Effect of Electrolytes on Foaming of Nonionic Surfactant Solutions

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The effect of electrolytes and other additives on the foaming of solutions of the nonionic surfactant octoxynol 9 (Triton X-100) was investigated and correlated with their effect on the cloud point. Foams were generated by pouring solutions as a thin stream into a vertical tube. The height of the generally fast-draining foam columns was measured as a function of time, and their stability was rated according to the damage sustained within 13 min. The surfactant concentrations used, 0.050, 0.100 and 2.00%, were above the critical micelle concentration. Increasing concentrations increased foam height but not foam stability.

The electrolytes NaCl and Na_2SO_4 salted the surfactant out. They reduced its cloud point in proportion to their concentration. They also reduced the foam height, albeit to a lesser extent than the cloud point, but hardly reduced the foam stability below the cloud point.

Electrolytes which salted the surfactant in, raising its cloud point by complexation of their cations with the ether oxygens of the surfactant, namely HCl, H_2SO_4 and $Mg(NO_3)_2$, produced no major changes in either foam height or foam stability. The exception was $Al(NO_3)_3$, which reduced the foam height by increasing the viscosity of the solutions. Urea and NaSCN, which raised the cloud point by breaking the structure of water, and to a lesser extent citric acid, reduced the foam stability but produced no major changes in foam height.

Heating the solutions below their cloud point reduced the stability of all foams, especially of those which were the least stable at the lower temperatures. When the cloud point was exceeded by 5 C through a combination of added NaCl and heating, foam height and foam stability decreased significantly. At 10 C above the cloud point, the foam height was reduced to 1/6 of that at 12 C below the cloud point, but the former foam was slow draining and rather stable.

Previous studies dealt with the effect of electrolytes on the following properties of polyoxyethylated nonionic surfactants: Their solubility, limited by the cloud point on heating (1-4) and, for some, also by the Krafft point on cooling (5); the critical micelle concentration (CMC) and the surface properties of their aqueous solutions (6), and the stability of emulsions (7) and suspensions (8) prepared with these surfactants. The present study deals with the effect of electrolytes on the foaming properties of solutions of a polyoxyethylated surfactant.

Salting-in and salting-out electrolytes exerted only minor effects on the stability of oil-in-water emulsions prepared with the nonionic surfactant, octoxynol 9, provided that the surfactant was insoluble in the oil phase (7). This unexpected observation prompted the present investigation, designed to gain information on the effect of electrolytes on interfacial octoxynol films without the oil phase, i.e., foams.

Both foams and hexadecane-water emulsions (7) have multilayer interfacial surfactant films. In both systems, the polyoxyethylene moiety of the adsorbed surfactant molecules is immersed in the aqueous phase, where it is subjected to the influence of dissolved electrolytes. Therefore, foams constitute a useful model system to study that influence without the interference by the oil phase which occurs in emulsions (9).

EXPERIMENTAL

The surfactant, octoxynol 9 (Triton X-100 of Rohm & Haas Co.) has been described (10). The solid additives were ACS reagent grade or USP/NF grade. Their concentrated stock solutions were analyzed (1-3) and weighed out to the nearest milligram. Hexadecane was Eastman practical grade, and xylene was Baker purified.

Mixtures of octoxynol and electrolyte solutions were prepared with 10.00% surfactant solutions previously aged for $\geqslant$ 48 hr. These mixtures were stored at the foaming temperature 48 hr before the measurements except for the few measurements made above the cloud point, where the mixtures were stored at 10-15 C below the cloud point for 48 hr, followed by adjustment to the foaming temperature for 30-40 min before the measurements. Concentrations are based on the weight of water present, expressed as % (w/w) for the surfactant and as molality for the additives.

To saturate a 2.00% octoxynol solution with solubilized hexadecane without emulsifying an excess hexadecane, 260 g of the surfactant solution and four g of hexadecane were stored in a separatory funnel at 25 C for a week. The aqueous phase, drawn from the bottom of the funnel, contained 0.4% hexadecane (3). Xylene has a much higher solubilization limit than hexadecane (3). At the 1.57% xylene level used here, the 2.00% octoxynol solution was undersaturated with respect to xylene. The cloud point of a 2.00% octoxynol solution containing 1.57% xylene was 20 C, and a white precipitate formed at 25 C. Therefore, foaming experiments with this solution were performed at 15 ± 1 C. In the 10-18 C range, 2.00% octoxynol + 1.57% xylene form an almost clear solution with a bluish haze.

