and σ_0 are the respective equilibrium values of the surface concentration Γ and the surface tension σ corresponding to the concentration of surfactant in the film c_0^* . The quantity B is obtained from the solution of the hydrodynamic equation for the dispersion phase and is very slightly dependent on h through the parameter $\kappa \approx 1 - (\partial \ln V / \partial \ln h)$ (see Ivanov & Traykov 1976; Traykov & Ivanov 1977). In the calculations below we are using the steady flow value $B = 2.82$. Form [1], with $\epsilon^e = 0$, is obtained the expression for the velocity of thinning of a foam film (Radoev, Dimitrov & Ivanov 1974) and with $\epsilon^f = 0$ —the corresponding expression for an emulsion film in the absence of surfactant (Ivanov & Traykov 1976).

The value of the parameter ϵ^f is strongly dependent on the concentration c_0^* and surface activity of the surfactant, but even at the lowest experimentally accessible concentrations it does not fall below 0.1 (Manev *et al.* 1976, as well as the experimental data adduced in Section 3). In the experiments with thin liquid films, the quantities in [4] have the following characteristic values: $\rho = 1 \text{ g/cm}^3$; $\mu = \mu^* = 10^{-2} P$; $h = 10^{-5} \text{ cm}$; $R = 10^{-2} \text{ cm}$ and $\Delta P = 10^3 \text{ dyne/cm}^2$. If $\epsilon^f \geq 0.1$, then $V' \leq 10 V_0$ so that (see [3] and [4]) $\epsilon^e \leq 10^{-4}$. Accordingly, with a surfactant soluble in the film,

$$V'/V_0 \approx 1 + 1/\epsilon^f, \quad [6]$$

and although the velocity V' can be significantly greater, it still is of the order of Reynolds' velocity V_0 . In this case the only difference between the emulsion film and the corresponding foam film is due to the altered values of σ_0 , ΔP and D_s . With the surfactant soluble in the drops $\epsilon^e = (2/3B)(\rho\mu h^4 \Delta P / \mu^{*3} R^2)^{1/3}$ (Traykov & Ivanov 1977) and

$$\frac{V''}{V_0} \approx \frac{1}{\epsilon^e} = \frac{3B}{2} \left(\frac{\mu^{*3} R^2}{\mu \rho h^4 \Delta P} \right)^{1/3} \gg 1. \quad [7]$$

It follows from [6] and [7] that the ratio of the velocities of thinning V' and V'' for a given pair of liquids will be

$$V'/V'' \approx (\epsilon^f / \epsilon^e) \gg 1. \quad [8]$$

The present work is intended to verify experimentally the basic theoretical results adduced above. When the surfactant is only soluble in the drops, or when the dispersion phase and the dispersion medium are pure liquids, the films live only a fraction of a second and it proved to be impossible to obtain properly reproducible results for the velocity of thinning. Besides the difficulties associated with carrying out measurements for such a brief period of time, the scattering of the results is also due to the considerable deformations of the films (their surfaces not being plane-parallel) and to alterations of their radius during the thinning. Even an insignificant surfactant contamination of the dispersion medium which persists after the most painstaking purification will substantially reduce the velocity of thinning with respect to the theoretical velocity, as calculated after [7]. All these difficulties preclude any precise quantitative verification of the theory. On the other hand the differences of the velocities of thinning in the two abovementioned cases are so great (see [8]) that the basic deductions from the theory can be corroborated even only on the basis of the qualitative differences in the behaviour of the two kinds of emulsion.

For this purpose we have carried out two kinds of experiments. In the first 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 a concentration of surfactant in the dispersion medium, 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 the others at finite concentrations, one of them being sufficiently high to ensure a velocity of thinning close to Reynolds' velocity in the reverse emulsion. It turned out, in complete conformity with the theory that the velocity of thinning was not dependent on the concentration of surfactant in the dispersion phase.

The experiments of the second kind were carried out at zero concentrations of surfactant in the dispersion medium and different concentrations of surfactant in the dispersion phase. In this case, as the films 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 (Sheludko 1962). Like the velocity of thinning, the lifetimes proved to be practically independent of the concentration of surfactant in the dispersion phase.

