

Effect of the surfactant concentration on the kinetic stability of thin foam and emulsion films

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The thinning and the lifetime of foam and emulsion films formed in a model experimental cell have been investigated. The foam films were stabilised by either sodium dodecyl sulfate or sodium dodecyl polyoxyethylene-2 sulfate. The emulsion films contained either Tween 20 or Span 20. The time of hydrodynamic drainage of the films increased linearly as the logarithm of the surfactant concentration. This linear dependence was valid whatever the type of film or surfactant and not only below the critical micelle concentration (c.m.c.) but also much above this concentration threshold. The experimental results are relevant to the hydrodynamic basis of foam and emulsion stabilisation. They are compared with the earlier hydrodynamic theories of film drainage. A reasonable, but not excellent, agreement between the experimental data and the theory could be achieved in the region below the c.m.c. of the surfactant. The data about the complex system above the c.m.c. still remain unexplained by an adequate theory. The investigation provides some guidelines for choosing the optimal type and concentration of surfactant in colloid systems of practical importance.

The stability of foams and emulsions is of high importance for many practical systems in the food, paint, oil, pharmaceutical and other industries. The breakdown of these colloid systems occurs mainly because of the rupture of the thin liquid films which form between the bubbles or droplets when these are pressed against each other either in collisions or by buoyancy.^{1,2} Therefore, the behaviour and the stability of these thin liquid films is a problem of major experimental and theoretical importance.^{1,2} It has been established, in principle, that one can distinguish between two types of foam and emulsion film stability, thermodynamic and kinetic.^{1,3} The thermodynamic stability is associated with the repulsive intermolecular interactions that act between the film surfaces and oppose their approach.¹ The kinetic stability arises from the hydrodynamic friction in the film, that delays its thinning. Although the kinetic stabilisation is transient, it has been recognised¹ that, in many cases, the hydrodynamic forces alone, or through enhancing the thermodynamic factors are the key to the stability of the foam or emulsion systems.

There are many theoretical and experimental investigations dedicated to the hydrodynamics of thinning of foam and emulsion films^{4–7} (for a detailed review of the recent advances in this field see also ref. 1). The majority of these studies, however, deal with the case of fixed surfactant concentration (and usually below the c.m.c.). Of major practical importance is investigation of the effect of the surfactant concentration on the stability of thin films, foams and emulsions. The quantity of surface-active agent, that is introduced in practical foams and emulsions, is usually quite large and orders of magnitude higher than the c.m.c. Finding ways of reducing this quantity could be advantageous from both financial and environmental view points.

Our study is dedicated to the effect of the surfactant concentration on the kinetic stability of foam and emulsion films. The first step in such an investigation is to define a clear, measurable set of thin-film parameters that are strongly dependent on the surfactant concentration. The main stages of thinning of liquid films greater than 100 μm in diameter are shown

schematically in Fig. 1, adapted from Ivanov and Dimitrov.² Generally, after the film is formed, one first observes the formation of a dimple [thick lens-like formation, Fig. 1(b)] which, after some time, flows out, leaving a plane-parallel film behind [Fig. 1(d)]. The plane-parallel film thins further until a transition to a secondary ('black') film or rupture occurs (this depends predominantly on the surfactant concentration^{8,9}). The two most important parameters that describe the process are the film thinning rate, $V(h)$ and the lifetime, τ_1 . The relation between these two parameters is

$$\tau_1 = \int_{h_{cr}}^{h_i} \frac{dh}{V(h)} \quad (1)$$

where h_i denotes the thickness of film formation and h_{cr} is the 'critical' or 'transition' thickness at which the film becomes

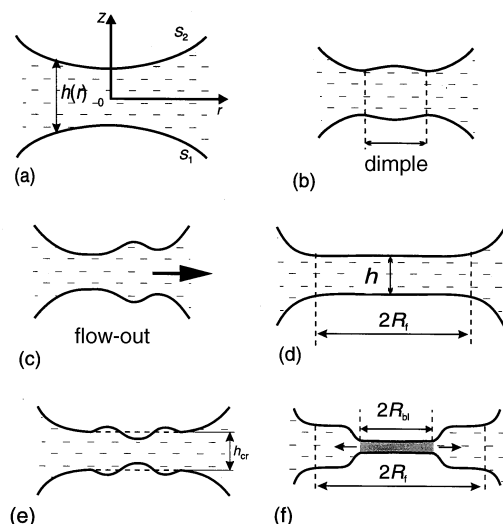


Fig. 1 Schematics of the basic stages of thinning of a liquid film formed between bubbles or droplets (modified after Ivanov and Dimitrov²): (a) approach of the non-deformed fluid particles; (b) below the thickness of film formation, h_i , a film with a dimple is formed; (c) the flowing out of the dimple results in a plane-parallel film; (d) thinning of the plane-parallel film; (e) when the transition thickness, h_{cr} , is reached, a transition to a thin black film occurs; (f) the black film expands radially, until it occupies the whole area

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unstable and either ruptures or undergoes a transition to a very thin secondary film.

