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SHORT COMMUNICATION

Thinning of foam films of micellar surfactant solutions

Nonionic surfactants $C_{10}H_{21}(OC_2H_4)_8OH$ and $C_{12}H_{25}(OC_2H_4)_8OH$

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Abstract Drainage in microscopic circular foam films depends significantly on the radial (tangential) mobility of the film surfaces and is accelerated as compared to the limiting case of tangentially immobile surfaces, where velocity of thinning is described by the classical Reynolds' equation (outflow of viscous fluid from a cylindrical gap between two solid plates). The structure and composition of the adsorption layer and the interfacial mass transfer determine the tangential mobility of the film surfaces and, hence, the measured velocity of film thinning. Experiments with soluble surfactants below the critical micelle concentrations (CMC) have exhibited the effect of dynamic interfacial elasticity. At relatively low bulk concentrations, the interfacial mass transfer is governed by surface diffusion; close to CMC (saturated adsorption layer), the limiting case of tangentially immobile surfaces can be reached and at concentrations above the CMC the film thinning is accelerated again. Here, we report freshly established data on the kinetic behavior of foam films from micellar solutions of soluble nonionic surfactants (decyl-octaoxyethylene alcohol and dodecyl-octaoxyethylene alcohol) in a wide range of concentrations above the CMC aiming to investigate the effect of partially disintegrated micelles acting as sources of surfactant molecules at the surface.

Keywords Foam films · Surface micelles · Dynamic interfacial elasticity

Introduction

Thinning of microscopic circular foam films depends significantly on the radial (tangential) mobility of the film surfaces. The structure and composition of the adsorption layer and interfacial mass transfer determine the tangential mobility of the film surfaces and, hence, the measured velocity of film thinning.

Previous experiments with soluble surfactants below the critical micelle concentration (CMC) have proven the effect of dynamic interfacial elasticity. At relatively low bulk concentrations, the interfacial mass transfer is governed by surface diffusion; the limiting case of tangentially immobile surfaces can be reached close to CMC (saturated adsorption layer) and at concentrations slightly above the CMC the film thinning is accelerated again [1–4]. Foam films of liposome suspensions (lipid molecules practically insoluble as monomers in the bulk) exhibit an accelerated thinning due to the presence of interfacial lipid aggregates acting as sources of surfactant molecules during film thinning [5–7]. In monolayer experiments, the presence of such lipid aggregates at the interface was proven both indirectly (see e.g., [8, 9]) and directly [10–14] and has stimulated theoretical treatment of equilibrium and kinetic aspects of this phenomenon [15–19]. Interfacial aggregates were found also in more complex systems of biological interest [20–23].

In recent years, much scientific effort, both experimental and theoretical, was invested in order to understand the

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transients of the surface tension of soluble surfactants below and above the CMC ('dynamic surface tension'—see e.g., [24–33], and references therein). The effects of disintegration of micelles in the bulk solution on the velocity of thinning of circular microscopic foam films were studied theoretically by Dushkin [32] (see references therein). Most of these theoretical models neglect the existence of partially disintegrated micelles at the interface ("adsorbed micelles"). At high concentration of micelles in the bulk, their concurrent adsorption and disintegration at the interface may block the surface before the disintegration is completed and the closely packed adsorption layer will contain both monomers and aggregates (see Fig. 1). It was shown that even at concentrations below the CMC some peculiarities of the interfacial layer might be explained with the existence of interfacial aggregates [9, 34, 35].

Hydrodynamics of foam films (cylindrical film with planar surfaces)

The starting point has been the Reynolds' equation for the laminar flow of a viscous fluid pressed between two solid disks (cylindrical planar film with tangentially immobile surfaces [36–38]). However, the hydrodynamic "no-slip" boundary condition at the foam film surfaces is not always fulfilled.