2. EXPERIMENTAL AND MATERIALS

The experiments were carried out by the dynamic method of Sheludko and his collaborators (see e.g. Sheludko & Exerova 1959; Sheludko 1966, 1969), the capillary tube in which the film forms (figure 1) being slightly modified to make it appropriate for emulsion systems. A biconcave drop of the dispersion medium (liquid 2) forms in the capillary tube 1, as shown in figure 1. Thereupon the capillary tube, which is attached to the lid of the measurement cell, is introduced into the cell, which has previously been filled with the dispersion phase (liquid 5). Suction of a small quantity of liquid through the lateral tube 3 causes the two interfaces to draw close and then a thin film of radius R forms at the centre of the capillary tube (see also figure 1 in Ivanov & Traykov 1976); Traykov & Ivanov 1977). As the capillary tube walls must be fully wetted by the dispersion medium liquid, when operating with the cell with emulsion films of the *W/O* kind (oil film), a plastic bushing (which was well wetted by the oil phase) was introduced into the capillary tube. The cell for *O/W* emulsions (aqueous film) has no such bushing and

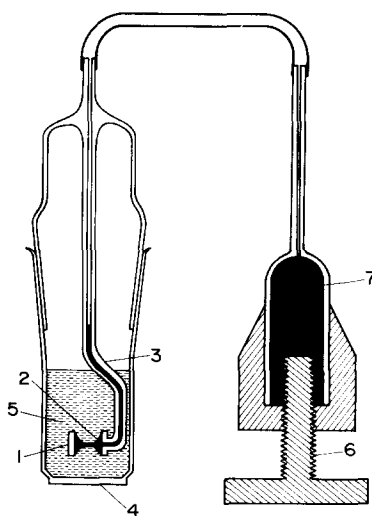


Figure 1. Scheme of the measuring cell for formation and investigation of emulsion films. 1—capillary tube, 2—biconcave meniscus (dispersion medium), 3—lateral tube, 4—plane-parallel glass bottom 5—liquid forming the dispersion phase, 6—piston (micro-screw) for sucking the liquid 2 and 7—mercury reservoir of the piston.

good wetting is ensured by previous vertical scouring of the glass capillary tube with a steel core. For a more convenient comparison of the results, the internal radii R_c of the capillary tubes of both cells (i.e. the internal radius of the bushing of the first cell) were very similar—0.135 cm for the first cell and 0.145 cm for the second. For the same reason, all the investigated films had the same radius $R = 10^{-2}$ cm, assumed to be equal to the distance from the centre of the film to the first Newtonian ring. The measurements were carried out at a constant temperature $20 \pm 0.1^\circ\text{C}$. The thickness of the film was measured interferometrically (Sheludko 1966; Sonntag & Strenge 1970) with a photomultiplier (Zeiss M12FS35); the photocurrent vs time curves were photographed with a camera on the screen of an oscilloscope (Orion TR4602). Photometric measurements were made of the light reflected from the central part of the film, of radius about $3 \cdot 10^{-3}$ cm. The thickness was calculated with the formula (see, e.g. Sonntag & Strenge 1970)

$$h = \frac{\lambda}{2\pi n_0} (l\pi \pm \arcsin \Delta^{1/2}). \quad [9]$$

Here $\lambda = 546$ nm is the wavelength of the monochromatic light used, l is the order of the interference, n_0 is the refractive index of the liquid in the film and $\Delta = (I - I_{\min}) / (I_{\max} - I_{\min})$; I being the momentary value of the photocurrent, I_{\min} and I_{\max} being the minimum and maximum values for the respective order of interference. The thickness range $0.8 \cdot 10^{-5} \text{ cm} \leq h \leq (1.5 \div 2.0) \cdot 10^{-5} \text{ cm}$ proved to be most suitable for investigating the velocity of thinning. At greater thicknesses the film is not plane-parallel and at the lesser thicknesses there arises the so-called "secondary dimpling" (Sonntag & Strenge 1970). Moreover, with $h > 0.8 \cdot 10^{-5} \text{ cm}$, van der Waals' disjoining pressure (see, e.g. Sheludko 1966) (on which reliable experimental data are still lacking) is small which permits to assume in [3] that $\Delta P = P_c$. We calculate the capillary pressure by the formula $P_c = 2\sigma_0/R_c$ (Sheludko & Exerova 1959) and measured the surface tension σ_0 by the stalagmometric method (Aveyard & Haydon 1965; see also Shermann 1968).