There are numerous papers, that deal with the effect of the film dimensions, pH and presence of electrolyte on the lifetime of foam and emulsion films.^{6,10,11} Strangely enough, very little attention has been given to the effect of the surfactant concentration on the film lifetime and stability. In the case of a liquid-liquid film Danov *et al.*¹² have proposed simple expressions that link the increase of the emulsifier concentration in the continuous phase up to the c.m.c. with the incurred decrease in the kinetic rate of emulsion coalescence. Though this theory includes a number of assumptions and expects an idealised surfactant behaviour, it is the only one we are aware of that deals with the question of correlating the concentration of surfactant with the stability of the emulsion. There is also a lack of pertinent experimental data in the literature that would allow us to extend the theoretical research further. Such experimental data on the stability of model liquid-liquid and liquid-air films as a function of the surfactant concentrations are reported in this paper.

We have carried out experiments with foam and emulsion films, formed in a model cell of Scheludko and Exerowa.^{13,14} The method is described in the Experimental section. The data from the investigations of the film lifetime are presented in the Results section. In the Discussion section we present the major theoretical background of the hydrodynamics of film thinning and compare the theoretical predictions with the new experimental results. The data are then discussed from the viewpoint of the practical implications of the results.

Experimental

Materials

In the experiments with model foam films in air we used the ionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecyl polyoxyethylene-2 sulfate (SDP-2S) as stabilisers. The SDS was a Sigma product. SDP-2S was used as an ethanol solution containing 73.6 wt.% pure substance, kindly provided by Colgate-Palmolive Inc.

The water for the solutions was obtained from a Milli-Q Organex system (Millipore). The electrolyte concentration was adjusted to 0.1 M by addition of NaCl (Merck, analytical grade, heated for 5 h at 450 °C).

In the experiments with model emulsion films as an oil phase, we used xylene (isomeric mixture from Riedel, Germany). The water for these solutions was obtained from a D-Ionstill double distiller unit (Jencons Sci., England).

The emulsion films were stabilised with either Tween 20 or Span 20. Both substances are typical non-ionic stabilisers of industrially produced emulsions and are widely used for research purposes.^{15,16} The emulsifier samples were supplied by ICI, Italy. Tween 20 (polyoxyethylene 20 sorbitan monolaurate) is water soluble and was dissolved in the aqueous phase.¹⁶ Span 20 (sorbitan monolaurate) is predominantly oil soluble^{17,18} and was dissolved in the xylene phase.

Earlier, it was found that mass-transfer effects, driven by emulsifier redistribution between the phases, can significantly change the film behaviour and stability.^{19,20} In order to avoid such effects, the oil-water pairs of solutions prepared for the experiments were allowed to pre-equilibrate by staying in contact in a wide flask for not less than 24 h.

Methods

The model water films between air or oil simulate the contact and the possible coalescence of two bubbles or drops, respectively. The films were investigated with the use of cells analogous to those proposed by Scheludko and Exerowa.^{13,14} A schematic presentation of the cell capillary and film geometry is given in Fig. 2. In the first cell, the capillary, of diameter

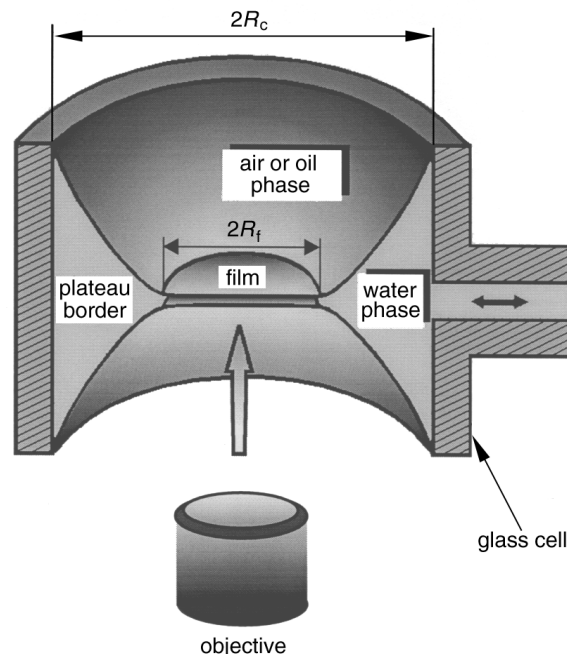


Fig. 2 Schematics of the geometry of the film and the capillary in which it is formed (highly enlarged and not to scale)

