# Foam Stability: The Effect of Surface Rheological Properties on the Lamella Rupture

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Liquid foams are colloids in which a large volume of a gas is dispersed in a small volume of a liquid. Foams consist of bubbles, each of which is a lamella that encloses the gas. A lamella consists of two surface layers with a liquid core between them. The surface active material is preferentially adsorbed at the surface, and the composition and properties of the liquid core are similar to those of the bulk solution from which the foam has been generated. The rupture of a foam film or lamella is preceded by its thinning, due to drainage of the liquid core under the influence of gravity and capillary suction. The rate and extent of drainage, however, have been shown to be governed by a complex interplay among the properties of the surface and of the bulk.

Recently, reliable techniques for determination of surface rheological properties such as surface viscosity and elasticity have been developed. Consequently, it is possible to measure accurately the dynamic properties of adsorbed surfactant systems. Hence, the purpose of this study, which is continuing (Rao et al., 1982; Manev et al., 1982), is to assess the influence of surface rheological properties in the stabilization of thin liquid surfactant films or lamellae associated with aqueous foam systems. In the present note we establish a direct relationship between the lamella rupture time and the trends in surface viscosity and elasticity, which, in turn are dependent on the molecular packing and molecular interactions at the gas-liquid surface.

Aqueous solutions of sodium lauryl sulfate and of sodium lauryl sulfate-lauryl alcohol were selected for the study of the single and the mixed surfactant systems, respectively. The procedure for purifying these surfactants is given elsewhere (Djabbarah, 1978). A procedure similar to that of Brown et al. (1953) was employed in preparing sodium lauryl sulfate-lauryl alcohol solutions. They were prepared at three constant mass ratios of sodium lauryl sulfate-lauryl alcohol, K (100, 250, and 500). At each value of K, the bulk concentration of sodium lauryl sulfate was varied from 3.58 g/L to 0.10 g/L.

Surface tension, surface viscosity, and surface elasticity were measured using the procedures described by Djabbarah and Wasan (1982a, 1982b). Surface excess concentrations were determined using the single bubble foaming apparatus, originally conceived by Bikerman (1973).

The same apparatus that was used for the determination of

of the rupture time of foam lamellae (Djabbarah and Wasan, 1982a). Placed in the triple-neck flask was 500 mL of the solution under study. Bubbles were generated in the flask by means of a high purity-prehumidified nitrogen gas flowing into the solution through a 0.4 cm-dia. glass tubing. A typical run began by adjusting the gas flow rate of 20 cm³/min so that the bubbles generated rose in the glass tubing as single lamella. A few minutes were allowed for the flow to become steady and the spacing between the rising bubbles up the tube to become equal. Subsequently, a bubble was picked for the stability study just as it entered the tube, and the timer was turned on. The flow of nitrogen was turned off so that the bubble came to a standstill around the middle of the tube. The time of bubble rupture was recorded. This procedure was repeated ten times for each system.

surface excess concentration was also utilized in the determination

It should be pointed out that since the bubble received fluid from lamellae draining above it, we measured the rupture time of a given lamella at the top, middle, and bottom of the tube and found negligible effects concerning the location of the lamella rupture on its rupture time. We also monitored the direction of lamella rupture (i.e., whether the rupture of a single lamella began with lamellae at the top and then proceeded downward, or the other way around). We found no preferred direction for the lamella rupture. The spacing of the lamella depended on the gas flow rate, the surfactant system, and concentration of surfactant.

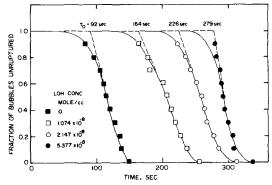


Figure 1. Distribution curve for fraction of bubbles unruptured for solutions containing  $3.468 \times 10^{-6}$  mol/cm³ sodium lauryl sulfate at different concentrations of lauryl alcohol.

