

☛ Synergism in Binary Mixtures of Surfactants. 7. Synergism in Foaming and its Relation to Other Types of Synergism¹

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The relationship between synergism in Ross-Miles foaming and the existence of other types of synergism in binary mixtures of surfactants has been investigated. All studies were conducted in solutions of constant ionic strength (0.1 M NaCl) at 25 and/or 60°C. Six anionic-zwitterionic or anionic-nonionic mixtures and a sodium dodecylbenzenesulfonate (LAS)-soap mixture, all consisting of commercial surfactants, were studied. Synergism in foaming effectiveness, measured by initial foam heights, appears to be related to synergism in surface tension (γ) reduction effectiveness, but not to synergism in γ reduction efficiency or in mixed micelle formation. The LAS-soap system showed negative synergism in foaming effectiveness, correlated with negative synergism in γ reduction effectiveness, the conditions for which are defined. There appears to be no correlation between synergism in foaming efficiency and synergism in either γ reduction efficiency or mixed micelle formation. There also appears to be no unambiguous relationship between foam stability, measured by the ratio of the 5-minute to the initial foam height, and the average area per surfactant molecule at the aqueous solution/air interface.

In previous publications on synergism in binary mixtures of surfactants in aqueous solution (1-4), we have discussed surface tension reduction and mixed micelle formation. In this paper we investigate synergism in foaming and its relationship to the types of synergism previously studied. In addition, we apply our treatment of synergism for the first time to commercial materials, rather than to highly purified surfactants. We also encounter and discuss the phenomenon of negative synergism.

Three types of synergism for binary mixtures of surfactants in aqueous solution have been distinguished and investigated in previous publications: (i) surface tension reduction efficiency, when a given surface tension (reduction) is attained at a total mixed surfactant concentration less than that required for either component of the mixture; (ii) synergism in mixed micelle formation, when the cmc of the mixture is less than that of either component by itself; (iii) synergism in surface tension reduction effectiveness, when the surface tension of the mixture at its critical micelle concentration (cmc) is less than that attained with either component by itself. Synergism of the first type depends upon the value of β^o , the interaction parameter for mixed monolayer formation at the aqueous solution/air interface; of the second type, on the value of β^M , the

interaction parameter for mixed micelle formation in aqueous solution; of the third type, on the values of both β^o and β^M .

These parameters are evaluated from surface tension (γ)-molar concentration (C) data for the two individual surface-active components of the system and at least one mixture of them, by use of the equations:

$$\frac{X^2 \ln(C_{12}\alpha/C_1X)}{(1-X)^2 \ln [C_{12}(1-\alpha)/C_2(1-X)]} = 1 \quad [1]$$

and

$$\beta = \frac{\ln(C_{12}\alpha/C_1X)}{(1-X)^2} \quad [2]$$

For the determination of β^o , C_1^o , C_2^o and C_{12} are the total molar concentrations of surfactant 1, surfactant 2 and their mixture, at mole fraction, α , of surfactant 1 in the total surfactant in the aqueous phase, respectively, required to attain the same surface tension value at a given temperature. Using these quantities, equation 1 is solved numerically for X, the mole fraction of surfactant 1 in the mixed monolayer of surfactant at the aqueous solution/air interface [(1-X) is the mole fraction of surfactant 2], and this is used in equation 2 to evaluate β^o . For evaluating β^M , C_1^M , C_2^M , and C_{12}^M are the cmcs of surfactant 1, surfactant 2 and their mixture, respectively, at a mole fraction, α , in the aqueous phase at a given temperature. Equation 1 is solved in this case for X^M , the mole fraction of surfactant 1 in the mixed micelle, and this is used in equation 2 to evaluate β^M .

The conditions for the existence of synergism in these three respects are (1,4):

- γ reduction efficiency: β^o is negative; $[\beta^o > \ln(C_1^o/C_2^o)]$.
- mixed micelle formation: β^M is negative; $\beta^M > \ln(C_1^M/C_2^M)$.
- γ reduction effectiveness: β^o is negative; $\beta^o - \beta^M$ is negative; $\beta^o - \beta^M > (\gamma^o \text{ cmc}_1 - \gamma^o \text{ cmc}_2)/S$.

