

# ✿Foaming of Nonionic Surfactant Solutions: Effect of Surfactant Concentration and Temperature

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**Foaming of solutions of the nonionic surfactant, octoxynol 9, was investigated in the concentration range of 0.010 to 5.00% and in the temperature range of 7-37 C, well below the cloud point of 65 C, by measuring the height and stability of foams generated by pouring thin streams of surfactant solutions into a glass column. All foams were fast-thinning. Their height increased monotonically with surfactant concentration. The rate of change of foam height with log surfactant concentration underwent no change at the CMC of 0.018%, but was four times lower above 0.146% than below 0.146%. Foams at lower temperatures generally thinned somewhat more slowly and were stronger or more cohesive and more stable than foams generated at higher temperatures by surfactant solutions of comparable concentrations. Oxidative degradation reduced foam height somewhat. Octoxynol 9 and sodium lauryl sulfate, rated as a good foamer, produced foams of comparable volume and stability.**

Most published foaming studies deal with anionic surfactants (1, 2). Nonionic surfactants generally are rated as low to moderate foamers (3, 4), and their foaming properties have not been investigated extensively. In particular, most foaming studies of nonionic surfactants have been conducted at one or two fixed concentrations: The effect of concentration has rarely been examined systematically.

In order to extend our studies of the effect of electrolytes on nonionic surfactant solutions to foaming, it first became necessary to understand the foaming of the surfactant without added electrolytes. This is the subject of the present study.

## EXPERIMENTAL

**Materials.** The surfactant octoxynol 9 N.F. (Triton X-100 of Rohm & Haas Co., Philadelphia, Pennsylvania) is a branched octylphenol with an average of 9-10 ethylene oxide units. It is a viscous, anhydrous liquid with an HLB of 13.4. The cloud points of the three batches used were 64, 65 and 65.5 C, respectively, at either 1.00 or 2.00%.

One sodium lauryl sulfate sample was U.S.P. grade and old. Its bottle had been opened repeatedly. The other sample (Kodak 5967) was fresh and in a sealed bottle. The water was double distilled. Surfactant concentrations are based on the amount of water present: % (w/w) represents g octoxynol/100 g water. All nonionic surfactant solutions were held for  $\geq 48$  hr at the foaming temperature before the measurements were made.

**Methods.** Preliminary experiments indicated that the height and stability of foams generated by pouring a stream of the solutions from a fixed height into a cylinder gave reproducible results that demonstrat-

ed differences among different types of electrolytes. Therefore, the Ross-Miles test (5,6) was used, with the following modifications. The jacketed glass tube was a modular chromatography column of 2.5 cm i.d. After a 50-ml aliquot at the desired temperature was charged into a separatory funnel that was fastened coaxially to the top of the glass tube, the stopcock was fully opened so that the liquid issued as a continuous stream. When the funnel was almost empty and the jet began to break up into drops, the stopcock was closed.

Efflux times were  $18 \pm 1$  sec. A variation of two sec did not affect the foam height. Larger liquid volumes required excessive efflux times, during which foam was destroyed as well as generated, which increased the relative standard deviation of the foam height. Smaller liquid volumes generated proportionally less foam: 30-ml volumes of 2.00% octoxynol produced initial foam heights of  $7.9 \pm 0.2$  cm, compared with  $12.7 \pm 0.3$  cm for 50 ml.

Liquid draining rapidly from the freshly generated foam column caused the boundary between liquid and foam to rise so fast that the initial upwards motion could be detected with the naked eye. This rapid initial rise of the boundary lasted up to  $\sim 30$  sec, depending on the height of the foam. As soon as the boundary ceased to rise visibly, the initial foam height was measured. At that point, the distance between the tip of the separatory funnel and the liquid-foam boundary was 61 cm, the smallest height through which the jet impinged on the liquid surface to generate the foam.

Subsequent measurements of foam height were taken every odd minute, starting from the time the stopcock was closed and continuing for at least 13 min. Frequently, foams underwent sudden partial breakdown during this period, such as the sudden collapse of a portion of the column or the appearance of a hole. When this occurred, the foam height measurements were discontinued. The time at which the first gross damage appeared was noted. Partial collapse and hole formation usually occurred near the top of the foam column.