$D = 3.20 \pm 0.05$ mm, is placed in an air environment that is closed and saturated with water vapour (to prevent evaporation from the studied film). The films are formed by sucking out aqueous phase from the biconcave meniscus held in the capillary. This arrangement allows us to simulate the evolution of foam films. In the second cell arrangement, designed to study liquid-liquid (emulsion) films, the capillary, of diameter $D = 2.95 \pm 0.05$ mm, is encapsulated in a glass chamber with an optically clear upper window filled with the xylene phase.

The foam or emulsion films formed are observed by a microscope (Zeiss, Germany) in reflected light. The microscope is equipped with a videocamera (Sony DXC-1821P or Panasonic, WV-BP50/G) and a calibrated monitor. The diameter of the films is measured on the monitor and is controlled with a pressure-control system. The temporal evolution of the films is recorded on a tape (with a video-system Panasonic, AG-7355) to be analysed further.

In order to obtain reliable and reproducible data, a number of experimental parameters need to be fixed throughout the experiments. The film diameter was sustained at 330 ± 20 μ m for emulsion films and at 200 ± 20 μ m for the foam film. The films were formed by decreasing the meniscus pressure within a period of 1–3 s. The timer was started at the moment of the appearance of the interference film picture. Data for 50 ± 20 films were measured for each surfactant type and concentration. In order to enhance the formation of interfacial adsorption layers of surfactant, the phases were allowed to remain in contact for 10 min after loading the cell with the solutions and for 2 min after each film rupture. The experiments were carried out at 27.5 ± 1.0 °C.

To suppress the long-range electrostatic repulsion between the film surfaces, which otherwise may change the film thinning rate and stability through thermodynamic factors,^{11,21} 0.1 M NaCl was added to the aqueous phase.

Results

The presence of surfactants is a decisive factor for the film stability. We found out that films from pure phase(s) survive less than 2–6 s and do not possess a defined and measurable pattern of thinning. When a surfactant was added to the films, we observed all of the basic stages of thinning presented in Fig. 1. Pictures of the typical appearance of foam films

throughout the phases of the thinning are presented in Fig. 3. When the transition thickness is reached, the films either rupture immediately or first form a black film. The lifetime of the film after this transition is governed by stochastic rather than by hydrodynamic factors. For this reason, we defined and measured the hydrodynamic contribution to the film lifetime as the time elapsed from the film formation until the critical thickness is reached, even if the resulting black films are more or less stable. In the few cases where the films broke down before the transition to a black film, the moment of rupture was taken as the final moment of the film lifetime. It is easy to notice that the so-defined hydrodynamic lifetime (denoted hereafter simply as 'lifetime') is related only to the hydrodynamic motion of the film fluid and interfaces which, in their turn, are controlled by the type and concentration of surfactant.

The results for the lifetime of foam films, stabilised by SDS and SDP-2S are presented in Fig. 4(a) and (b), respectively. The surfactant concentration is varied over a wide range, 3 orders of magnitude. It is seen that, even within this very wide range, there is a remarkably good linear dependence between the film lifetime, τ_1 , and the logarithm of the concentration, $\ln(C)$. The linear dependence is even more surprising, bearing in mind that the studied range of concentrations encompasses the c.m.c. of the two surfactants (c.m.c. = 1.0×10^{-3} M for

SDS^{22,23} and 5.32×10^{-5} M for SDP-2S, measured by the static light scattering method on Malvern equipment).

The measured lifetime of the films is not to a full extent, a measure of their stability, as it does not take into account the effect and probability of black film rupture. To provide information on the mechanism of film breakage, we have distinguished four different patterns of film rupture: (1) the rupture occurs during the thinning, before the critical thickness is reached; (2) the rupture occurs instead of transition to a black film, when the critical thickness is reached; (3) the rupture occurs after a black film has formed and is spreading or (4) the black film formed occupies the whole film area and lasts for more than 60 s.