Benzene, used as basic component of the oil phase, was prepared from a p.a. grade reagent, successively washed with concentrated sulphuric acid and a 30% KOH solution, dried over solid KOH and then distilled. The distillate obtained was redistilled in a glass unit with a rectifying column. Particular care was devoted to obtaining surfactant-free water—this was reached by three successive distillations and reduction to a minimum of any contact of the purified liquid and the ambient air. In order to eliminate the electrostatic disjoining pressure, in all the experiments the aqueous phase contained electrolyte (NaCl) of concentration 0.3 mol/dm^3 . The sodium chloride used was obtained from a p.a. grade reagent, thrice recrystallized in thrice distilled water and then calcined at 700°C .

The surfactants used—lauryl alcohol and sodium octylsulfonate—were so chosen as to be mainly soluble in one of the phases. One of the reasons for this choice is that the hydrodynamic theory for the effect of surfactants on the thinning of emulsion films (Traykov & Ivanov 1977) was evolved for the limiting cases, where the surfactant is soluble only in the dispersion medium or only in the dispersion phase. Another reason is that the surfactants, used usually in preparing emulsions, are preferably soluble in one of the phases (Becher 1965; Shermann 1968). Lauryl alcohol is mainly soluble in benzene, with $c_0^o/c_0^w \approx 10^5$, whereas sodium octylsulfonate with $c_0^o/c_0^w \approx 10^{-25}$ is practically insoluble in the oil phase (here c_0^o and c_0^w are the respective equilibrium concentrations in the oil and aqueous phases. The above distribution coefficients were calculated on the basis of the data on the hydrophilic-lipophilic balance (HLB) (Shermann 1968). The lauryl alcohol and sodium octylsulfonate used were of p.a. grade and were not further purified.

3. RESULTS AND DISCUSSION

The basic results obtained from the measurements of the velocity of thinning are presented in table 1. The concentrations of sodium octylsulfonate c^w in water and of lauryl alcohol c^o in

Table 1. Effect of surfactant concentration on the rate of thinning of emulsion films

No.	Emulsion type	c^w (mol . dm ⁻³)	c^o (mol . dm ⁻³)	σ_0 (dyn . cm ⁻¹)	$\Delta h^{-2}/\Delta t$ $\cdot 10^{-9}$ (cm ⁻² sec ⁻¹)	$(dh^{-2}/dt)_{V=V_0}$ $\cdot 10^{-9}$ (cm ⁻² sec ⁻¹)	V/V_0
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	3.8
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

c^w —concentration of sodium octylsulfonate in aqueous phase, c^o —concentration of lauryl alcohol in benzene phase.

benzene used for the different kinds of emulsion (column 2) are given in columns 3 and 4 respectively. The slope $(dh^{-2}/dt)_{(V=V_0)}$ corresponding to Reynolds' velocity V_0 of the dependency h^{-2} vs t is calculated on the basis of [3] (with $\Delta P = P_c = 2\sigma_0/R_c$) and the data for σ_0 , given in column 5. The mean slope $(\Delta h^{-2}/\Delta t)$ in column 6 and the dimensionless velocity of thinning $(V/V_0) = (\Delta h^{-2}/\Delta t)/(dh^{-2}/dt)_{(V=V_0)}$ in column 8 are calculated from the experimental data for $h(t)$. Typical experimental curves h^{-2} vs t for emulsions W/O are given in figure 2, and for emulsions O/W in figure 3. The data in table 1 are obtained by averaging $\Delta h^{-2}/\Delta t$ for five experimental curves. In systems 1, 2, 4 and 5, the concentration of surfactant in the dispersion phase is zero; for them, consequently, V coincides with the velocity V' in [1]. The situation is more complex in the other systems, as with them there is surfactant in the dispersion phase as well. We shall dwell on this point further on, and will demonstrate that, in that case too, the measured velocity should correspond to the case in which the drops contain no surfactant.

The data in table 1 indicate that at a sufficiently high concentration c_0^* of surfactant in the dispersion medium, the film surfaces are practically immobile tangentially—for systems 1 and 4, the ratio V/V_0 is 1.06 and 1.7 respectively. The rise of V/V_0 when c_0^* falls by several orders of magnitude (see systems 2 and 5) can be explained by the reduction of ϵ^f (for these systems ϵ^f is very small—see section 1). In this case the behaviour of emulsion films is wholly similar to that of foam films.