At the end of the measurements, the aged foam columns were removed through the bottom fitting of the glass tube by suction, while their mechanical strength and cohesiveness were rated qualitatively.

## RESULTS AND DISCUSSION

Table 1 lists average values for the initial foam height and for the foam height after five min, their standard deviations, and the number of measurements on which these values are based, as a function of surfactant concentration and temperature. Foam height values after five min are listed only for intact columns. Where the number of measurements for the initial foam height exceeds that for the foam height after five min, the difference represents the number of foam columns that underwent a sudden partial col-

## FOAMING OF NONIONIC SURFACTANT SOLUTIONS

**TABLE 1**  
**Foaming of Surfactant Solutions**

No.	Octoxynol 9 conc'n. [% (w/w)]	Temp. (°C)	Foam height (cm) <sup>a</sup>		Remarks <sup>b</sup>
			initial	after 5 min	
1	0.010	25	2.48 ± 0.11 (5)	2.30 ± 0.16 (5)	
2	0.015	25	3.81 ± 0.10 (4)	3.55 ± 0.14 (4)	
3	0.020	25	4.50 ± 0.31 (6)	4.22 ± 0.31 (6)	
4	0.050	25	8.11 ± 0.32 (9)	7.79 ± 0.25 (9)	1/9 HF at 7 min
5	0.100	25	9.96 ± 0.27 (11)	9.57 ± 0.25 (11)	
6	0.126	25	10.10 ± 0.08 (7)	9.66 ± 0.08 (7)	2/7 PC at 9 - 10 min
7	0.200	25	11.08 ± 0.26 (5)	10.48 ± 0.29 (5)	
8	0.64	25	12.36 ± 0.17 (11)	11.88 ± 0.13 (11)	1/11 PC at 12 min
9	0.64 <sup>c</sup>	25	11.75 ± 0.16 (6)	11.25 ± 0.19 (6)	2/6 PC in ≤ 9 min <sup>d</sup>
10	2.00	25	12.73 ± 0.32 (19)	12.23 ± 0.43 (15)	4/19 PC or HF in ≤ 10 min <sup>e</sup>
11	5.00	25	13.60 ± 0.26 (6)	12.67 ± 0.32 (6)	
12	2.00	15	12.34 ± 0.21 (5)	11.60 ± 0.23 (5)	
13	0.100	7	8.69 ± 0.20 (7)	8.14 ± 0.33 (7)	
14	2.00	7	11.76 ± 0.11 (7)	11.21 ± 0.11 (7)	
15	0.050	36	7.98 ± 0.17 (8)	7.70 ± 0.18 (6)	3/8 PC in ≤ 9 min
16	0.100	36	10.18 ± 0.24 (6)	- (0)	6/6 PC in ≤ 3 min
17	0.500	36	12.10 ± 0.34 (10)	11.8 ± 0.57 (2)	8/10 PC in ≤ 4 min
18	2.00	36	12.80 ± 0.36 (9)	12.34 ± 0.34 (5)	4/9 PC in ≤ 3 min
	<b>Sodium lauryl sulfate conc'n. [% (w/w)]</b>				
19	1.00 <sup>f</sup>	25	11.48 ± 0.13 (5)	11.02 ± 0.15 (5)	
20	1.00 <sup>g</sup>	25	12.52 ± 0.13 (5)	12.10 ± 0.19 (5)	

<sup>a</sup>Mean ± standard deviation; number of measurements between parentheses.

<sup>b</sup>Absence of remarks indicates that all foam columns remained intact within the observation period of 13 min.

<sup>c</sup>Prolonged exposure to light and air.

<sup>d</sup>Partial collapse of 2 columns from a total of 6 studied within 9 min.

<sup>e</sup>Partial collapse or hole formation for 4 of 19 columns within 10 min.

<sup>f</sup>Fresh sample.

<sup>g</sup>Old sample.

lapse or developed a hole within five min. Information on foam stability is contained in the last column of Table 1.