The tangential radial outflow of liquid from a foam film perturbs the equilibrium surfactant distribution. The perturbation in the surface concentration, $\Delta\Gamma$, creates a gradient $\partial\Gamma/\partial r$ and consequently a gradient in the surface tension σ, which governs an effective "dynamically elastic" behavior of the fluid surface. In the case of a "completely rigid" insoluble monolayer, this effect may immobilize tangentially the foam film surfaces. Compensating surfactant fluxes (surface and bulk diffusion, adsorption, sources of surfactant monomers) can lower $\partial\Gamma/\partial r$ and the gradient in σ, thus leading to changes in the "dynamic elasticity", an increase of the tangential mobility of the film surfaces, and hence to an increase in the measurable overall velocity of thinning of the foam film. The lowest velocity of thinning is obtained with "rigid" surface layers ensuring the hydrodynamic "no-slip" boundary condition at the film surfaces. This is closely related to many interfacial phenomena known as Marangoni–Gibbs effects (see e.g., the already classical book by Levich [39] and [40, 41]). The experimentally registered rate of thinning of a cylindrical plane-parallel thin foam films, governed by interfacial mass transfer, can be used to find rate-determining processes and to estimate interfacial kinetic constants [3, 5, 41–46]. An analogous procedure can be applied to the rate of flattening of an axisymmetric dimple in foam films [6, 47].

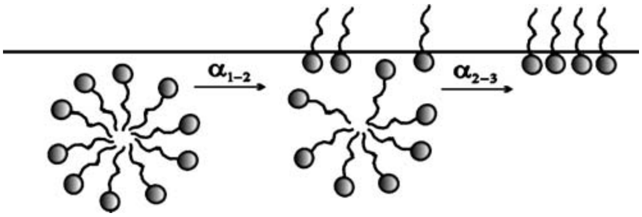

Fig. 1 The surfactant layer at the air–water interface can consist of monomers and aggregates

Under conditions where the film thinning follows regular pattern and the cylindrical film is almost plane-parallel, the following equations can be used to quantify experimental data:

Film with tangentially immobile surfaces—'rigid' surface layers [2, 36–38]

$$\left(\frac{dh}{dt}\right)_{Re} = -\frac{2h^3(P_c - \prod)}{3\eta r^2} \tag{1}$$

where t is time, h is film thickness, P_c is capillary pressure, Π is disjoining pressure (in our case Π is the negative attractive van der Waals disjoining pressure, which increases the driving pressure—see e.g., [48]), η is dynamic viscosity, and r is film radius. The subscript 'Re' refers to the 'Reynolds velocity' [36–38]. It is convenient to express the velocity of thinning as $\left(dh^{-2}/dt\right)_{Re}$. With this notation, Eq. 1 has been rewritten as

$$\left(\frac{dh^{-2}}{dt}\right)_{Re} = \frac{4(P_c - \prod)}{3\eta r^2} \tag{2}$$

It is instructive to rewrite this equation in an integral form for larger thicknesses, where $\Pi << P_c$ ($h > 55$ nm). After integration and rearrangement this equation yields

$$\Delta t = \frac{3\eta r^2}{4P_c}\Delta\left(h^{-2}\right) \tag{3}$$

Film with tangentially mobile surface—"dynamically elastic" surface layers

With soluble surfactants the essential theoretical treatment of the kinetics of surface layer formation below the CMC (diffusion and adsorption in series) is given by Ward and Tordai [49].

The case of monomer bulk diffusion controlled process, considered theoretically in [43, 46, 50], was also found experimentally for solutions of water-soluble surfactants (soluble both as monomers and micelles) [43, 50]. For liposomes, this case is excluded (water insoluble lipid molecules). At very low concentrations below the CMC, surface diffusion is solely responsible for the surface mobility (see "Appendix").

The case of monomer adsorption controlled surface "dynamic elasticity," was considered theoretically in [46]. With lipid vesicles and micelles the "adsorptive" flux can be provided by surface aggregates acting as sources of surfactant molecules at the film surface, perturbed by radial liquid flow beneath the surface. A simplified kinetic scheme is presented in Fig. 1.