Foams were generated by a modified (10) Ross-Miles test (11, 12). Initial foam height and heights at two-min intervals were recorded every odd minute for 13 min or until the foam column suffered visible damage such as the formation of a hole, usually down the center of the column, or partial collapse. The age of the foam column when it sustained such damage also was recorded. The transparency and rate of thinning of foams and their strength or cohesiveness during removal by aspiration at the end of the experiments (10) were noted.

RESULTS

General observations. Tables 1-3 list average initial foam heights and heights after five min, their standard deviations, and the number of measurements on which the averages are based. Foam heights after five min are listed only for intact columns. In those cases where the number of measurements listed for the initial foam

TABLE 1

Foaming of Octoxynol 9 Solutions with Salting-in Electrolytes at 25 C

No.	Additive, concentration (ΔCP, degrees C)[a]	Octoxynol 9 concentration [% (w/w)]	Foam height (cm)[b]		Remarks[c]
			initial	after 5 min	
1	none (0)	2.00	12.73 ± 0.32 (19)[d]	12.23 ± 0.43 (16)	4/19 PC or HF in ≤ 10 min[e]
2	none	0.100	9.96 ± 0.27 (11)	9.57 ± 0.25 (11)	
3	none	0.050	8.11 ± 0.32 (9)	7.79 ± 0.25 (9)	1/9 HF at 7 min
4	HCl, 2.00 m	2.00	12.75 ± 0.24 (6)	12.16 ± 0.05 (5)	3/6 HF or PC in ≤ 7 min
5	(15)	0.100	9.98 ± 0.26 (6)	9.60 ± 0.29 (6)	2/6 HF in ≤ 7 min
6		0.050	8.25 ± 0.29 (6)	8.02 ± 0.26 (6)	2/6 HF in ≤ 7 min
7	H_2SO_4, 3.00 m	2.00	12.47 ± 0.29 (3)	11.80 ± 0.17 (3)	1/3 PC at 12 min
8	(28)	0.100	8.89 ± 0.28 (5)	8.40 ± 0.33 (5)	
9		0.050	6.60 ± 0.60 (6)	6.28 ± 0.61 (6)	
10	H_2SO_4, 1.50 m (7)	0.100	9.75 ± 0.24 (6)	9.27 ± 0.18 (6)	1/6 HF at 9 min
11	$Mg(NO_3)_2$, 2.00 m	2.00	13.42 ± 0.19 (5)	12.84 ± 0.29 (5)	
12	(12.5)	0.100	9.72 ± 0.33 (5)	9.28 ± 0.35 (5)	
13		0.050	7.28 ± 0.34 (4)	6.98 ± 0.32 (3)	3/4 HF in ≤ 7 min
14	$Al(NO_3)_3$, 2.00 m	2.00	11.59 ± 0.31 (7)	10.34 ± 0.20 (7)	
15	(10.4)	0.100	4.85 ± 0.10 (6)	4.42 ± 0.12 (6)	
16		0.050	3.64 ± 0.09 (5)	3.40 ± 0.08 (4)	
17	NaSCN, 2.00 m	2.00	12.83 ± 0.33 (6)	12.05 ± 0.35 (2)	6/6 PC in ≤ 6 min
18	(>30)	0.100	9.57 ± 0.26 (6)	8.95 ± 0.49 (2)	5/6 PC or HF in ≤ 7 min
19		0.050	7.34 ± 0.51 (7)	7.03 ± 0.57 (7)	3/7 HF in ≤ 9 min
20	NaSCN, 1.25 m (24)	2.00	13.23 ± 0.15 (3)	12.50 ± 0 (2)	3/3 PC in ≤ 7 min

[a] Δ CP defined by eqn. [1]. CP is cloud point of solution containing 2.00% octoxynol.