Here, $\gamma^o \text{ cmc}_1$ and $\gamma^o \text{ cmc}_2$ are the surface tensions of surfactants 1 and 2, respectively, at their cmcs, and S is the larger of the slopes of the γ -ln C plots for the two individual surfactants.

We define synergism in foaming effectiveness as existing when the initial foam height attained by the mixture of surfactants at a given total concentration in the liquid phase exceeds that attained by the individual surfactants, by themselves, at that same concentration in the liquid phase. Six systems, all either anionic-zwitterionic or anionic-nonionic mixtures, have been investigated: sodium linear dodecylbenzenesulfonate (LAS)- $C_{12}N^+(CH_3)_2CH_2COO^-$, LAS- $C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$, LAS- $C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2O^-$, LAS- $C_{11}H_{23}CON(CH_2CH_2OH)_2$, LAS- $C_{12}H_{25}(OC_2H_4)_{10}OH$, and $C_{12}H_{25}(OC_2H_4)_2SO^-Na^+-C_{12}H_{25}$

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(OC₂H₄)₁₀OH. In addition, the system LAS-C₁₅H₃₁COO-Na⁺, has been investigated.

EXPERIMENTAL

All surfactants were commercial-grade materials, used as received: sodium linear dodecylbenzenesulfonate (LAS) - C-550 LAS (Vista Chemical Co., Ponca City, Oklahoma); C₁₁H₂₃CONH(CH₂)₃N⁺(CH₃)₂O⁻ - Monalux CAO (Mona Industries, Paterson, New Jersey); C₁₂H₂₅N⁺(CH₃)₂CH₂COO⁻ - Mirataine CDMB (Miranol Chemical Co., Dayton, New Jersey); C₁₁H₂₃CON(C₂H₄OH)₂ - Monamid 150 LWA (Mona Industries); C₁₂H₂₅(OC₂H₄)₂SO⁻Na⁺ - Texapon N25; C₁₂H₂₅(OC₂H₄)₁₀OH - Dehydrol 100 (Henkel, KGaA, Düsseldorf, Germany); palmitic acid (Eastman Kodak Co., Rochester, New York). Sodium chloride (analytical reagent) was baked at red heat for at least eight hr before use, to decompose any surface-active material.

To ensure that comparisons between solutions of different ionic surfactants would be made at the same ionic strength, all surfactant solutions were made in 0.1N NaCl.

β^o and β^M values were determined from plots of γ versus the log of the total molar concentration of surfactant (log C) in the aqueous solution in the manner described above. All surface tension measurements were at 25 C \pm 0.1 C, using the Wilhelmy plate technique described previously (3).

Foaming data in 0.1N NaCl were obtained by the Ross-Miles method (5). Initial and five-min foam heights were measured. The ratio of the five-min foam height to the initial foam height was termed the foam stability. Since foam heights generally fall off below the cmc, all foaming data were taken on solutions with surfactant concentrations at least 20 times the cmc. Values listed are the average of three or four runs in each case.

The area per molecule (A/mol) at the aqueous solution/air interface, in Å², was determined from the maximum slope of the γ -log C plot, by use of the relationship: A/mol = 2.303 \times 10¹⁶RT/slope \times N, where N is Avogadro's number, R is 8.31 \times 10⁷ ergs mol⁻¹ °K⁻¹, and γ is measured in dyne cm⁻¹. The cmc was taken as the point of intersection of the line of maximum slope of the γ -log C plot with the linear portion of the plot above the discontinuity.

RESULTS AND DISCUSSION

From plots of γ versus log C for the individual surfactants and their mixtures in 0.1N NaCl at 25 C, β^o and β^M were evaluated using equations 1 and 2. These were compared with $\ln C_1^o/C_2^o$, $\ln C_1^M/C_2^M$, and $(\gamma^o \text{ cmc}1 - \gamma^o \text{ cmc}2)/S$, to determine whether synergism in surface tension reduction efficiency, micelle formation, or surface tension reduction effectiveness, could exist.