The results from the observations of the patterns of the breakdown of foam films, based on the described stability scale, are presented in Fig. 5. With the exception of the lowest concentration of SDP-2S (data for SDS at these concentrations were not available), all the systems end up with a long-lived black film. Such a behaviour is expected owing to the good saturation of the surfaces with a surfactant adsorption layer. Increase of the surfactant concentration, above the c.m.c., eventually leads to a step-wise layering ('stratification') of the foam films.^{24,25} When such a phenomenon was noticed, we measured the last experimental point and did not perform any experiments at higher concentrations.

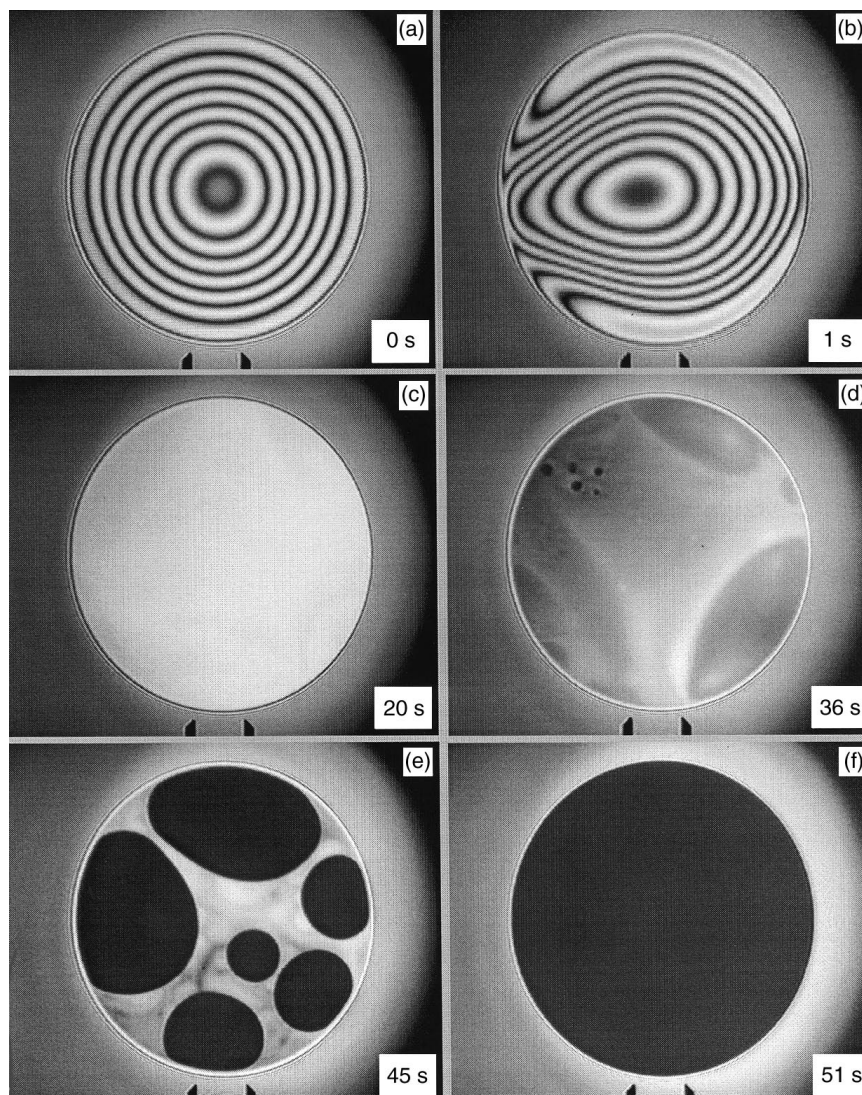


Fig. 3 Typical interference pictures of the thinning of a foam film containing 2×10^{-4} M of SDS: (a) big dimple between the film surfaces; (b) flow-out of the dimple; (c) thinning plane-parallel film; (d) appearance of the first black 'spots'; (e) enlargement of the spots; (f) final stable black film. The time elapsed from the moment of the film formation is indicated in the lower right corner of each picture. The film diameter is 220 μm .

