Direct measurement of the transversal elasticity modulus of foam films

Anatoly I. Rusanov,* Valery V. Krotov and Aleksandr G. Nekrasov

*Mendeleev Center, St. Petersburg State University, 199034 St. Petersburg, Russian Federation.
Fax: +7 812 428 6939; e-mail: rusanov@AR1047.spb.edu*

The transversal elasticity modulus and the film thickness have been measured in an equilibrium foam by an optical method to verify the theoretical prediction of the behaviour of these properties near the critical micelle concentration.

Earlier,[1–3] we reported experimental evidences for the sharp maxima of foaminess and foam stability near a critical micelle concentration (CMC). The explanation was given only recently[4] by analysing the behaviour of the film elasticity modulus as a function of concentration. The film stability is related to the elasticity modulus for a closed film when the Gibbs elasticity is pronounced in both thick and thin films. Therefore, the explanation was based on the Gibbs elasticity. In addition, the transversal elasticity modulus was introduced[4]

$$E_\perp \equiv -\frac{\mathrm{d}\Pi}{\mathrm{d}\ln h}, \qquad (1)$$

where Π is the disjoining pressure and h is the total film thickness (including the adsorbed layers). The transversal elasticity modulus is a specific characteristic of a thin film with overlapping surface layers and is manifested even in the absence of Gibbs elasticity. Equilibrium foams under gravity is a typical case. Although the film thickness diminishes with increasing height, the temperature and composition of the mother phase (from which foam films originate) is practically the same for all films. These are other conditions than considered earlier,[4] so that the Gibbs elasticity is excluded. The definition of the transversal elasticity modulus for a binary foam (containing water and a surfactant) can be refined in this case as

$$E_\perp \equiv -h\left(\frac{\mathrm{d}\Pi}{\mathrm{d}h}\right)_c, \qquad (2)$$

where c is the surfactant concentration, and we keep in mind that the temperature is also fixed.

The measurement of the disjoining pressure Π in an equilibrium foam is very simple because of the formula[5]

$$\Pi = \rho g H, \qquad (3)$$

where ρ is the surfactant solution density, g is the acceleration of gravity, and H is the height. Actually, it is only necessary to measure the film thickness as a function of height to evaluate the transversal elasticity modulus. Every measurement is carried out at a given surfactant concentration. However, measurements can be repeated for various concentrations to obtain the concentration dependence of the transversal elasticity modulus. The theoretical and experimental investigation of this dependence is the goal of this work.
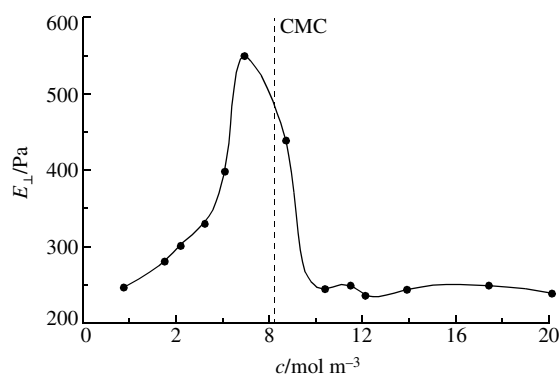
Let us consider a binary film containing a surfactant and a solvent at a fixed temperature. We assume the disjoining pressure to be a function of the concentration c and thickness h: $\Pi = \Pi(c,h)$. By differentiating both of the sides of equation (2) with respect to concentration at a fixed disjoining pressure, we have

$$\left(\frac{\mathrm{d}E_\perp}{\mathrm{d}c}\right)_\Pi = -\left(\frac{\mathrm{d}h}{\mathrm{d}c}\right)_\Pi \left(\frac{\mathrm{d}\Pi}{\mathrm{d}h}\right)_c = \left(\frac{\mathrm{d}\Pi}{\mathrm{d}c}\right)_h. \qquad (4)$$

This remarkable relationship shows that the concentration dependence of the transversal elasticity modulus of a film with a fixed disjoining pressure coincides with the concentration dependence of the disjoining pressure of the film with a fixed thickness. The latter dependence is expected to pass through a maximum of the disjoining pressure in the case of an ionic surfactant. There are two opposing tendencies in this case, the growth of charge and the decrease of the surface layer thickness and of the surface layer overlapping with increasing concentration, the former enhances and the latter weakens the disjoining pressure. This can be illustrated by the following equation for the disjoining pressure of a film of a solution of a symmetrical electrolyte:[6]