[b] Mean ± standard deviation; number of measurements between parentheses.

[c] Absence of remarks indicates that all foam columns remained intact within the observation period of 13 min.

[d] Blank foams 1-3 from Ref. 10.

[e] Four foam columns of 19 studied underwent partial collapse (PC) or hole formation (HF) within ≤ 10 min.

heights is greater than the number of measurements listed for five-min heights, the difference in the number of measurements represents the number of foam columns that suffered visible damage in the first five min. Additional damages, up to 13 min, are listed in the last column, which gives additional information about foam stability.

Cloud points refer to solutions with 2.00% octoxynol. Blank solutions from three surfactant lots had cloud points of 64, 65 and 65.5 C (10). Cloud points are generally independent of surfactant concentration between 0.2 and 5%. They are ca. 1-2 C higher at the two lower concentrations used here (13). Because the three lots of octoxynol 9 used had slightly different cloud points and because of the small variations in cloud point with surfactant concentration, the tables list changes in cloud point, ΔCP:

$$\Delta \mathrm{CP} = \begin{pmatrix}\text{cloud point of 2.00\%} \\ \text{octoxynol sol'n + additive}\end{pmatrix} - \begin{pmatrix}\text{cloud point of 2.00\% octoxynol} \\ \text{sol'n of same lot of octoxynol}\end{pmatrix} \quad [1]$$

Additives which increase the cloud point, i.e., whose ΔCP is positive, expand the temperature range in which the surfactant is soluble in water, i.e., they salt it in. Salting-out additives lower the cloud point (1-3). While 3.0 m H_2SO_4 raised the cloud point of octoxynol by 28 C, 0.4 m Na_2SO_4 lowered it by 29 C. These were, therefore, the maximum concentrations used for these two electrolytes. $Mg(NO_3)_2$ and $Al(NO_3)_3$ could not be used at concentrations high enough to boost the cloud point by 29 C.

The ratios of initial foam height to height after five min ranged from 1.02 to 1.08, averaged 1.054, and were not influenced systematically by the presence of salting-in or salting-out additives, surfactant concentration, or temperature. Foams 14, 29 and 52 had significantly higher ratios (see below). Foams 14 and 52 were also the slowest draining foams. Most other foams were fast draining. After 5-10 min, the top 2/3 of their columns turned gossamer thin and transparent, but generally showed no interference colors.

$Al(NO_3)_3$ solutions produced relatively slow-draining and stable foams because they were more viscous than other solutions of comparable electrolyte content. For instance, the density of a 2.00 m $Al(NO_3)_3$ solution with a 29.9% (w/w) solids content was 7% higher than that of 2.00 m $Mg(NO_3)_2$ with 22.9% solids, while the efflux time of its 50-ml volume from the separatory funnel at 25 C, 20.5 sec, was 28% higher than the 16 sec of $Mg(NO_3)_2$. Hence, its viscosity was 38% higher. As a

TABLE 2

Foaming of Octoxynol 9 Solutions with Nonionic Additives or Salting-out Electrolytes at 25 C