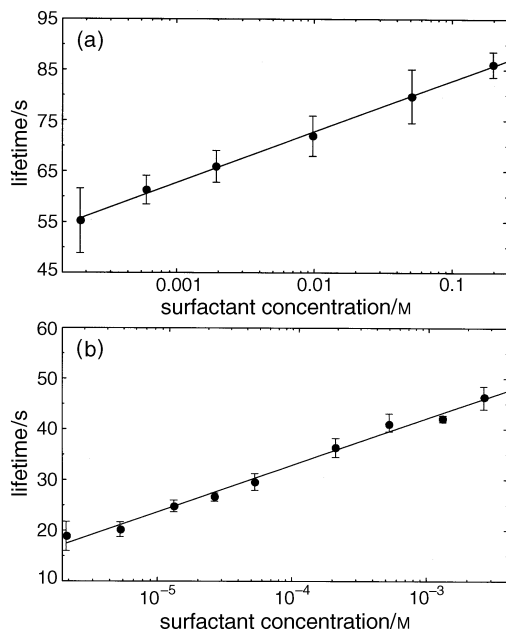


Fig. 4 Mean hydrodynamic lifetime of foam films vs. surfactant concentration: (a) films stabilised by SDS; (b) films stabilised by SDP-2S

The data on the lifetime of emulsion films as a function of surfactant type and concentration are presented in Fig. 6. It is seen that the film lifetime for the non-ionic, water-soluble Tween 20 also follows a straightforward linear increase vs. the

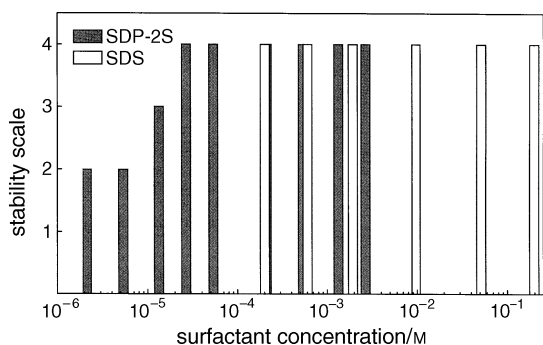


Fig. 5 Pattern of rupture of foam films vs. the surfactant concentration. The scale on the y-axis reads: (1) the rupture occurs during the thinning, before the critical thickness is reached; (2) the rupture occurs instead of transition to a black film, when the critical thickness is reached; (3) the rupture occurs after a black film has formed and is spreading or (4) the formed black film occupies the whole film area and lasts for more than 60 s.

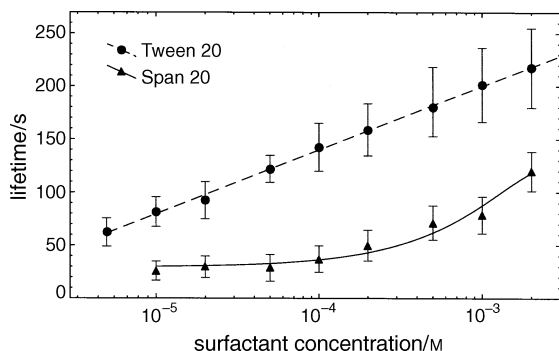


Fig. 6 Mean hydrodynamic lifetime of aqueous emulsion films vs. surfactant concentration. Tween 20 was initially dissolved in the aqueous phase, while Span 20 was dissolved in the xylene phase. The experiments were performed with phases pre-equilibrated for not less than 24 h.

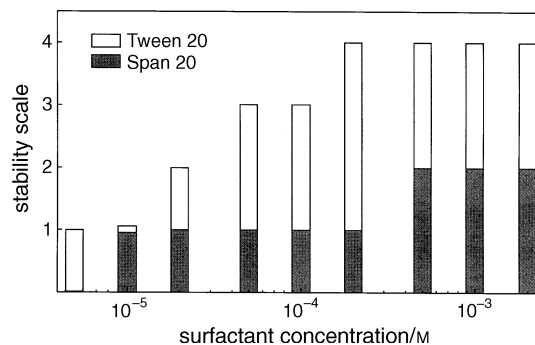


Fig. 7 Pattern of rupture of emulsion films vs. the surfactant concentration. The scale on the y-axis reads: (1) the rupture occurs during the thinning, before the critical thickness is reached; (2) the rupture occurs instead of transition to a black film, when the critical thickness is reached; (3) the rupture occurs after a black film has formed and is spreading or (4) the formed black film occupies the whole film area and lasts for more than 60 s.

logarithm of the surfactant concentration, both below and above the c.m.c. point ($5 \times 10^{-5} \text{ M}^{18}$). In the case of Span 20, the lifetime below $5 \times 10^{-4} \text{ M}$ of surfactant is very short and does not depend on the surfactant concentration. This is the only case where the thinning pattern (1) is recorded and the final thickness of rupture is higher than the transition thickness, as defined in Fig. 1. The lifetime in this case is very short and the films rupture prematurely. The reason for this short lifetime is revealed below. Above $5 \times 10^{-4} \text{ M}$ the data for Span 20 also seem to follow a linear increase.