The ratio of initial foam height to foam height after five min ranged from 1.04 to 1.08 and showed no trend with surfactant concentration or temperature. This value agrees with the ratio of 1.08 reported for 0.10% solutions of various octoxynols at 20 C (7).

**Effect of surfactant concentration.** As expected, the concentration of octoxynol affected the foam properties significantly. Foams 1-6, generated by solutions containing between 0.010 and 0.126% at 25 C, thinned very fast. Within seven to nine min, the top 60% of their foam columns were gossamer thin and transparent. Foams 8, 10 and 11, generated by 0.64-5.00% solutions, while still fast draining (1, 2), did not thin as fast.

Because the critical micelle concentration (CMC) of octoxynol 9 at 25 C is  $2.9 \times 10^{-4}$  mol/l or 0.018%, Foams 1 and 2 were generated by solutions below the CMC and Foam 3 by one above it. The thinning rate and stability of the three foams were similar. However, Solutions 1 and 2 wetted the wall of the glass tube poorly and beaded, while Solution 3 wetted it with a uniform film.

Foam heights increased monotonically with octoxy-

nol concentration. However, for the three parameters whose data cover a wide enough concentration range, namely, initial heights at 25 and 36 C and 5-min height at 25 C, semilogarithmic plots consist of two linear segments which intersect at 0.146% octoxynol (Fig. 1). For the initial foam height (FH) at 25 C, the two regression lines are:

$$\text{FH} = 17.05 + 7.264 \log (\% \text{ octoxynol}) \quad [1]$$

between 0.010 and 0.13% (Foams 1 - 6) ( $r = 0.995$ ), and

$$\text{FH} = 12.40 + 1.691 \log (\% \text{ octoxynol}) \quad [2]$$

between 0.20 and 5.00% (Foams 7, 8, 10, 11) ( $r = 0.979$ ), where  $r$  is the correlation coefficient.

The surfactant concentration at which the abrupt decrease in slope of plots of foam height versus log octoxynol concentration occurred, namely, 0.146%, is eight times larger than the CMC. However, accumulation of adsorbed surfactant at the extensive air-water interface may have reduced the bulk concentration to the level of the CMC. To examine this possibility, the size of cells of Foam 6 were measured. The mean volume-surface height of 131 foam polyhedra was 0.117 cm. Most cells were pentagonal dodecahedra (2), whose mean edge length was  $L = 0.117 \text{ cm} / 1.55 = 0.0755 \text{ cm}$ .

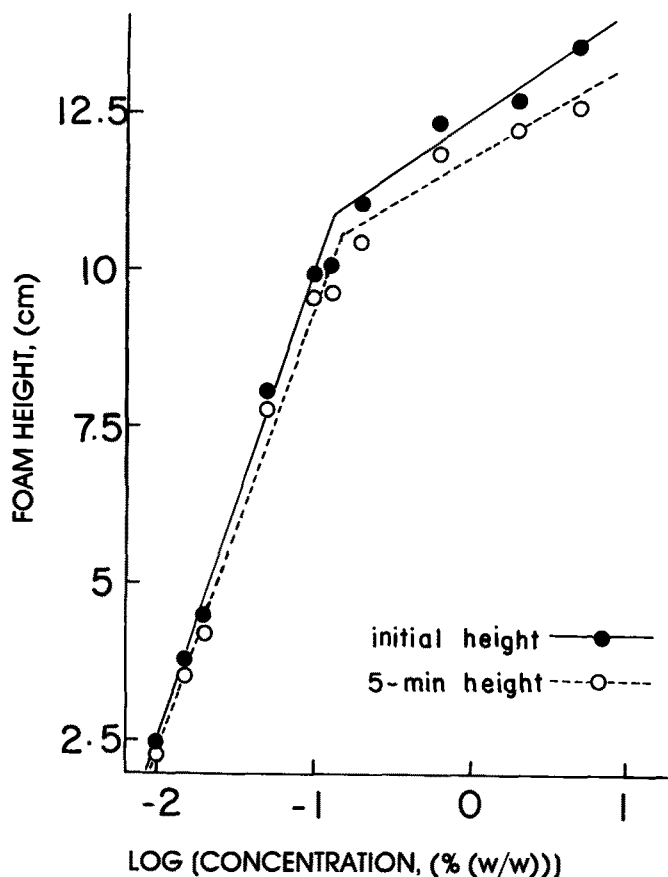


FIG. 1. Foam height of octoxynol 9 solutions as a function of the logarithm of concentration at 25 C.