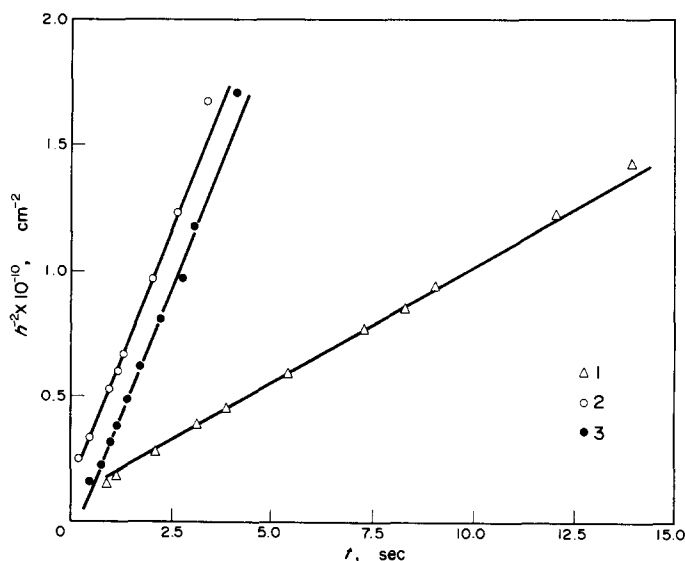


Figure 2. Typical experimental curves h^{-2} vs t for benzene films. Curve 1: film, benzene + 0.1 mol dm⁻³ lauryl alcohol; dispersion phase, water + 0.3 mol dm⁻³ sodium chloride. Curve 2: film, benzene + 5 . 10⁻⁷ mol dm⁻³ lauryl alcohol; dispersion phase, water + 0.3 mol dm⁻³ sodium chloride. Curve 3: film, benzene + 5 . 10⁻⁷ mol dm⁻³ lauryl alcohol; dispersion phase, water + 2 . 10⁻³ mol dm⁻³ sodium octylsulfonate + 0.3 mol dm⁻³ sodium chloride.

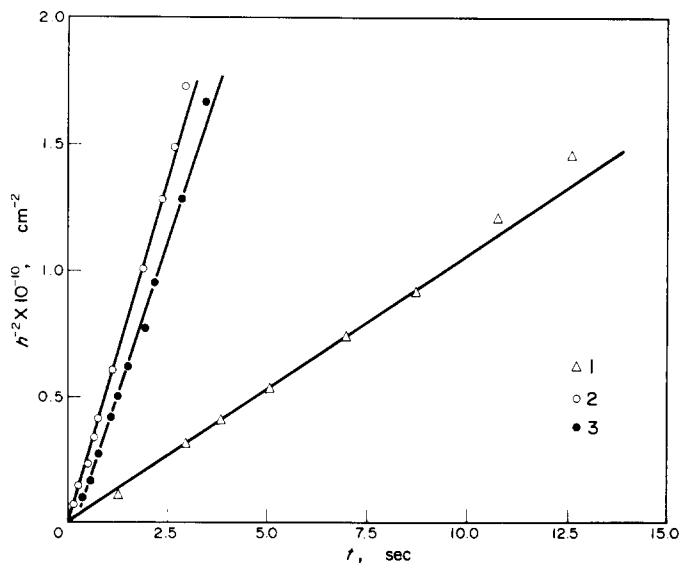


Figure 3. Typical experimental curves h^{-2} vs t for aqueous films. Curve 1: film, water + $2 \cdot 10^{-3}$ mol dm^{-3} sodium octylsulfonate + 0.3 mol dm^{-3} sodium chloride; dispersion phase, benzene. Curve 2: film, water 10^{-7} mol dm^{-3} sodium octylsulfonate + 0.3 mol dm^{-3} sodium chloride in water; dispersion phase, benzene. Curve 3: film, water + 10^{-7} mol dm^{-3} sodium octylsulfonate + 0.3 mol dm^{-3} sodium chloride; dispersion phase, benzene + 0.1 mol dm^{-3} lauryl alcohol.