The data for the pattern of rupture of the emulsion films are presented in Fig. 7. It is noticed that the films containing the oil-soluble Span are much less stable and much more inclined to rupture prematurely, even at comparatively high concentrations. This provides a clue to the horizontal part of the curve for Span 20 in Fig. 6, it is seen that at concentrations below $5 \times 10^{-4} \text{ M}$ of Span 20 film rupture occurs early, before the critical thickness is reached. Hence, the lifetime of these films is low and not dependent on the hydrodynamic parameters alone.

Theoretical considerations and Discussion

It is known that higher concentrations of surface active agents should increase the film stability through a number of complementary factors. All these factors arise from the increased adsorption on the surfaces at higher surfactant concentrations in the bulk. The increased adsorption, in its turn, causes surface immobilisation and a lower rate of hydrodynamic thinning,^{2,4} higher sterical repulsion²⁶ *etc.* The data obtained on the film lifetime and moment of rupture are in full accord with these expectations.

Turning to the quantitative side of the results, the most striking feature of all the investigated systems is the linear increase in the film lifetimes, even above the c.m.c. point of the surfactants. The film lifetime for the water soluble surfactants as a function of $\ln(C)$, where C is normalised by the respective c.m.c. value, is plotted in Fig. 8. It is well known that, at the c.m.c., some of the first derivatives of the properties related to the surfactant concentration, such as interfacial tension or osmotic pressure, undergo a jump-wise transition.²⁷ Therefore, one would intuitively expect a breakpoint in the slope of the obtained dependence; however, such a breakpoint was not observed experimentally (Fig. 8). Such behaviour in surfactant systems is revealed and investigated for the first time here.

To calculate the film lifetime, τ_1 , one needs to find an explicit solution of eqn. (1). We shall assume that the films thin down as plane-parallel ones and shall neglect the effect of the dimpling as long, as it has been suggested,²⁸ that the

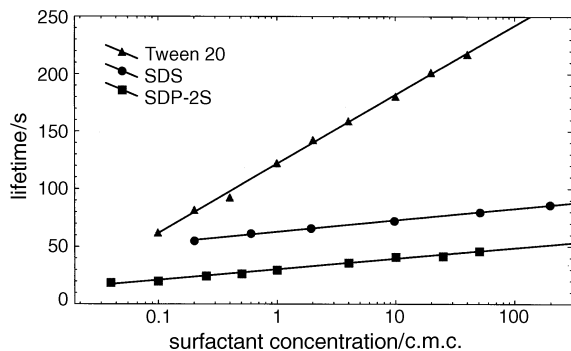


Fig. 8 Mean hydrodynamic lifetime of aqueous films stabilised by different water soluble surfactants vs. the surfactant concentration, normalised by the respective c.m.c. value (5×10^{-5} M for Tween 20, 5.3×10^{-5} M for SDP-2S and 1×10^{-3} M for SDS)

occurrence of the dimple through the film thinning does not change significantly the thinning rate, $V(h)$ and the lifetime, τ_1 . Appropriate formulae for the rate of thinning of foam and emulsion films have been derived in the hydrodynamic theory of thin-film drainage of Ivanov and co-workers^{2,29,30} and the theoretical treatment below is based on these formulae. The solution for the case of surfactant soluble in the film only is:

$$\frac{V(h)}{V_{re}} = 1 + b + \frac{h_s}{h} \quad (2)$$

where the velocity of thinning is normalised by the Reynolds velocity, V_{re} , of approach of circular, tangentially immobile plane-parallel surfaces³¹

$$V_{re} = \frac{2h^3}{3\eta R_f^2} \Delta P \quad (3)$$

where η is the viscosity of the liquid in the film, R_f is the film radius and ΔP is the driving pressure of film thinning.

The parameters b and h_s , in eqn. (2), are expressed through the bulk and surface diffusion coefficients of the surfactant, D and D_s , respectively; the adsorption, Γ ; the interfacial tension, σ ; the surfactant concentration, C ; and the Gibbs elasticity, E_G :

$$b = -\frac{3\eta D}{\Gamma \left(\frac{\partial \sigma}{\partial C} \right)}; \quad h_s = \frac{6\eta D_s}{E_G}; \quad E_G = -\frac{\partial \sigma}{\partial \ln \Gamma} \quad (4)$$

