

Notes

Effect of the Rheology on Foam Drainage

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When a foam is formed from a surfactant solution, it contains excess liquid that drains out until equilibrium is eventually reached between the capillary and gravity forces. In view of the importance of this process for the stability of the foam, it has often been studied by measuring the rate of accumulation of the liquid drained from the foam. However, because of the complexity of this process, no satisfactory model has been proposed until now to quantitatively describe the drainage rate.¹ Recently, a new type of experiment was proposed in which the surfactant solution is poured from above to wet a foam column. It was observed that the front separating the wet from the dry part of the foam does not broaden with time.² This result indicates that the hydrodynamic motion of the liquid front is of the "soliton" type. A model has been worked out to explain this behavior, idealizing the complex network of Plateau borders as a set of N identical tubes with a cross section that depends on height and on time. A soliton type propagation has indeed been found, whose velocity V is

$$V^2 = A Q \rho g / \eta \quad (1)$$

where Q is the volumetric flow rate, g is the acceleration of gravity, ρ is the solution density, η is the solution viscosity, and A is a constant that depends on the foam structure.³ The theory predicts that A should be independent of the surface tension or its derivatives, in particular the Gibbs elasticity. This prediction is made because the surfactant layer, covering the soap bubbles and the Plateau borders, is assumed to be rigid; that is, the tubes of the model behave as rigid pipes. For a recent

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(1) Bikerman, J. J. *Foams*; Springer Verlag: Berlin, 1973.

(2) Weaire, D.; Pittet, N.; Hutzler, S.; Paldal, D. *Phys. Rev. Lett.* **1993**, *71*, 2670.

(3) Verbist, G.; Weaire, D. *Europhys. Lett.* **1994**, *26*, 631.

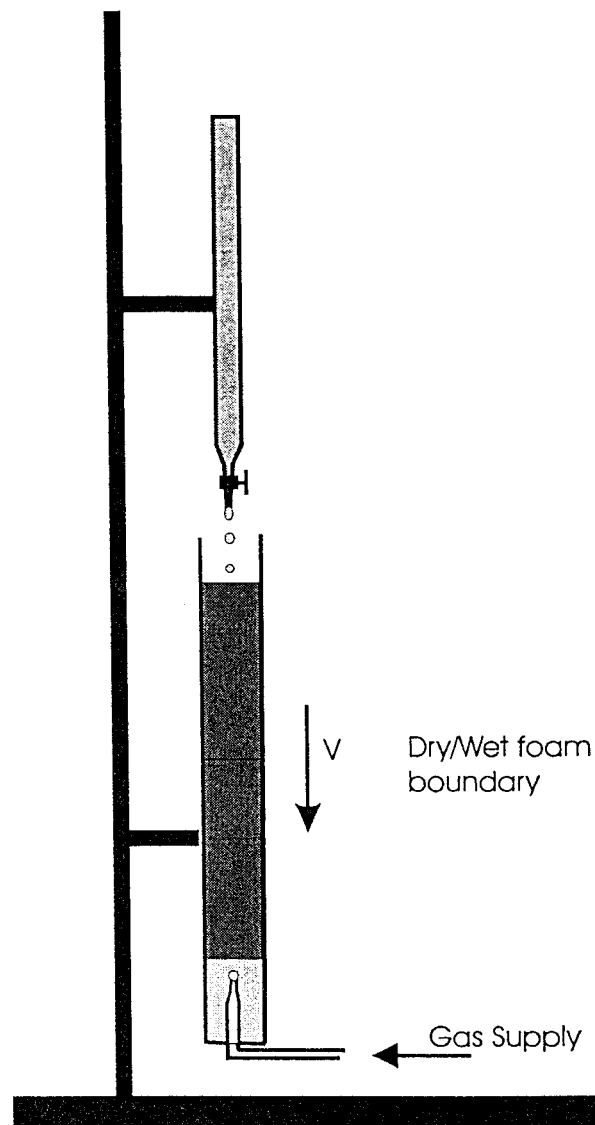


Figure 1. Sketch of the experimental setup.

review of both theoretical and experimental work, see Weaire et al.⁴

To check the validity of this prediction, we measured the velocity of drainage of foams prepared from water solutions of different surfactants with different surface tension and Gibbs elasticity. In these experiments, the foam is formed in a 50-cm-long graduated glass column by bubbling gas (nitrogen) through a porous glass disk at the bottom of the column (Figure 1). The gas rate is adjusted in such a way that monodisperse foam is created with a bubble size of ~ 5 mm. The gas supply is stopped once the foam reaches a height of ~ 30 cm, and the foam is allowed to reach a dry state for ~ 5 min. The surfactant solution is then added on the top of the column with the

(4) Weaire, D.; Hutzler, S.; Verbist, G.; Peters, E. A. J. *Adv. Chem. Phys.* **1997**, *102*, 315.