The equation for the case of adsorption controlled process, derived for small expansion perturbations (linear approximation in the simplest relevant geometry of a cylindrical foam film with plane-parallel surfaces), is sophisticated enough [46]. A useful limiting case is when bulk and surface diffusion are negligible:

$$\frac{\left(dh^{-2}/dt\right)}{\left(dh^{-2}/dt\right)_{Re}} = \frac{3\eta r^2\alpha}{4hE_{\mathrm{G}}} \tag{4}$$

Where the derivative $\left(dh^{-2}/dt\right)$ contains the actual measured values of h and t, $E_{\mathrm{G}} = -(\partial\sigma/\partial\ln\Gamma)_0$ is the equilibrium Gibbs' surface elasticity, the kinetic constant α is defined as $j_{\mathrm{ads}} = -\alpha\Delta\Gamma$ j_{ads} is the adsorption flux of surfactant molecules, and $\Delta\Gamma$ is the perturbation in the equilibrium surface concentration. According to the simplified kinetic scheme (see Fig. 1), α should be redefined as $\alpha_{1\text{–}2}$ for the process 1–2 or as $\alpha_{2\text{–}3}$ for the process 2–3 (in cases of an order of magnitude difference or more). The rate constant $\alpha_{1\text{–}2}$ describes the adsorption of soluble intact micelles or liposomes and $\alpha_{2\text{–}3}$ describes the disintegration of insoluble surface aggregates acting as sources of lipid molecules at the interface, when the equilibrium adsorption layer is disturbed by the tangential flow in the film.

It is instructive to rewrite Eq. 4 in integral form for larger thicknesses, where $\Pi << P_{\mathrm{c}}$ (h >55 nm). Then combining Eqs. 4 and 2 after integration yields (film thinning is influenced only by the presence of partially disintegrated micelles serving as sources of surfactant molecules).

$$\Delta t = \frac{2E_{\mathrm{G}}}{\alpha P_{\mathrm{C}}}\Delta\left(h^{-1}\right) \tag{5}$$

Equation 2 predicts a decrease in the rate of thinning with the film size (film area ~ r^2) due to viscous drag (friction) in the film with "rigid" surface layers. Equation 4 predicts a relative acceleration of the thinning due to the "dynamic elasticity" of the surface layers: Eq. 4 takes into account only the compensating flux due to surface sources—the "dynamically elastic" effect is proportional to r^2.

In the integral form of Eq. 5, obtained from Eqs. 2 and 4, the "viscous" and the "elastic" effects, both proportional to r^2, work in opposite directions and render $\Delta t/\Delta\left(h^{-1}\right)$ insensitive to the film area. These predictions are tested experimentally further on.

Materials and methods

Commercial nonionic surface active substances decyl-octaoxyethylene alcohol ($C_{10}E_8$) and dodecyl-octaoxyethylene alcohol ($C_{12}E_8$) were used without further purification. Solutions with different concentrations were prepared with doubly distilled water containing sodium chloride (0.1 mol/dm^3). NaCl was doubly recrystalised and subsequently heated for 5 h at temperature 450°C in order to remove possible traces of organic contaminants. Electrolyte was added to suppress the positive electrostatic disjoining pressure. The glassware was processed with bichromic cleaning mixture and extensively rinsed with doubly distilled water.

The measurements were carried out with solutions of the following concentrations: 5.10^{-4} mol/dm^3, 10^{-3} mol/dm^3, 10^{-2} mol/dm^3, and 10^{-1} mol/dm^3 for $C_{10}E_8$ and 5.10^{-5} mol/dm^3, 10^{-4} mol/dm^3, 10^{-3} mol/dm^3, and 10^{-2} mol/dm^3 for $C_{12}E_8$.

The measured values of the surface tension coincided within experimental accuracy with data of Meguro et al. reported in [51] giving for $C_{10}E_8$ CMC=1.10^{-3} mol/dm^3 and for $C_{12}E_8$ CMC=7.5.10^{-5} mol/dm^3.

Hence, the respective concentrations are 0.5 CMC, 1 CMC, 10 CMC, and 100 CMC for $C_{10}E_8$ and 0.665 CMC, 1.33 CMC, 13.3 CMC, and 133 CMC for $C_{12}E_8$.

A computerized version of the microinterferometric set up of Scheludko and Exerowa for studying thin foam films was used. The established experimental procedure is described in detail elsewhere (see e.g., [40, 52–55]): the registered time trace of the intensity of monochromatic light reflected from the lower and the upper film surfaces is governed by light interference from an optically denser film of diminishing thickness; the interferograms are used to obtain the time trace of the film thickness. The same phenomenon is responsible for the colorful appearance of soap bubbles in polychromatic light.