The driving pressure, ΔP , is a sum of the sucking capillary pressure in the cell, P_c , and the disjoining pressure between the film surfaces, Π ,

$$\Delta P = P_c - \Pi(h) \quad (5)$$

The capillary pressure in the cell can be expressed via the cell radius, R_c :

$$P_c = \frac{2\sigma R_c}{R_c^2 - R_f^2} \quad (6)$$

The disjoining pressure between the film surfaces is a sum of the van der Waals, electrostatic and steric contributions. The investigated films, however, had a high electrolyte concentration (0.1 M) and were thicker than 20 nm. This allows us to neglect the electrostatic and the steric interactions. To account for the van der Waals attraction between the surfaces we used the expression from ref. 32

$$\Pi(h) = -\frac{A_H}{6\pi h^3} \quad (7)$$

where A_H is the Hamaker constant. It is easy to estimate that, for the typical range of film thicknesses, starting from $h = h_i \approx 200$ nm and going down to $h = h_{cr} \approx 20$ nm, the integral in eqn. (1) is practically independent of the upper boundary of integration. Therefore, we can set $h_i = \infty$. The critical or transition film thickness, h_{cr} can be evaluated on the basis of the expression derived by Vrij³³

$$h_{cr} = 0.264 \left(\frac{A_H^2 R_f^2 R_c}{2\pi\sigma^2} \right)^{1/7} \quad (8)$$

Introducing the above eqn. (2)–(7) into eqn. (1), we can integrate to obtain

$$\begin{aligned} \tau_1 = & \frac{3\pi\eta R_f^2}{2(1+b)A_H} \frac{1}{a(\beta^3 - 1)} \\ & \times \left\{ \sqrt{3(\beta^2 - 1)} \left[\pi - 2 \arctan \left(\frac{2\xi_{cr} - 1}{\sqrt{3}} \right) \right] \right. \\ & - (\beta - 1)^2 \ln(\xi_{cr}^2 - \xi_{cr} + 1) \\ & \left. + 2(\beta^2 + \beta + 1) \ln(\xi_{cr} + 1) - 6\beta \ln(\xi_{cr} + \beta) \right\} \quad (9) \end{aligned}$$

where

$$a = \left(\frac{12\pi\sigma}{A_H R_c} \right)^{1/3}; \quad \beta = \frac{ah_s}{1+b}; \quad \xi_{cr} = ah_{cr}$$

The above equation can, in principle, be simplified further for surfactants with high Gibbs elasticity ($E_G \approx 10$ – 100) where $\beta \ll 1$ and $b \ll 1$.

We have compared our experimental results for SDS up to the c.m.c. with the calculations from eqn. (9). The data for the interfacial tension, the adsorption and the Gibbs elasticity were estimated, based on a numerical approximation of the literature data of the SDS isotherm of Exerowa *et al.*⁹ The Hamaker constant was used as an adjustable parameter. The results obtained are presented in Fig. 9 with the value obtained for $A_H = 8.0 \times 10^{-13}$ erg [which is in agreement with the literature data for foam films, $(4$ – $30) \times 10^{-13}$ erg^{26,34}]. It is seen that the theoretical curve can approximate the experimental data reasonably in the region below and around the c.m.c. To describe the data above the c.m.c., one should account for the influence of the micelles present and the resulting change in the surfactant adsorption layers. Note, also that the theory used approximates the linear relation obtained between τ and $\ln(C)$, but this relation is not explicitly derived from the above equations. Therefore, we have to conclude that, although the currently available theoretical predictions are close to the obtained data, there is agreement in the region up to the c.m.c. A complete description appears to be very difficult as long as one has to account for the presence of

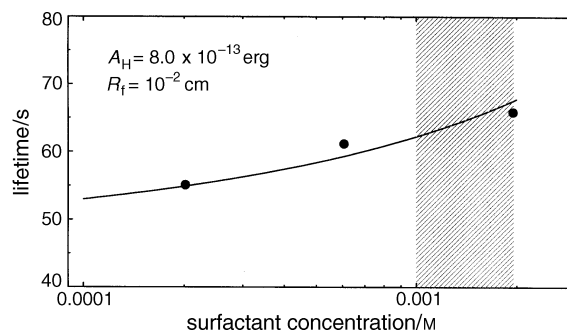


Fig. 9 Comparison between experiment and theory for foam films stabilised with SDS. The c.m.c. region of the surfactant is denoted by the shaded area.

the micelles that, in their turn, may cause structural or osmotic contributions to the disjoining pressure between the surfaces. We hope that this study may catalyse such future theoretical developments. From a numerical viewpoint, the water-air films thin much faster than emulsion ones. Despite the quicker thinning of the foam films, the final black films, which they form at lower surfactant concentration, appear to be more stable than those in emulsions.