Because the volume of a pentagonal dodecahedron is  $7.66312 \text{ L}^3$  and the area of its surface is  $20.64578 \text{ L}^2$ , the specific surface area of the foam is  $20.64578 \text{ L}^2/7.66312 \text{ L}^3 = 2.694/\text{L cm}^2/\text{cm}^3$ . The initial volume of the column of Foam 6 was  $\pi R^2 FH = \pi (1.25 \text{ cm})^2 (10.2 \text{ cm}) = 50.0 \text{ cm}^3$ , making the surface area of the foam  $1,800 \text{ cm}^2$ . Because the foam lamellas are two-sided, the total surface area of the foam column was  $3,600 \text{ cm}^2$ .

The area per molecule of octoxynol 9 adsorbed at the air-water interface at saturation adsorption, i.e., in a close-packed monolayer, was calculated from the linear portion of Figure 2 in reference (8). Its regression line, based on the data points of the graph, is:

$$\gamma_{\text{AW}} = 4.856 - 6.468 \ln c \quad [3]$$

with the surface tension  $\gamma_{\text{AW}}$  in dyne/cm and  $c$  in percent. Using the slope,  $d\gamma_{\text{AW}}/d \ln c = -6.468 \text{ erg}/\text{cm}^2$  in the Gibbs adsorption equation gives an area of  $63.6 \text{ \AA}^2$  per molecule adsorbed octoxynol 9 at 25 C. This value corresponds to  $1.63 \times 10^{-7} \text{ g}$  adsorbed octoxynol 9/ $\text{cm}^2$  and, for  $3,600 \text{ cm}^2$ , to  $5.87 \times 10^{-4} \text{ g}$  adsorbed octoxynol. Thus, less than one mg octoxynol has accumulated in a duplex film of foam, compared to the 63 mg octoxynol present in  $50 \text{ cm}^3$  of a 0.126% solution.

The value of  $3,600 \text{ cm}^2$  is a low estimate because it is based on regular dodecahedra. Distortion would in-

crease the surface area, but less than double it. Furthermore, the foam lamellas could contain several monolayers instead of two. Assuming a surface area of  $7,200 \text{ cm}^2$  for the foam and an interfacial film with a thickness of eight monolayers instead of two as upper limits would result in a maximum of five mg octoxynol in the foam interface, leaving  $63 - 5 = 58 \text{ mg}$  in  $50 \text{ cm}^3$ . The bulk octoxynol concentration would still be over six times the CMC. Thus, the increase in slope in Figure 1 occurs at a low multiple of the CMC and is not related to it.

In one of the few foaming studies of nonionic surfactants covering a range of concentrations, foam volume and foam stability of polyoxyethylated tridecanols seemed to reach a plateau in their semilogarithmic plots at concentrations of 0.05-0.15%, corresponding to  $\sim 10$  times the CMC (9). In Figure 1, there is merely a four-fold decrease in slope at eight times the CMC.

*Effect of temperature.* As nonionic surfactant solutions are heated above the cloud point, their ability to foam drops precipitously (10, 11), not only because the surfactant loses its solubility but also because the liquid, surfactant-rich phase that separates acts as an antifoaming agent (4, 12). The present studies were conducted between 7 and 36 C, so that even the highest temperature is 29 C below the cloud point and free of incipient phase separation effects.

The rate of thinning of Foam 12 (2.00% octoxynol at 15 C) was not noticeably lower than that of Foam 10 (2.00% octoxynol at 25 C), but foams at 7 C thinned more slowly than foams of comparable concentration at 25 C. The top half of foam columns at 7 C remained considerably more opaque than the top half of the corresponding 25 C columns after comparable observation times. Foam 14 required about 30 min to turn as transparent as Foam 10 turned in seven to nine min.