With soluble surfactants, initially the foam film drains irregularly; at smaller thickness (below approximately 130 nm and sufficiently small radii), an almost plane-parallel film is observed, followed by film rupture or black film formation (see e.g., [37, 40, 54, 56, 57]).

The rate of thinning was measured at room temperature 23°C. The film radius was determined from the position of the first dark Newton fringe.

According to Eq. 3, at the lowest studied concentrations, the straight lines in Figs. 2a and 3a were drawn with an intercept fixed to zero; according to Eq. 5, at the highest studied concentrations the straight lines depict the mean values of Δt.

Results and discussion

Here, we present only the newly established data for the time interval (Δt) in which the film thins from 103 to 55 nm because in this thickness interval the drainage pattern are closest to the plane-parallel mode of thinning. The range of foam film radii is also limited: from

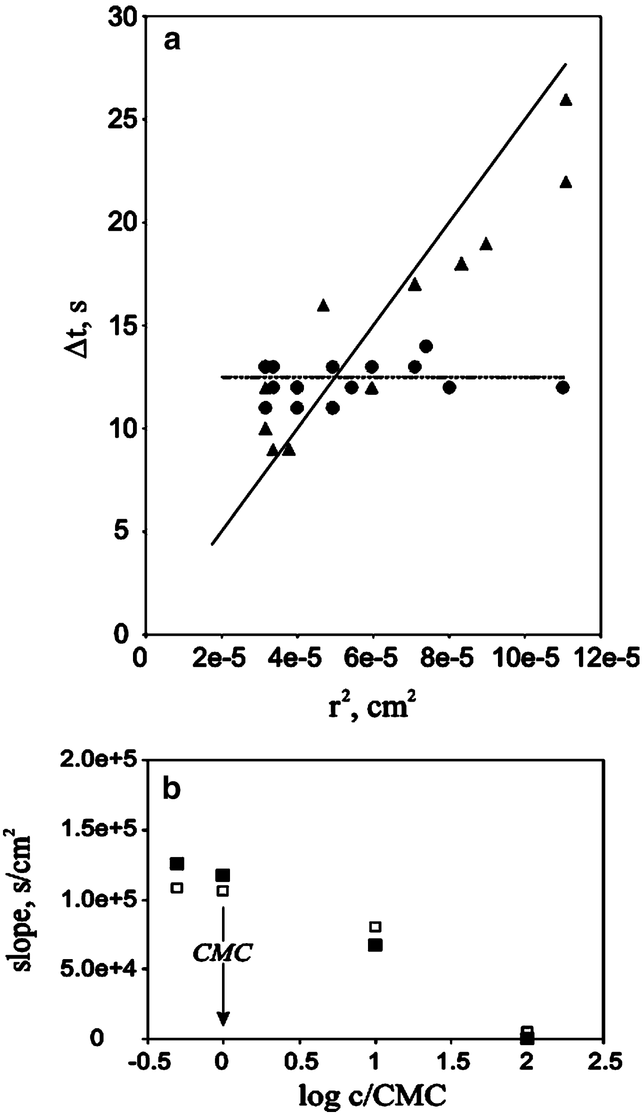

Fig. 2 Data for $C_{10}E_8$: **a** time of film thinning (Δt) for the thickness interval 103–55 nm as a function of film area (r^2); *triangles*: c=0.5 CMC, *circles*: c=100 CMC; **b** slopes of the straight lines Δt (r^2) vs. log (c/CMC); see Eqs. 3 and 5 (*full* and *open symbols* depict results from two different independent experimental series)

approximately 5.10^{-3} cm to approximately 15.10^{-3} cm; at smaller radii, the films tend to shrink while at higher values irregular domains form and the film drainage is additionally accelerated [56, 57].

The concentration range of the studied solutions includes solutions under CMC (0.5 CMC for $C_{10}E_8$ and 0.665 CMC for $C_{12}E_8$), close to CMC (1 CMC for $C_{10}E_8$ and 1.33 CMC $C_{12}E_8$), and up to two orders of magnitude above CMC (100 CMC for $C_{10}E_8$ and 133 CMC for $C_{12}E_8$).