No.	Additive, concentration (ΔCP, degrees C)[a]	Octoxynol 9 concentration [% (w/w)]	Foam height (cm)[b]		Remarks[c]
			initial	after 5 min	
21	urea, 2.00 m	2.00	12.98 ± 0.24 (5)[d]	12.40 ± 0.26 (3)	5/5 PC in ⩽ 8 min
22	(ca. 15)	0.100	9.60 ± 0.22 (6)	9.20 ± 0.12 (5)	4/6 PC in ⩽ 12 min
23		0.050	7.28 ± 0.18 (5)	6.88 ± 0.22 (4)	3/5 PC in ⩽ 12 min
24	citric acid,	2.00	13.15 ± 0.43 (6)	12.16 ± 0.47 (5)	5/6 HF or PC in ⩽ 10 min[d]
25	2.00 m	0.100	7.00 ± 0.68 (6)	6.47 ± 0.72 (6)	2/6 HF in ⩽ 12 min
26	(> 30)	0.050	5.44 ± 0.15 (5)	5.10 ± 0.18 (4)	2/5 HF or PC in ⩽ 12 min
27	NaCl, 3.125 m	2.00[e]	11.45 ± 0.24 (6)	10.60 ± 0.24 (6)	
28	(-38; CP = 27 C)	0.100	3.24 ± 0.18 (5)	2.8 ± 0 (2)	3/5 HF at 1 min
29	NaCl, 2.00 m	2.00	11.98 ± 0.16 (6)	11.47 ± 0.19 (6)	
30	(-28.5)	0.100	6.47 ± 0.32 (6)	6.17 ± 0.33 (6)	
31		0.050	4.3 ± 0.1 (2)	4.1 ± 0.1 (2)	3/5 HF initially
32	NaCl, 1.00 m	2.00	12.53 ± 0.16 (6)	11.93 ± 0.34 (6)	
33	(-16.5)	0.100	8.70 ± 0.13 (6)	8.32 ± 0.13 (5)	2/5 HF in ⩽ 6 min
34	Na_2SO_4, 0.40 m	2.00	12.10 ± 0.14 (6)	11.40 ± 0.09 (6)	
35	(-29.5)	0.100	5.78 ± 0.16 (5)	5.42 ± 0.28 (5)	3/5 HF in ⩽ 12 min
36		0.050	3.57 ± 0.31 (7)	3.50 ± 0.57 (2)	5/7 HF in ⩽ 2 min and 7/7 HF in ⩽ 8 min
37	hexadecane, 0.4%[f] (14.5)	2.00	12.72 ± 0.56 (5)	12.30 ± 0.55 (4)	3/5 PC in ⩽ 6 min
38	xylene, 1.57%[g] (-45; CP = 20 C)	2.00	10.35 ± 0.10 (4)	- (0)	4/4 pr. C at 20 sec[h]

[a] Δ CP defined by eqn. [1]. CP is cloud point of solution containing 2.00% octoxynol.

[b] Mean ± standard deviation; number of measurements between parentheses.

[c] Absence of remarks indicates that all foam columns remained intact within the 13-min observation period.

[d] Five foam columns of 6 suffered hole formation (HF) or partial collapse (PC) within ⩽ 10 min.

[e] At 2 C below its cloud point, Solution 27 was slightly turbid.

[f] Saturated solution (see text).

[g] At 15 C because phase separation occurred at 25 C.

[h] Progressive collapse in all 4 columns starting at ca. 20 sec.

result of the higher solution viscosity, Foam 14 was denser and more opaque after 21 min than most other foams after only ⩽ 5 min.

Solutions 26 and 47 wetted the wall of the glass tube poorly and formed a few drops that did not spread. Both solutions contained 0.050% octoxynol. The beading was not as severe as that of a 0.010% octoxynol solution at 25 C, whose concentration was well below the CMC of 0.018% (w/v) (10). While $Mg(NO_3)_2$ raised the CMC of octoxynol at 25 C by as much as 15% (6), it is doubtful that the presence of 2.00 m $Mg(NO_3)_2$ at 37 C, or of 2.00 m citric acid at 25 C, could nearly triple the CMC. Thus, even Solutions 26 and 47, despite the poor wetting, were probably above their CMC.

Effect of surfactant concentration on foaming. Foam heights increased with increasing surfactant concentration in solutions without additives (10), as well as in solutions with salting-in and salting-out additives (Tables 1-3). However, foam stability was not related to surfactant concentration.

Foams of solutions of various additives containing octoxynol at the 2.00% level were generally less transparent than foams of solutions of the same additive and of comparable age but containing only 0.100 or 0.050% octoxynol. However, the former were just as likely to sustain damage on standing as the latter.

Effect of additives and their concentration on foaming. Most salting-in additives produced no major changes in initial and five-min foam heights. Exceptions are $Al(NO_3)_3$ (see above) and citric acid with 0.100 and 0.050% octoxynol (Nos. 25 and 26).

Urea and NaSCN affected foam stability adversely at all octoxynol concentrations, but reduced the foam height significantly only at the lowest octoxynol concentration.