The greater strength of the foam columns at 7 C was demonstrated by the fact that they descended intact when the chromatography tube was emptied by suction at the end of the observation periods. Aged foam columns at room temperature frequently ruptured during emptying.

Foams generated at 36 C thinned and became transparent faster than foams at 25 C. Many columns at 36 C underwent partial collapse within five min, and those which remained intact turned noticeably coarser. The poor foam stability at 36 C is illustrated by the fact that none of the six foam columns generated by 0.10% octoxynol (Foam 16) survived intact for five min at 36 C, whereas all of the 11 columns generated at 25 C (Foam 5) did.

Neither the initial foam heights nor the five-min heights of foams generated by surfactant solutions of comparable concentrations at 25 and 36 C were significantly different, because the average values differ by less than one standard deviation (Table 1). Moreover, at 0.050% octoxynol, the initial and five-min foam heights at 25 C were greater, while at the other three concentrations the corresponding 36 C values were greater. The values of 11.89 [Equation (2)] and 11.43 cm, interpolated for the initial and five-min foam heights of a 0.50% octoxynol solution at 25 C, are not significantly different from the 36 C values of  $12.10 \pm 0.34$  and  $11.8 \pm 0.6 \text{ cm}$ , respectively, of Foam 17.

The foregoing confirms the well-known observation (2) that foam height and foam stability are not necessarily related.

According to t-tests, the differences between the initial heights of Foams 10 (2.00% octoxynol at 25 C) and 12 (2.00% octoxynol at 15 C) are statistically significant, as are the differences between their five-min heights. The differences between the heights of the 7 C foams and the corresponding 25 C foams are also significant. Application of the F-test to foam heights measured at 7, 15, 25 and 36 C for solutions of equal surfactant concentrations shows that the overall trend of increasing foam height with increasing temperature is significant.

The modest increase in foam height and/or the reduction in foam stability caused by the 29 C increase in temperature have been corroborated by all studies which covered a wide enough temperature range sufficiently below the cloud point (7, 11, 12). Both effects are ascribed to the more extensive hydration of the polyoxyethylene moiety of the nonionic surfactant at the lower temperatures. More extensive hydration increases the radius of gyration of that moiety and, hence, the viscosity of the surfactant solutions, and decreases the rate of drainage of the foams, increasing their stability. Less extensive hydration at higher temperatures, by reducing the solubility of the surfactant in water, renders it more surface-active and hence increases the foam height.

*Effect of surfactant degradation.* The many ether groups promote oxidative degradation of nonionic surfactants, producing decreases in surface tension, CMC and cloud point (13). Solution 9 was exposed to sunlight in a half-filled volumetric flask lightly closed with a cotton wad for six weeks, followed by two weeks storage in darkness at 25 C before the foaming measurements. This procedure reduced its cloud point from 65 to less than 50 C and produced small but statistically significant drops in initial and five-min foam heights compared to the fresh, unexposed solution (Foam 8). The thinning rates of Foams 8 and 9 were comparable, but the latter foam was somewhat less stable.

*Comparison of foaming of the nonionic and an anionic surfactant.* Even though nonionic surfactants are generally rated as low to moderate foamers (3, 4), octoxynol 9 solutions produced voluminous and stable foams. This observation prompted us to compare

its foaming properties with those of a surfactant rated as a good foamer, namely, sodium lauryl sulfate.

The aged and presumably more extensively hydrolyzed sodium lauryl sulfate sample (Foam 20) produced a 9-10% greater foam height than the fresh and less hydrolyzed sample (Foam 19), presumably owing to complex formation between the hydrolysis product, lauryl alcohol, and the surfactant. The interpolated initial and five-min foam heights of a 1.00% octoxynol solution, 12.40 and 11.91 cm, are practically identical with the values of the aged sample. Being equivalent to sodium lauryl sulfate, octoxynol 9 must be rated a good foamer.

Other nonionic surfactants fall into the same category: Comparable foam volumes and foam stability were reported for sodium dodecylbenzene sulfonate and nonionic surfactants of optimum polyoxyethylene chain length. These foams were generated by a plunger consisting of a perforated disk (9).

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