The data for the lowest and highest concentrations studied are shown as Δt as a function of r^2 in Figs. 2a and 3a for $C_{10}E_8$ and $C_{12}E_8$, respectively. Data for the intermediate concentrations are not shown in order not to overcrowd the figures. Below the CMC, Δt increases with the film area (as required by Eq. 3), while for the highest surfactant levels, approximately 100 CMC, Δt becomes independent of the film size (in accord with Eq. 5).

For all studied concentrations, the resulting values of the slopes of the straight lines of the plots Δt vs. r^2 are shown as a function of surfactant concentration in Figs. 2b and 3b (for $C_{10}E_8$ and $C_{12}E_8$, respectively). The slopes decrease with increasing surfactant concentration above the CMC. With the highest concentrations studied (100 CMC for $C_{10}E_8$ and 133 CMC for $C_{12}E_8$), the slopes are practically zero.

These findings strongly corroborate the applicability of Eq. 3 to describe the film thinning at concentrations slightly

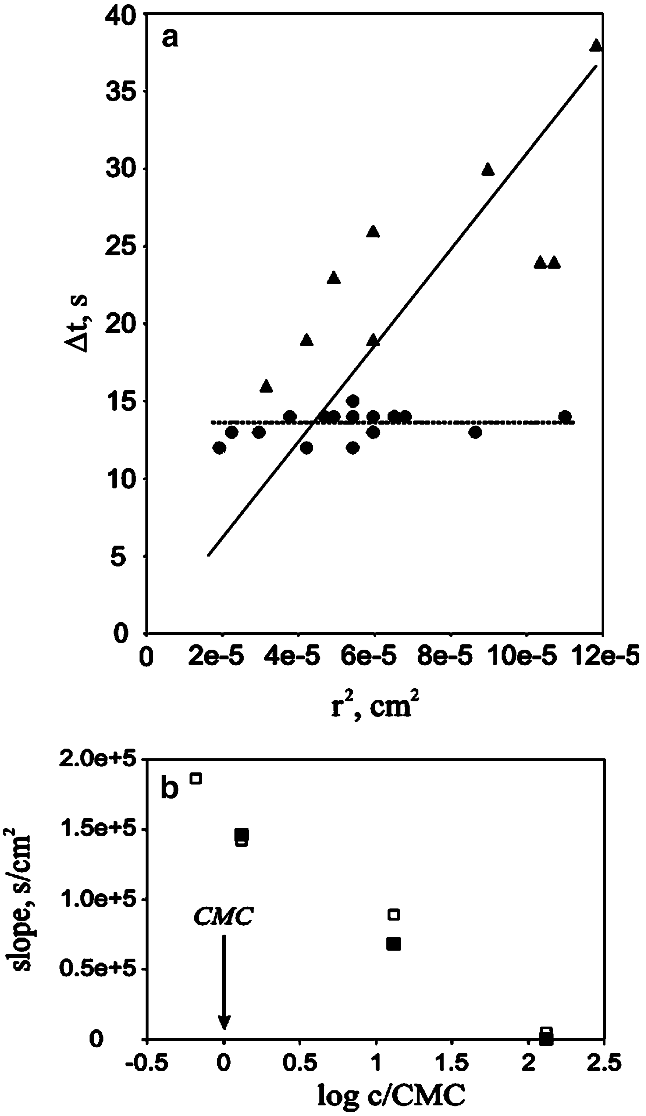

Fig. 3 Data for $C_{12}E_8$: **a** time of film thinning (Δt) for the thickness interval 103–55 nm as a function of film area (r^2); *triangles*: c=0.665 CMC, *circles*: c=133 CMC; **b** slopes of the straight lines Δt (r^2) vs. log (c/CMC); see Eqs. 3 and 5 (*full* and *open symbols* depict results from two different independent experimental series)