Most salting-out electrolytes reduced the initial and five-min foam heights of 0.100 and 0.050% octoxynol solutions, more so at higher electrolyte concentrations. They caused only minor reductions in foam stability. Solubilized xylene, which is very effective in lowering the cloud point of octoxynol, produced coarse and transient foams: The foam columns collapsed in sections, starting from the top, at 10-20-sec intervals, beginning ∼ 20 sec after pouring. None of the other foams was this unstable.

Effect of temperature on foaming. Raising the temperature from 25 to 37 C produced only minor changes in foam height but reduced the stability of all foams

TABLE 3

Foaming of Octoxynol 9 Solutions with Electrolytes at 37 C

No.	Additive, concentration (ΔCP, degrees C)[a]	Octoxynol 9 concentration [% (w/w)]	Foam height (cm)[b]		Remarks[c]
			initial	after 5 min	
39	- (0)	2.00	12.80 ± 0.36 (9)[d]	12.34 ± 0.34 (5)	4/9 PC in ≤ 3 min
40	-	0.100	10.18 ± 0.24 (6)	- (0)	6/6 PC in ≤ 3 min
41	-	0.050	7.98 ± 0.17 (8)	7.70 ± 0.18 (6)	3/8 PC in ≤ 9 min
42	HCl, 2.00 m	2.00	13.09 ± 0.21 (9)	12.42 ± 0.30 (4)	9/9 PC in ≤ 8 min
43	(15)	0.100	9.49 ± 0.10 (8)	9.07 ± 0.12 (6)	5/8 PC in ≤ 10 min
44		0.050	8.13 ± 0.21 (7)	7.78 ± 0.23 (6)	4/7 PC in ≤ 7 min
45	$Mg(NO_3)_2$, 2.00 m	2.00	13.89 ± 0.17 (7)	12.95 ± 0.23 (6)	7/7 PC in ≤ 10.5 min
46	(12.5)	0.100	9.20 ± 0.14 (7)	8.67 ± 0.12 (6)	6/7 PC in ≤ 13.5 min
47		0.050	7.15 ± 0.15 (6)	6.55 ± 0.19 (4)	6/6 PC or HF in ≤ 11 min[e]
48	NaSCN, 2.00 m	2.00	12.97 ± 0.24 (9)	- (0)	9/9 pr. C at 1.5-3 min[f]
49	(> 30)	0.100	10.22 ± 0.22 (9)	- (0)	9/9 pr. C at 2-3 min
50		0.050	8.44 ± 0.21 (8)	- (0)	8/8 pr. C or HF at 1.5-2 min
51	NaCl, 2.40 m (-33; CP = 32 C)	2.00	7.84 ± 0.21 (5)	- (0)	5/5 pr. HF at 2-3 min[g]
52	NaCl, 2.40 m[h]	2.00	2.12 ± 0.20 (7)	1.86 ± 0.30 (6)	3/7 HF in ≤ 7 min
53	NaCl, 1.60 m (-24; CP = 41 C)	2.00	12.16 ± 0.25 (8)	11.57 ± 0.25 (3)	8/8 PC in ≤ 8 min

[a] Δ CP defined by eqn. [1]. CP is cloud point of solution containing 2.00% octoxynol.

[b] Mean ± standard deviation; number of measurements between parentheses.

[c] Absence of remarks indicates that all foam columns remained intact within the 13-min observation period.

[d] Blank foams 39-41 from Ref. 10.

[e] All 6 of 6 columns studied suffered partial collapse (PC) or hole formation (HF) within ≤ 11 min.

[f] Progressive collapse in all 9 columns starting at 1.5-3 min.

[g] Holes began to form at 2-3 min in all 5 columns and became gradually larger.

[h] At 42 C rather than 37 C.

including those from solutions without additives. The least stable foams at 37 C were those which were already less stable at 25 C, such as those containing NaSCN (Nos. 48-50), which were coarse, and 2.4 m NaCl (No. 51). Blank foams without additives at 37 C (Nos. 39-41) had stabilities comparable to 25 C foams of solutions containing NaSCN (Nos. 17-20).