$$\Pi = 64ckT\Phi\exp(-\kappa h/2) - 4A_{\mathrm{H}}/27\pi h^3, \qquad (5)$$

where $\Phi = \tanh(\psi ze/2kT)$, ψ is the surface potential, ze is the ionic charge, κ is the reciprocal Debye length, A_{H} is the Hamaker constant, and kT is of usual meaning. According to equation (5), the disjoining pressure depends on the concentration as $c\exp(-c^{1/2})$, and this function has a maximum. The effect is enhanced in the presence of the CMC. Below the CMC, almost the whole amount of a surfactant added is incorporated into the surface layers of a film. By contrast, the surfactant mainly enters the interior of the film above the CMC, which creates the screening effect and leads to a steeper decrease of the disjoining pressure after the maximum. Similar speculations can be found in the literature.[7] Accounting for equation (4), we can say that the behaviour of the transversal elasticity modulus should be the same. In other words, we expect the existence of a maximum of the transversal elasticity modulus close to the CMC.
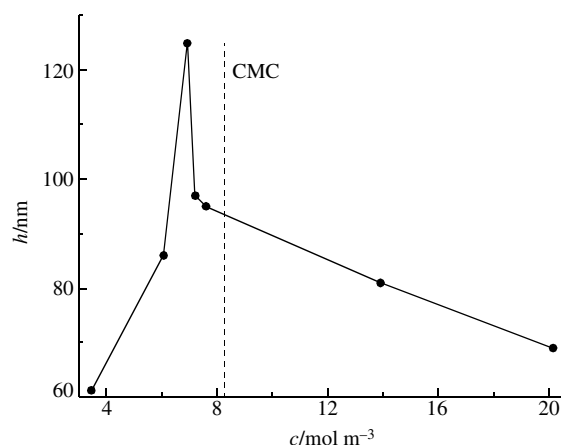

Figure 1 The dependence of the transversal elasticity modulus of foam films on the concentration of sodium dodecyl sulfate.

Figure 2 The dependence of the foam film thickness on the concentration of sodium dodecyl sulfate.

We consider how the film thickness depends on the surfactant concentration if the disjoining pressure of the film is fixed. The latter condition is expressed as

$$\mathrm{d}\Pi = \left(\frac{\mathrm{d}\Pi}{\mathrm{d}h}\right)_c \mathrm{d}h + \left(\frac{\mathrm{d}\Pi}{\mathrm{d}c}\right)_h \mathrm{d}c = 0. \tag{6}$$

From the equation (6) we obtain

$$\left(\frac{\mathrm{d}h}{\mathrm{d}c}\right)_\Pi = -\left(\frac{\mathrm{d}\Pi}{\mathrm{d}c}\right)_h / \left(\frac{\mathrm{d}\Pi}{\mathrm{d}h}\right)_c. \tag{7}$$

Since the derivative $\partial\Pi/\partial h$ is negative by the stability condition of a thin film, it follows from equation (7) that extremes of the disjoining pressure and of the film thickness should occur simultaneously at the same concentration. As we know that the transversal elasticity modulus duplicates the behaviour of the disjoining pressure [see equation (4)], we can also say that the extremes of the transversal elasticity modulus and of the film thickness should coincide in concentration.

The experiments were carried out with an aqueous solution of sodium dodecyl sulfate (Fluka, > 99% purity). The foam with a cell radius of about 1 mm was produced by blowing air through a porous membrane. The foam film thickness was measured optically as described elsewhere.[2] To evaluate the transversal elasticity modulus, the film thickness was measured in the foam column at heights $H_1 = 50$ mm and $H_2 = 79$ mm, and the following equation was used:

$$E_\perp = \frac{\rho g(H_2 - H_1)[h(H_1) + h(H_2)]}{2[h(H_1) - h(H_2)]}. \tag{8}$$

The concentration dependence of the film thickness was determined at a height of 60 mm.

The results are presented in Figures 1 and 2, where well pronounced maxima can be seen near the CMC, as predicted by the above theory. It is of interest that the maxima are located approximately at the same place on the concentration axis as the maxima of foaminess and foam stability,[1–3] although the mechanism of elasticity is different for closed and completely open (as in this work) films. These similar locations of the maxima are explained by the leading role of the CMC in both the cases.

References

1 V. V. Krotov, A. G. Nekrasov and A. I. Rusanov, *Mendeleev Commun.*, 1996, 178.
2 V. V. Krotov, A. G. Nekrasov and A. I. Rusanov, *Mendeleev Commun.*, 1996, 220.
3 A. I. Rusanov, V. V. Krotov and A. G. Nekrasov, *J. Colloid Interface Sci.*, 1998, **206**, 392.
4 A. I. Rusanov and V. V. Krotov, *Mendeleev Commun.*, 2004, 16.
5 V. V. Krotov and A. I. Rusanov, *Physicochemical Hydrodynamics of Capillary Systems*, Imperial College Press, London, 1999, p. 372.
6 D. O. Shah, N. F. Djabbarah and D. T. Wasan, *Colloid Polym. Sci.*, 1978, **256**, 1001.
7 D. Exerova and P. Kruglyakov, *Foam and Foam Films*, Elsevier, Amsterdam, 1998.