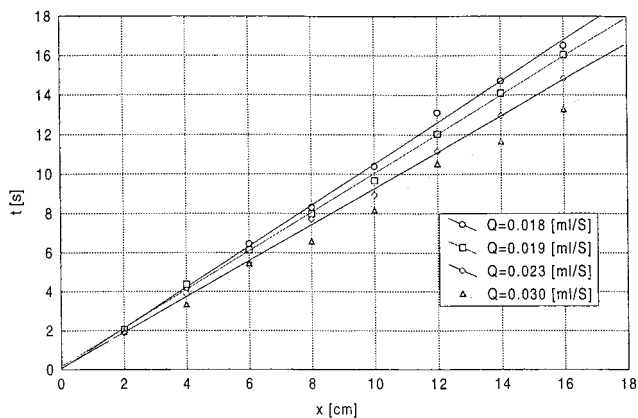


Figure 2. Motion of the boundary between wet and dry foam as determined from the distance x to the top of the liquid column for an SDS solution at 10 cmc and 0% glycerol; variation of x with the time t .

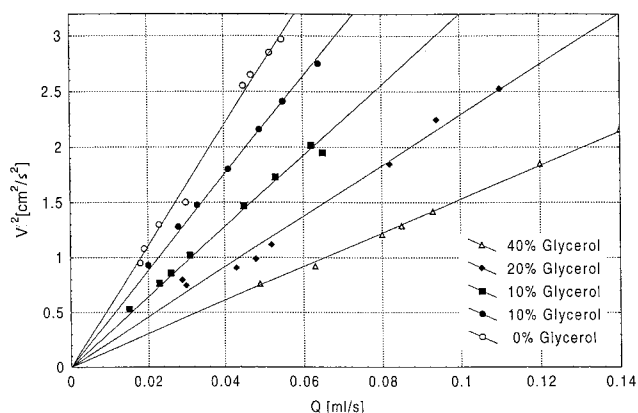


Figure 3. Drainage of SDS solutions containing different amounts of glycerol; variation of the square of the velocity of drainage V^2 versus flow rate Q . The slopes are 55.05, 43.87, 31.98, 22.89, and 15.29 for 0, 10, 20, 30, and 40% concentrations of glycerol.

help of a pipet that delivers drops of calibrated volume (1 to 10 drops/s). The motion of the front is observed visually.

We used two surfactants, sodium dodecyl sulfate (SDS) from BDH, England, and cetyltrimethylammonium bromide (CTAB) from Aldrich. The surfactants were recrystallized twice to ensure good purity. No minimum of surface tension around the critical micellar concentration (cmc) was observed. Both surfactants give stable foams that can last a few hours. Several trials were made with dodecyltrimethylammonium bromide (DTAB), but the foam was not stable enough and was rapidly destroyed when the liquid was added on the top.

We first checked the effect of flow rate Q . As seen from Figure 2, the ratio $B = V^2/Q$ remains constant within the experimental error. The deviations from this rule come mainly from difficulties in controlling the bubble size and the flow rate. To minimize the fluctuations, each experiment has been repeated five times, and an average of these results has been taken. This procedure allows us to estimate the experimental error on the coefficient B at $\sim 10\%$.

Next, we checked the role of bulk viscosity by adding glycerol to the SDS solutions (see Figure 3). The measured ratios $B = V^2/Q$ are given in Table 1 together with kinematic viscosity (Q is in mL/s and V is in cm/s). The results in Table 1 indicate that B is inversely proportional to the bulk viscosity, as predicted by eq 1.

We also checked the role of surfactant type, and in the case of CTAB, surfactant concentration. In the latter case,

Table 1. Values of $B = V^2/Q$ for SDS Solutions in Water/Glycerol Mixtures of Different Viscosities^a

surfactant	C/CMC	$B = V^2/Q$ (cm ⁻¹ s ⁻¹)	B/B_0	$(\eta/\eta_0)(\rho/\rho_0)$
SDS	10	55 ± 5		
		43.9	1.25	1.28
		32	1.72	1.68
		22.9	2.4	2.32
		15.3	3.6	3.38

^a V is in cm/s and Q is in mL/s; the data correspond to glycerol concentrations of 0, 10, 20, 30 and 40% from top to bottom; the respective values for η and ρ are taken from *Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1994. The subscript zero corresponds to solutions without glycerol.