Effect of cloud point on foaming. Increasing the NaCl concentration of 2.00% octoxynol solutions reduced their cloud point. Solution 53, containing 1.60 m NaCl, has a cloud point of 41 C; at the foaming temperature of 37 C, it was 4 C below the cloud point. The initial and five-min foam heights of Solution 53 were identical with the respective (interpolated) foam heights at 25 C. However, its foam stability was considerably lower: All columns suffered sudden and substantial collapses within eight min, while none of the columns of the corresponding 25 C foams, Nos. 29 and 32, suffered any damage in ≥ 13 min. The 37 C foams thinned more slowly than the 25 C foams, remaining fairly opaque at the time of their partial collapse.

Solutions 51 and 52, containing 2.4 m NaCl, were 5 C and 10 C above their cloud point at the respective foaming temperatures of 37 C and 42 C. The two solutions were about equally white opaque at their foaming temperatures. The precipitated surfactant-rich phase creamed only slightly and was easily redispersed. The initial height of the 37 C foam, 7.84 cm, was considerably below the interpolated 25 C value of 11.79 cm. The 37 C foam was comparatively unstable: In two to three min, all columns developed holes that grew.

The foam generated at 10 C above the cloud point, No. 52, was different from all other foams. Its height was much smaller than that of foams produced by solutions of the same composition at only 5 C above and 7 C below the cloud point, but it was considerably more stable than the latter. On aging, it did not thin noticeably or turn more transparent, but the foam cells became coarser. The ratio of initial height to five-min height, 1.14, was higher than that of other foams. The holes that eventually developed within 13 min in three of the seven columns did not grow larger as they did for Foam 51. Apparently, the precipitated surfactant phase increased the viscosity of the foam lamellas, minimizing drainage.

DISCUSSION

The present results are compared below with the brief published data on the effect of electrolytes on foaming of a surfactant similar to the one used here, namely, a polyoxyethylated nonylphenol with an HLB (hydrophilic-lipophilic balance) of 13.6 (almost identical with the 13.4 value of octoxynol 9) (14). In that study, a fixed surfactant concentration of 0.10% and a single electrolyte concentration of 3% (corresponding to 0.2-0.8 M for the various electrolytes) were used. Salting-in HCl at 3%, which raised the cloud point by 6 C, did not affect foam height (14), in agreement with present observations.

Examination of the data indicates that the salting-out additives NaOH, Na_2CO_3, Na_3PO_4 and NaCl at a 3% concentration reduced the foam height approximately in the same proportion in which they lowered the cloud point, i.e., foam height was proportional to ΔCP (14).

For the salting-out additives NaCl and Na_2SO_4 at 25 C used in the present work with 2.00% octoxynol (Nos. 27, 29, 32 and 34) and with 0.100% octoxynol (Nos. 28, 30, 33 and 35), there is a somewhat less than linear relationship between foam height and the lowering of the cloud point compared to the respective blank solutions (Nos. 1 and 2).

For 2.00% octoxynol solutions, the average slope in Figure 1 for the initial and five-min foam heights is a mere -0.035 cm/degree C. The average slopes are -0.169 and ca. -0.14 cm/degree C for the 0.100 and 0.050% octoxynol solutions, respectively. The lesser sensitivity of foam height to cloud point change in the more concentrated octoxynol solution parallels the smaller increase in foam height with octoxynol concentration for the more concentrated octoxynol solutions observed in the case of blank solutions (10). Figure 1 was not extended to positive ΔCP values because the salting-in electrolytes produced neither large nor systematic changes in foam height compared to blank solutions of comparable octoxynol concentrations (see above).