Turning now to the data for the emulsion films, it is interesting to compare the lifetimes of emulsion systems where the films stabilised by Tween last much longer than those with Span. This set of data can be explained on the basis of two empirical rules, well known to the emulsion investigator. The first is the Bancroft rule,³⁵⁻³⁹ which postulates that the phase into which the emulsifier is dissolved will become the continuous one, when the dispersion is prepared. The second guideline is the so-called hydrophile-lipophile balance (HLB) scale,^{15,17} based upon the chemical composition and hydrophilicity of the surfactants. Both these empirical rules are also in good correlation with the expectations of the hydrodynamic theories of film thinning and stability. Indeed, according to Ivanov and co-workers^{2,4} the rate of thinning is lower (respectively, the lifetime is higher) when the surfactant is dissolved in the continuous (film) phase and possesses a higher Gibbs elasticity. To make sure that the Bancroft rule is applicable, we have to make certain that both of the surfactants are predominantly distributed into only one of the phases throughout all the investigated concentrations and at the working temperature.³⁷⁻³⁹ This is based on our measurements with Tween 20^{19,20} and Span 20 (unpublished data). This conclusion is supported also by the HLB values of the two surfactants¹⁷ and the literature data on their solubilities,¹⁸ both reported at temperatures close to that in these experiments. The difference in the film stability can also be correlated with the interfacial tension isotherms of Span 20 and Tween 20 obtained earlier (Fig. 3 from ref. 16). These isotherms show that Tween 20 has a much higher adsorption at lower concentrations. The interfacial tension (and the adsorption) of Tween continues to decrease above the c.m.c., which may be the reason for the measured increase in the lifetimes in that region. Considering Span 20, an important correlation is noticed from ref. 16: the increase in its interfacial activity starts from the region where the film lifetime in our experiments (Fig. 6) increases, *ca.* 5×10^{-4} M. This correlation is direct evidence for the impact of the interfacial activity on the film lifetime, as postulated in the above theories.

In spite of their different chemical nature, all four investigated surfactants demonstrate a good linear increase in the lifetime, when plotted *vs.* the logarithm of the concentrations. Thus, the observed dependence seems to hold for a wide range of surfactant types and concentrations (Fig. 8). At present, it can hardly be claimed that this linear dependence will be followed by any available surfactant, but the wide diversity of the four systems studied suggests that many more surfactants of practical importance may exhibit the same behaviour. Further studies with alternative surfactant types should be important for assessment of the generality of the observed dependences.

The data obtained can provide clues for the formulation of the emulsion and foam systems used in practical applications. Usually, such emulsions are produced with concentrations of surfactants that are quite high and orders of magnitude above the c.m.c. Most of the surfactant initially dissolved in the water will be depleted by adsorption on the highly developed droplet interfaces. The data obtained can be viewed as describing the effect of the residual surfactant concentration on the emulsion stability. They demonstrate, that, if the residual concentration falls below the c.m.c., the interdroplet films will be unstable for both hydrodynamic and thermodynamic reasons. If a properly chosen stabiliser slightly above

the c.m.c. is used, the final (black) films, as well as the whole emulsion system, will probably be stable. However, the hydrodynamic stability of this emulsion (which may be important *e.g.* in the case of hydrodynamic shear stresses) could still be improved further by increasing the surfactant concentration. Therefore, the minimal required condition for obtaining a practically stable emulsion will be to complete the homogenisation with a residual surfactant concentration slightly above the c.m.c., but the hydrodynamic stability of the system could be improved with further increase in concentration.

Conclusions

The experimental results on the rate of thinning of foam and emulsion films, stabilised with four typical surfactants, demonstrated a linear increase in the film lifetime with the logarithm of the surfactant concentration. Notably, the film lifetime continues to increase even well above the c.m.c. of the water-soluble surfactants used. It appears that the observed functional dependence may be typical for many practical systems, though further studies with different surfactants will be required for a full verification. A large difference in the lifetime and the stability of model water-oil films is observed, when water-soluble (Tween 20) and oil-soluble (Span 20) surfactants are present. This difference is in correlation with the theoretical expectations and the empirical Bancroft rule.

The data obtained are compared with the theoretical predictions of the hydrodynamic theories of film thinning. It is shown that the theory is able to describe the experimental quantitative relations with acceptable, but not excellent, agreement. The origin of the measured increase in the lifetime above the c.m.c. still remains to be investigated and described theoretically, since the data obtained appear to hold numerous implications that are of practical importance.

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