The fact that the dependencies $h^{-2}(t)$ for systems 2 and 5 are linear (see figures 2 and 3) indicates that the surface diffusion of surfactant is less important than the bulk diffusion. In fact, if in [5] we put $D_s = 0$ and integrate [1] (with $\epsilon^e = 0$), by means of [3] (with $P = P_c$), we obtain a linear relation between h^{-2} and t :

$$h^{-2} = \frac{4P_c}{3\mu^*R^2} \left[1 + \frac{3\mu^*D^*}{\Gamma_0(-\partial\sigma_0/\partial c_0^*)} \right] t + \text{const.} \quad [10]$$

This appears to be a very likely explanation, bearing in mind that the surface diffusion coefficient at the boundary between two liquids ought to be smaller than at the boundary between liquid and gas, and that the effect of surface diffusion on the films investigated in the present work also should be reduced because of their comparatively great thickness.

System 3 differs from system 2 and systems 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_0 . In systems 3 and 6, 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_0 . The appreciable alteration of the mean slope in system 7 is due to some extent to the reduction of σ_0 and hence of P_c as well. So the ratio V/V_0 , being a true criterion of the influence of the Marangoni-Gibbs effect, is less changed. Although the absolute value of V/V_0 for system 7 differs perceptibly from the one for system 5, this alteration is only 6% and besides, its sign is the opposite of the one to be expected for the effect of the surfactant at these concentrations. It can therefore be assumed that in this case too, the presence of surfactant has no effect on the ratio V/V_0 .

The above experimental data cannot be directly interpreted on the basis of the theory advanced in the previous work (Traykov & Ivanov 1977), as it was assumed in it that the surfactant is only soluble in one of the phases. However, it is conceivable that the results of (Traykov & Ivanov 1977) can be readily generalized even in the case of two surfactants 1 and 2, each of them only soluble in one of the phases, provided their respective surface concentrations

Γ' and Γ'' are sufficiently low to allow that they are adsorbed independently on the interface. As the effect of the surfactant on the flow depends on the gradient of the local value of the surface tension $\sigma[\Gamma'(r), \Gamma''(r)]$ (r is the distance to the film axis (see figure 2 in Traykov & Ivanov (1977)), we can write for this case

$$\frac{\partial \sigma}{\partial r} = \left(\frac{\partial \sigma}{\partial \Gamma'} \right) \left(\frac{\partial \Gamma'}{\partial r} \right) + \left(\frac{\partial \sigma}{\partial \Gamma''} \right) \left(\frac{\partial \Gamma''}{\partial r} \right). \quad [11]$$

In each phase the diffusion flux towards the surface will be determined by the value of the respective surface concentrations Γ' and Γ'' at a given velocity of thinning V . Therefore if surfactant 2 is soluble in the dispersion phase, we can conclude, on the basis on the results obtained in Traykov & Ivanov (1977) that its diffusion flux towards the film surface will be so considerable as to easily eliminate any perturbation in the distribution of that surfactant on the film surface, i.e. in [11] we should set $\partial \Gamma'' / \partial r = 0$. Then the film will behave just as if the dispersion phase were a pure liquid and the velocity of thinning would again be described by [1]. These considerations are in complete accord with the experimental results given above.

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. The film lifetime is an important characteristic of liquid films, as it is directly associated with the stability of foams and emulsions (Biswas & Haydon 1962). It can provide information on the kinetics of film thinning, if data on the critical thicknesses of rupture are available. The investigated films drain extremely fast ($\tilde{t} \approx 1$ sec); of some 500 photocurrent-time curves for each kind of emulsion, only a few were more or less appropriate for measuring the critical thicknesses of rupture. For benzene films the latter proved to be $(3.5 \div 4) \cdot 10^{-6}$ cm and for aqueous films, $(2.5 \div 3) \cdot 10^{-6}$ cm. The corresponding values for such systems with a high concentration of surfactant in the dispersion medium, which practically ensures the tangential immobility of the surfaces (for benzene films $c^0 = 0.1$ mol/dm³, for aqueous films $c^w = 2 \cdot 10^{-3}$ mol/dm³; see systems 1 and 4 in table 1) were $4.1 \cdot 10^{-6}$ cm and 3.10^{-6} cm respectively, and the lifetimes were approx 20 sec and 33 sec (see figure 6). These results make it possible, in first approximation to disregard the dependence of the critical thicknesses on the concentration of surfactant and to consider the lifetime as a criterion of the velocity of thinning.