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TABLE I. DRAINAGE TIME, COLLAPSE TIME, AND SURFACE PROPERTIES OF LAMELLAE PRODUCED BY AQUEOUS SOLUTIONS OF SLS-LOH

SLS Conc.,	Purified SLS				SLS-LOH, K =500				SLS-KOH, K = 250				SLS-LOH, $K = 100$			
mol/	$\sigma^{\circ}$	E°	$ au_D$	$\tau_c$	σ°	Ε°	$ au_D$	$\tau_c$	$\sigma^{\circ}$	E°	$\tau_D$	$\tau_c$	$\sigma^{\circ}$	E°	$\tau_D$	$\tau_c$
cm <sup>3</sup> 10 <sup>6</sup>	mN/m		S		mN/m		s		mN/m		S		mN/m		S.	
0.693	67.8	4.6	9.3	5.5	53.6	6.8	42.2	18.5	50.5	10.1	106.1	28.5	45.5	9.5	171.2	7.5
1.732	62.8	11.9	28.2	14.4	46.8	14.3	95.6	24.6	42.4	19.5	137.9	28.3	37.8	16.8	212.2	12.3
2.600	56.4	17.0	63.5	28.2	41.7	21.7	162.8	28.2	37.3	26.1	218.0	28.3	33.4	20.8	269.6	8.9
3.468	52.9	24.4	92.0	13.0	38.4	31.9	164.2	41.6	34.1	31.8	226.3	32.2	28.6	20.9	279.2	14.2
5.208	45.6	29.2	128.2	18.5	37.1	40.7	217.4	21.3	30.5	35.8	258.3	41.1	29.4	6.8	270.4	21.6
6.092	_	44.8	158.6	14.5			224.7	10.5			261.0	38.5			280.0	18.2
6.935	41.1	_	_	_	33.2	32.7		_	31.3		_		29.9	5.6		_
6.976		67.5	175.1	16.3	-		223.8	36.6	_	20.7	242.3	21.3			270.3	22.6
8.669	39.3	17.8	183.2	16.1	33.8	20.5	219.7	38.2	32.2	15.2	261.1	16.6	30.0	4.8	270.2	25

Since the rupture time was not identical for all the lamellae that were generated from the same solution, the data were treated in a manner similar to that of Cockbain and McRoberts (1953). A time distribution curve of the fraction of bubbles unruptured was prepared for each system, as shown in Figure 1. The figure indicates that the rupture time of the lamella undergoes two stages. The first stage is one of the film thinning due to the drainage of the liquid core and is hydrodynamic in nature. The second stage is one in which the actual rupture takes place and is probably due to random molecular collisions. Drainage time is determined by the intersection of the extrapolated straight portion of the fraction of bubbles unruptured vs. time curve with the 1.0 fractioned ordinate. Both the drainage and collapse times are shown in Table 1. The rupture time of the lamella is the sum of the drainage and collapse times.

Table 1 clearly indicates the effect of the presence of lauryl alcohol on the total rupture time of a lamella. At a sodium lauryl sulfate concentration of  $3.468 \times 10^{-6}$  mol/cm³ and in the absence of lauryl alcohol ( $K = \infty$ ), the rupture time of the lamella is 105 s, while the drainage time is 92 s. When a small amount of lauryl alcohol is present  $(1.074 \times 10^{-8} \text{ mol/cm}^3; K = 500)$ , rupture time increases to 205 s, while the drainage time is 164 s. When the lauryl alcohol concentration is increased to  $2.147 \times 10^{-8} \text{ mol/cm}^3$  (K = 250), rupture time increases to 258 s and drainage time increases to 226 s. A further increase in the lauryl alcohol concentration to  $5.377 \times 10^{-8} \text{ mol/cm}^3$  (K = 100) causes the rupture and drainage

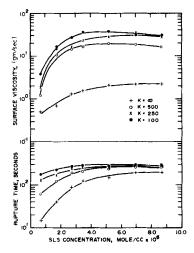


Figure 2. Surface viscosity and rupture time vs. bulk concentration for aqueous solutions of sodium lauryl sulfate-lauryl alcohol, K = conc. of SLS/conc. of LOH.

times to rise to 293 and 279 s, respectively. Similar trends were observed at other concentrations of sodium lauryl sulfate and lauryl alcohol.