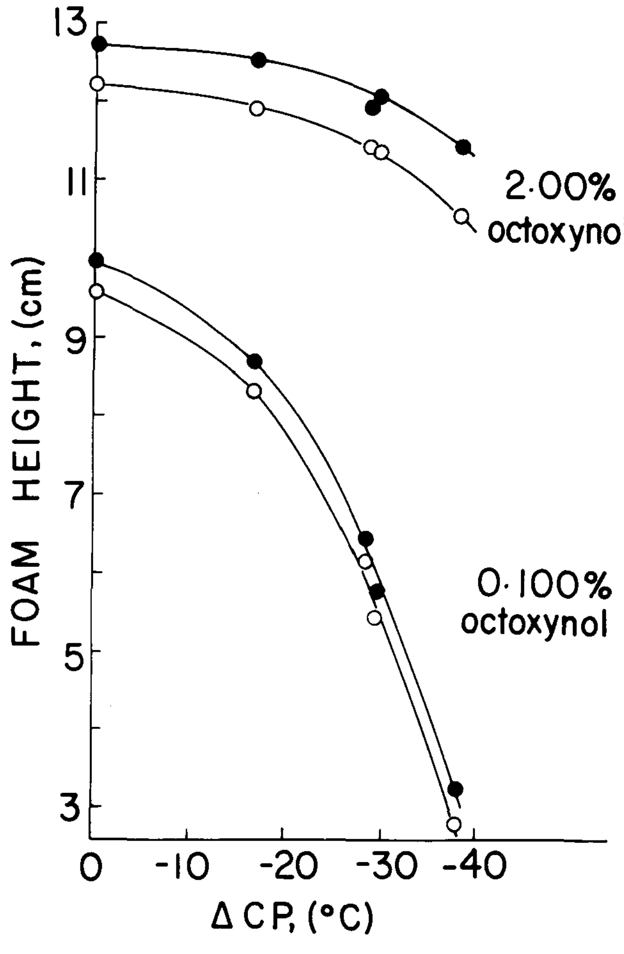

FIG. 1. Foam height of 0.100 and 2.00% octoxynol 9 solutions as a function of changes in cloud point at 25 C. ●, initial foam height; ○, 5-min foam height.

The salting-out electrolytes produced no significant adverse effects on foam stability except for No. 28, which was measured just 2 C below the cloud point. The stability of foams of a polyoxyethylated nonylphenol (HLB ≅ 12.6) was reported to drop considerably as the NaCl concentration was increased from 0 to 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} M (15). Even though the highest concentration used for that surfactant was only 0.11%, it seems surprising that Joos' low NaCl concentrations destabilized foams, whereas the higher NaCl concentrations used in the present study produced little or no adverse stability effects.

The nearly linear dependence of foam height on ΔCP (14; Fig. 1) is related to the nearly linear relation between the ΔCP of sodium salts with salting-out anions and the lyotropic number of these anions (16). Work with single films revealed no effect of various sodium salts on thinning in the region where the films were thick enough to exhibit interference fringes, but the time required for transforming the entire film area into a black film decreased almost linearly with decreasing lyotropic number of the anions (17). Black films are formed at the last stage of drainage, when their thickness becomes very small compared to the wavelength of light. In that case, the light reflected from their front and back surfaces interferes destructively at all visible wavelengths, rendering the film nearly invisible.

The destabilization of foams of solutions of a polyoxyethylated nonylphenol with HLB = 13.9 by sodium salts, expressed as the rate of decrease of the logarithm of foam height with time, followed approximately the order of the lyotropic series for the anions: NaSCN ⩽ NaCl < NaOH < 1/3 Na_3PO_4 < 1/2 Na_2SO_4 ≅ 1/2 Na_2CO_3 (18).

The underlying causes of decreasing foam height or foam stability with decreasing cloud point as salting-out electrolytes are added to the nonionic surfactant solutions, and their relation to the lyotropic number of the anions, are reduced hydration and lower solubility, and a related increase in activity of the polyoxyethylene moiety of the nonionic surfactant brought about by these electrolytes. They compress the coiled polyoxyethylene chains, decreasing the area per surfactant molecule adsorbed at the air-water interface in the saturation adsorption (6) and plateau regions, which is determined by the cross-sectional area of the polyoxyethylene moiety (19, 20). Compression or collapse of these random coils reduces the steric stabilization of the foam lamellas by the surfactant.

Reduced hydration and shrinkage of the polyoxyethylene coils of the surfactant molecules in the air-water film impaired the foaming tendency of the solutions only moderately. A possible reason why salting-out electrolytes did not destabilize the foams more extensively is that they may have increased the number of surfactant layers comprising the air-water interfacial film (7, 10). Such an increase in film thickness may have counteracted the compression of the polyoxyethylene coils and restored the steric stabilization of the foam lamellas.