Figure 4 shows the distribution curves for pure benzene films with concentration of surfactant in the dispersion phase $c^w = 0; 10^{-4}$ mol/dm³ and $2 \cdot 10^{-3}$ mol/dm³ (curves 1, 2 and 3 respectively); figure 5 shows the distribution curves of pure water films with concentration of surfactant in the dispersion phase $c^0 = 0; 10^{-3}$ mol/dm³ and 0.1 mol/dm³ (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 $\tilde{t} - \Delta \tilde{t} / 2$ to $\tilde{t} + \Delta \tilde{t} / 2$. Results were processed as described in (Sheludko 1962), with $\Delta \tilde{t} = 0.2$ sec in figure 4 and $\Delta \tilde{t} = 0.8$ sec in figure 5 (in figure 6 $\Delta \tilde{t} = 2.0$ sec); the total number of investigated films for each curve is $N \approx 150$. The mean value of \tilde{t} for benzene films for all three curves in figure 4 is $0.5 \div 0.6$ sec; the mean water film lifetime (figure 5)— $2 \div 3$ 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 on the concentration of surfactant in the dispersion phase is unquestionable, as well. The relatively higher value of the lifetime of surfactant-free aqueous films ($2 \div 3$ sec), when compared with that of surfactant-free benzene films, is probably due to the much more difficult elimination of surfactant contamination from water than from non-polar liquids, which inevitably leads to the presence of slight, undefined quantities of surfactant in the film. The latter conclusion is in accordance with the experimental results of Michels (1976) who has measured the life time of toluene droplets with continuous phase water. The film radii in his experiments can be calculated from the formula derived by Radoev & Ivanov (1977); they are of the order of 10^{-2} cm and the respective driving pressures $\Delta P \approx$

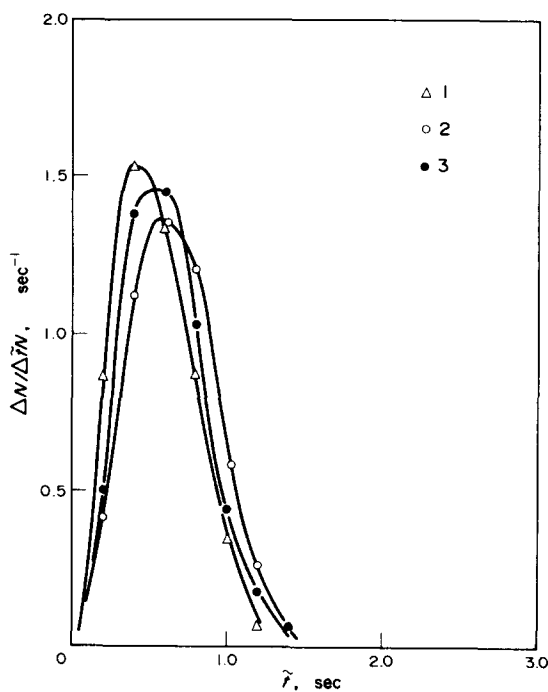


Figure 4. Distribution curves for the lifetime \bar{t} for surfactant-free benzene films. Dispersion phase respectively: Curve 1, water + 0.3 mol dm^{-3} sodium chloride; Curve 2, water + $10^{-4} \text{ mol dm}^{-3}$ sodium octylsulfonate + 0.3 mol dm^{-3} sodium chloride; Curve 3, water + $2 \cdot 10^{-3} \text{ mol dm}^{-3}$ sodium octylsulfonate + 0.3 mol dm^{-3} sodium chloride.