The preceding observations lead one to conclude that lauryl alcohol prolongs the lifetime of the films by prolonging the time for drainage, thus suggesting that luryl alcohol influences rupture time through its effect on the surface rheological properties of the films. In fact, a plot of surface viscosity versus the bulk concentration of sodium lauryl sulfate at several relative concentrations of lauryl alcohol (Figure 2) indicates that surface viscosity increases as the concentration of lauryl alcohol is increased (i.e., as K decreases). Furthermore, this increase occurs in a manner that is consistent with the increase in rupture time (Figure 2).

The knowledge of surface tension and surface excess concentration as function of bulk concentration permitted the determination of Gibbs elasticity (Djabbarah and Wasan, 1982b) defined as

$$E^{\circ} = -\Gamma^{\circ} \frac{d\sigma^{\circ}}{d\Gamma^{\circ}}$$

where  $\Gamma^\circ$  is the equilibrium surface excess concentration, and  $\sigma^\circ$  is the equilibrium surface tension. The values of  $E^\circ$  as a function of SLS bulk concentration with and without alcohol are tabulated in Table 1. It is seen that the rupture time, which is the sum of the drainage and collapse times, increases as the adsorbed surfactant film becomes more elastic. The concentration corresponding to the maximum rupture time is very close to the critical micelle concentration (CMC). Above CMC, the elasticity decreases as the concentration increases, as does the rupture time. These data clearly show that surface elasticity plays a major role in stabilizing foam lamellae or films.

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## NOTATION

CMC = critical micelle concentration

 $E^{\circ}$  = Gibbs elasticity

K = concentration ratio (ratio of concentration of sodium

lauryl sulfate to lauryl alcohol concentration)

LOH = lauryl alcohol N = Newton, force

SLS = sodium lauryl sulfate

## **Greek Letters**

 $\Gamma^{\circ}$  = equilibrium surface excess concentration

 $\sigma^{\circ}$  = equilibrium surface tension  $\tau_c$  = lamella collapse time

 $\tau_D$  = lamella drainage time

### LITERATURE CITED

Bikerman, J. J., Foams, Springer-Verlag, New York (1973). Brown, A. G., W. C. Thuman, and J. W. McBain, "Surface Viscosity of Detergent Solutions as a Factor in Foam Stability," J. Colloid Sci., 8, 491 (1953).

Cockbain, E. G., and T. S. McRoberts, "The Stability of Elementary Emulsion Drops and Emulsions," *J. Colloid Sci.*, 8, 440 (1953). Djabbarah, N. F., "Interrelationships Among Surface Composition, Surface Rheological Properties and Foam Stability," Ph.D. Thesis, Illinois Inst. of Technology (1978).

Djabbarah, N. F., and D. T. Wasan, "The Relationship Between Surface Viscosity and Surface Composition of Adsorbed Surfactant Films", *Ind. Eng. Chem. Fund.*, **21**, 27 (1982a).

Films", Ind. Eng. Chem. Fund., 21, 27 (1982a).

——, "Dilatational Viscoelastic Properties of Fluid Interfaces.
Part III. Mixed Surfactant Systems," Chem. Eng. Sci., 37, 175 (1982b).

Manev, E. D., S. V. Sazdanov, A. A. Rao, and D. T. Wasan, "Foam Stability—The Effect of a Liquid Crystalline Phase on the Dynamic Behavior of Foam Films," *J. Dispersion Sci. Technol.*, 3, 435 (1982).

Rao., A. A., D. T. Wasan, and E. D. Manev, "Foam Stability-Effect of Surfactant Composition on the Drainage of Microscopic Aqueous Films," *Chem. Eng. Commun.*, 15, 82 (1982).

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