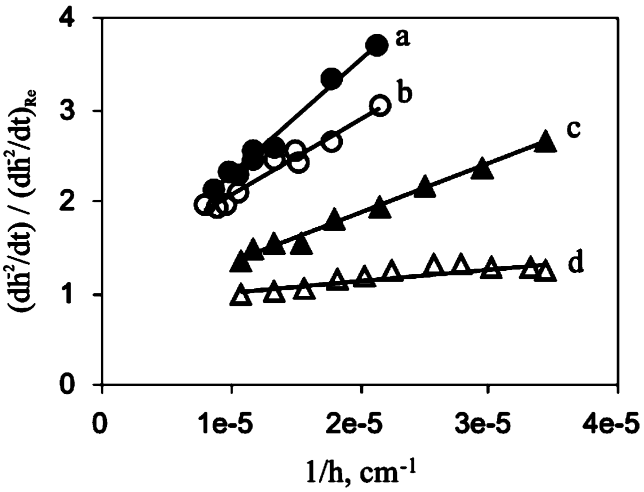

Fig. 4 Relative acceleration of film thinning according to Eq. 6, aqueous dilute electrolyte solutions of soluble surfactants: a, b valeric acid 2.10^{-3} mol/dm^3, 10^{-2} mol/dm^3; c, d sodium-dodecylsulphate 5.10^{-6} mol/dm^3, 10^{-3} mol/dm^3 (data summarized in [3])

below the CMC and of Eq. 5 at concentrations of the order of 100 CMC.

In the former case, the surfactant layer is practically saturated and the film surfaces are tangentially immobilized (Reynolds' equation is obeyed: viscous drag proportional to r^2 dominates). The experimental slopes are in reasonable agreement with values predicted by Eq. 3 with estimated parameter values. The applicability of Eq. 3 for foam films with saturated adsorption layers has been previously confirmed with many other surfactants and solvents [1–3, 37].

In the latter case, in accordance with Eq. 5, the viscous drag effect is compensated by dynamic elasticity due to surfactant release from surface aggregates. The established values of Δt give the possibility to estimate the value of the phenomenological rate constant of surfactant release α.

It is reasonable to assume a value of E_G in the range 50–100 mN/m [58]. The measured values of Δt are around 12 s for the thickness interval between 103 and 55 nm. The capillary pressure is estimated from $P_C = 2\sigma/R \approx 50\,\mathrm{Pa}$ (R denoting the radius of the cut glass capillary where the foam film is formed; in our case R=2 mm). With these values, Eq. 5 yields α values of the order of 10^{-3} s^{-1} (or a characteristic time $\tau = 1/\alpha$ in the millisecond range). Such values are reported in many studies of demicellization kinetics in bulk micellar solutions for the second much slower process 2–3 (see e.g., [27]). This corroborates the assumed schematic picture of interfacial demicellization kinetics (c.f. Fig. 1) analogous to that established in bulk micelle solutions. On the other hand, this order of magnitude agreement supports the idea of partially disintegrated micelles acting as sources of surfactant molecules at the surface when it is perturbed by small expansion.

Conclusions

At concentrations slightly below the CMC of the studied surfactants, the kinetics of foam film thinning (103>h>55 nm; 0.05<r<0.15 mm) are reasonably well described by Reynolds' equation (tangentially immobile foam film surfaces). The predicted linear increase of the time of film thinning on the film area is confirmed experimentally for the thickness interval of plane-parallel stage of drainage. At the highest concentrations studied (approximately 100 CMC), the time interval for film thinning (103>h>55 nm; 0.05<r < 0.15 mm) becomes insensitive to the film area and foam films drain up to four times faster. This is well explained with a predominant effect of interfacial surfactant aggregates acting as sources of monomer surfactant molecules at the hydrodynamically perturbed fluid interfaces of the foam film.

At intermediate concentrations above the CMC, the interfacial tangential mobility is most probably governed by a mixed diffusion–interfacial disaggregation mechanism.

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Appendix

Negligible sources of surfactant molecules and negligible bulk diffusion (surface diffusion being solely responsible for the surface mobility)

In this limiting, case the relative acceleration of foam film thinning is described by [44]

$$\frac{\left(dh^{-2}/dt\right)}{\left(dh^{-2}/dt\right)_{Re}} = 1 + \frac{6\eta D_S}{hE_G} \tag{6}$$

where D_s denotes monomer surface diffusivity.

The latter limiting case was found experimentally with soluble surfactants at very low degrees of surface coverage [3, 45, 59] (see Fig. 4). The values of D_s can be estimated from the slopes in Fig. 4. For all studied systems, they are collected in [3].

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