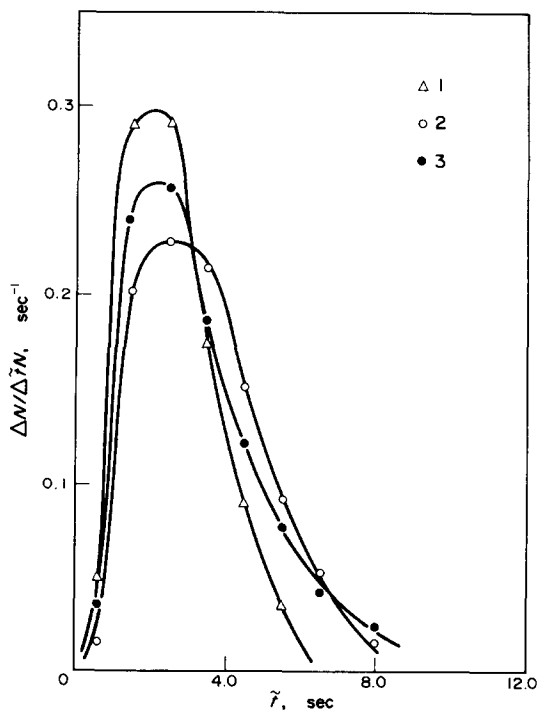


Figure 5. Distribution curves for the lifetime \bar{t} for surfactant-free aqueous films. Dispersion phase respectively: Curve 1, benzene; Curve 2, benzene + $10^{-3} \text{ mol dm}^{-3}$ lauryl alcohol; Curve 3, benzene + 0.1 mol dm^{-3} lauryl alcohol.

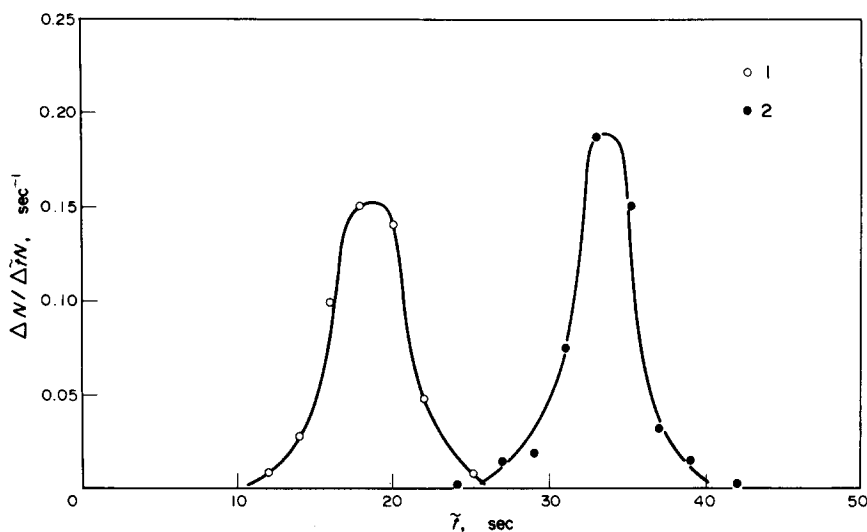


Figure 6. Distribution curves for the lifetime \bar{t} of films stabilized with surfactant. Curve 1: film, benzene + 0.1 mol dm^{-3} lauryl alcohol; dispersion phase, water + 0.3 mol dm^{-3} sodium chloride. Curve 2: film, water + $2 \cdot 10^{-3} \text{ mol dm}^{-3}$ sodium octylsulfonate + 0.3 mol dm^{-3} sodium chloride; dispersion phase—benzene.

500 dyn. cm^{-2} . Both quantities are close to those in our experiments. As a result of exceptionally careful purification of the water, Michels has measured lifetimes of $0.1 \div 0.3 \text{ sec}$. These values are about tenfold smaller than those obtained in our experiments with a similar system (benzene drops + lauryl alcohol in water) but are very close to those for the inverse emulsion (aqueous drops + sodium octylsulfonate in pure benzene).

Davis & Smith (1976) in a recent work have found like us that the presence of surfactants (fatty alcohols) soluble in the liquid of the drops (oil phase) does not affect the lifetime. In their experiments, however, the continuous phase (water) has contained small quantities of other surfactant (sodium lauryl sulfate) which can strongly reduce the mobility of the film surfaces and, respectively, can bring the rate of thinning down to Reynolds' V_0 . For this reason it is difficult to judge to what extent their results can be considered as a confirmation of our theory.

Although only qualitatively, the present experiments on the velocity of thinning and the lifetimes of emulsion films clearly point to the conclusion that a surfactant soluble in the dispersed phase has much less effect on the velocity of thinning than a surfactant soluble in the continuous phase. This corroborates the main conclusions reached in Traykov & Ivanov (1977) on the effect of surfactants on the thinning of emulsion films and on the need to take account of the hydrodynamic (collision) factor in the theoretical interpretation of Bancroft's rule (Bancroft 1913) as given by Davies (1957).

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