While salting-out electrolytes did not produce substantial adverse changes in the surface properties and foaming of the surfactant at temperatures below the cloud point, they did increase its bulk activity and lower its cloud point substantially. Once the cloud point of the nonionic solution is exceeded by the addition of salting-out electrolytes and/or by heating, the hydration of the polyoxyethylene chains of the surfactant molecules is insufficient to keep them in solution. At that point, the polyoxyethylene coils collapse completely. Lacking steric stabilization, foams do not form. Moreover, the precipitated concentrated surfactant phase actually acts as an antifoaming agent (21).

Overall, the effect of salting-out anions and cations on foaming is well understood. However, all cations except Na^+, K^+, NH_4^+, Rb^+ and Cs^+ promoted salting-in of nonionic surfactants by complexation with their ether groups, raising their cloud points (1, 2). Therefore, there was no correlation between ΔCP and the lyotropic number of the cations except for the alkali metal cations listed above (16). Similarly, no correlation was observed here between foam height and ΔCP of octoxynol solutions containing HCl, H_2SO_4, $Mg(NO_3)_2$ and $Al(NO_3)_3$ or the cloud point shift values (3, 4) of the individual cations. The eight salting-in additives used in this study did not change the foam height substantially, confirming the observation reported for HCl (14, 18).

Electrolytes with cations which salt the surfactant in by complexation with its ether oxygens, namely H^+, Mg^{2+} and Al^{3+}, did not affect the foam stability adversely despite the high concentrations at which they were added. Cation binding confers a cationic character to the surfactant, thereby adding repulsion between electric double layers as a foam stabilization mechanism. To what extent this mechanism is operative in the presence of elecrolytes at multimolal levels is not known: Most related investigations dealt with individual films (17, 22), whose stability is far greater than that of foams.

NaSCN and urea, which salt the surfactant in by reducing the self-association through hydrogen bonding among water molecules, breaking the structure of water (2, 3), lowered the foam stability. By increasing the activity of water, they reduced the activity of the surfactant as shown by increases in CMC (or, at least, smaller reductions than those produced by salting-out additives at comparable concentrations), increases in plateau surface tension (or, at least, no reductions) (6, 20), and by large increases in cloud point (2-4).

Citric acid, which at the prevailing pH $\leqslant 1.5$ is practically completely in the un-ionized form, salts octoxynol in very efficiently, either by reducing the dielectric constant and the solubility parameter of water and/or by associating with the surfactant through hydrogen bonding, increasing its effective HLB (3). Citric acid at 2.00 m or 28% (w/w) concentration reduced the foam height of solutions of 0.100 and 0.050% octoxynol (Nos. 24 and 25). It destabilized all three foams (Nos. 24–26) somewhat.

Of the two solvents, hexadecane dissolves only small amounts of octoxynol 9 while xylene and octoxynol 9 are miscible in all proportions (7). Xylene had a devastating effect on octoxynol foams because it distributed itself between the surfactant film at the air-water interface and the surfactant micelles.

Xylene present in the foam lamellas may have exerted a negative Marangoni effect. Indentation or stretching of a foam lamella caused by a disturbance prior to bursting reduces the surfactant concentration in the expanded portion of the surface film. The resultant local increase in surface tension tends to contract the expanded film area, repairing the damage before it bursts. This is the well-known Marangoni effect (23). Eventually, surfactant diffuses from the bulk solution to the expanded portion of the surface film to restore equilibrium surface excess and surface tension. Because xylene is volatile, it diffuses considerably faster than the surfactant to the expanded and underpopulated film area. When its temporary local concentration is high, it weakens the affected portion of the film by lowering its surface viscosity and surface tension below their equilibrium values, promoting bursting.

Because of its low miscibility with octoxynol, practically all of the hexadecane present in aqueous solution is solubilized in the hydrocarbon core of the micelles. It remains in the solution and does not partition itself into the surface film of octoxynol. Even if a little hexadecane could dissolve in that film, its diffusion from the bulk solution to a stretched portion would be slow because, unlike xylene, it has a low vapor pressure and will diffuse no faster than the surfactant.

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