Table 2. Values of the Ratio $B = V^2/Q$,^a Surface Tension (γ), and Gibbs Elasticity (ϵ) for SDS and CTAB

surfactant	C/CMC	$B = V^2/Q$ (cm ⁻¹ s ⁻¹)	γ (mN/m)	ϵ (mN/m)
SDS	10	55 ± 5	40	200
CTAB	0.6	76 ± 9	47	50
	10	60 ± 6	38	30

the foams formed from solutions below the cmc are stable enough for experimental utilization. The measured ratios $B = V^2/Q$ are given in Table 2 together with surface tension and surface elasticity. As seen from the results in Table 2, B does not change, although the surface tension and the Gibbs elasticity vary from one solution to another. The slight increase of B for CTAB below the cmc seems within experimental error.

It is known that the velocity of drainage of soap films is primarily determined by the Gibbs elasticity ϵ rather than by the surface tension γ .^{5,6} The Gibbs elasticity can be estimated by assuming that above the cmc, the elasticity remains close to its value at the cmc, because surfactant adsorption does not change much above the cmc. To estimate ϵ , we used the following expressions:

$$\epsilon = -\Gamma \partial \gamma / \partial \Gamma \quad \text{and} \quad 2kT\Gamma = -\partial \gamma / \partial \ln c \quad (2)$$

where Γ is the surface concentration and c is the bulk concentration of the surfactant, and kT is the thermal energy. For example, eq 2 gives value of ϵ for SDS at the cmc of ~ 200 mN/m with the surface tension data of Mysels⁷ and Thominet et al.⁸ Similarly, with the surface tension data of Bergeron⁹ and Monroy et al.,¹⁰ we have obtained ϵ values of ~ 50 mN/m at the cmc and ~ 30 mN/m at 0.6 cmc for CTAB.

Despite of the different values of ϵ , the ratios V^2/Q are essentially the same. The fact that the velocity of drainage of foams behaves differently from that of films is not so surprising. In the foam, most of the draining liquid flows through the Plateau borders and only minor amounts of liquid go through the films. The velocity of film drainage depends on the elasticity, because part of the surfactant is driven along the flow into the Plateau borders and, as a result, the film surfaces are depleted of surfactant. The amount of liquid in the film is very small, and there is not enough surfactant inside to replenish the surface. The situation is very different in the Plateau borders where there is plenty of surfactant to ensure that the surfaces are well covered by surfactant at any time. Most probably,

(5) Ivanov, I. B.; Dimitov, D. S. In *Thin Liquid Films, Surfactant Sci. Series Vol. 29*, Marcel Dekker: New York, 1988; p 379.

(6) Sonin, A. A.; Bonfillon, A.; Langevin, D. *J. Colloid Interface Sci.* **1994**, *162*, 323.

(7) Mysels, K. J. *Langmuir* **1986**, *2*, 423.

(8) Thominet, V.; Stenvot, C.; Langevin, D. *J. Colloid Interface Sci.* **1988**, *126*, 54.

(9) Bergeron, V. *Langmuir* **1997**, *13*, 3474.

(10) Monroy, F.; Kahn, J.; Langevin, D. submitted for publication in *Colloids Surf.*

this situation is the reason why the constant A in eq 1 does not depend on ϵ .

In conclusion, we have not seen any significant dependence of the velocity of the liquid front on properties of the surfactant monolayer, such as surface tension and Gibbs elasticity, as predicted by the theory of Weaire et al.² It is possible, however, that the profile of the liquid front could depend on the surface elasticity. Measurements of this effect are in progress with the technique introduced by Hutzler et al.¹¹ It must be stressed that all these measurements are only possible with sufficiently stable foams. In less stable foams, such as DTAB foams, film rupture occurs during the drainage, probably via the dimpling instability of the films known as marginal

regeneration.^{12,13} As a consequence, it is not possible to vary the surfactant layer properties (surface tension, Gibbs elasticity) too much, and the check of the validity of the theory can only be limited. On the other hand, we have verified that the front velocity was inversely proportional to the square root of the bulk viscosity, as predicted by the theory.

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(12) Mysels, K. J.; Shinoda, K.; Frankel, S. *Soap Films*; Pergamon: New York, 1959.

(13) Joye, J. L.; Hirasaki, G. J.; Miller, C. A. *Langmuir* **1994**, *10*, 3174; *ibid.*, *J. Colloid Interface Sci.* **1996**, *177*, 542.

(11) Hutzler, S.; Verbist, G.; Weaire, D.; van der Steen, J. A. *Europhys. Lett.* **1995**, *31*, 497.