These synergism parameters are listed in Table 1. They are consistent with previous data on mixtures of highly purified surfactants (2 - 4,6) indicating that: (i) anionic surfactants interact much more strongly with zwitterionics than with nonionics, especially at pH < 7; (ii) in anionic-polyoxyethylenated nonionic mixtures, attractive interaction between the two surfactants in mixed micelles is often stronger than in mixed monolayers (β^M is more negative than β^o); (iii) there is a small decrease in the strength of the attractive interaction between two surfactants with increase in temperature.

The somewhat larger than expected β^o and β^M values for the LAS-C₁₀CONH(CH₂)₃N⁺(CH₃)₂CH₂COO⁻ and LAS-C₁₁CONH(CH₂)₃N⁺(CH₃)₂O⁻ systems is probably due to the known presence of unreacted C₁₁CONH(CH₂)₃N(CH₃)₂ in these systems. (A large dip was observed near the CMC in the γ -log C plot of each of these

TABLE 1

Synergism Parameters for Systems Investigated in 0.1N NaCl at 25 C

System	γ Reduction efficiency		Mixed micelle formation		γ Reduction effectiveness	
	β^o	$[\ln(C_1^o/C_2^o)]$	β^o	$[\ln(C_1^M/C_2^M)]$	$(\beta^o - \beta^M)$	$[\gamma^o \text{ cmc}1 - \gamma^o \text{ cmc}2)/S]$
1. LAS-C ₁₂ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻ (pH = 5.8)	-3.8	0.091	-2.9	0.13	-0.9	0.045
2. LAS-C ₁₂ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻ (pH = 9.3)	-2.9	0.05	-1.7	0.29	-1.2	0.14
3. LAS-C ₁₁ CONH(CH ₂) ₃ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻ (pH = 5.8)	-5.8	0.51	-5.1	0.63	-0.7	0.10
4. LAS-C ₁₁ CONH(CH ₂) ₃ N ⁺ (CH ₃) ₂ O ⁻ (pH = 5.8)	-7.8 -6.3 ^a	0.49 0.51 ^a	-6.7 -5.6 ^a	0.79 0.30 ^a	-1.1 -0.7 ^a	0.17 0.37 ^a
5. LAS-C ₁₁ CON(C ₂ H ₄ OH) ₂ (pH = 5.8)	-2.4	0.19	-1.5	0.12	-0.9	0.44
6. LAS-C ₁₂ EO ₁₀	-2.4	1.24	-2.7	1.16	+0.3	0.081
7. C ₁₂ (EO) ₂ SO ₄ Na-C ₁₂ EO ₁₀ (pH = 5.8)	-2.1	0.9	-2.3	0.51	+0.2	0.13
8. LAS-C ₁₅ COO ⁻ Na ⁺ (pH = 10.6-10.7)	+2.4 ^a	1.04 ^a	+0.94 ^a	0.65 ^a	+1.46 ^a	0.83 ^a

^aAt 60 C.

SYNERGISM IN FOAMING

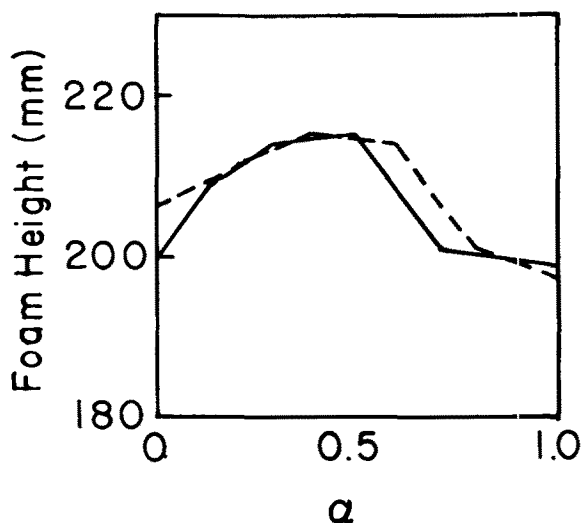


FIG. 1. Initial foam height at 60 C vs α for LAS- $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$ mixtures (0.25% conc). —, pH 5.8; ---, pH 9.3.

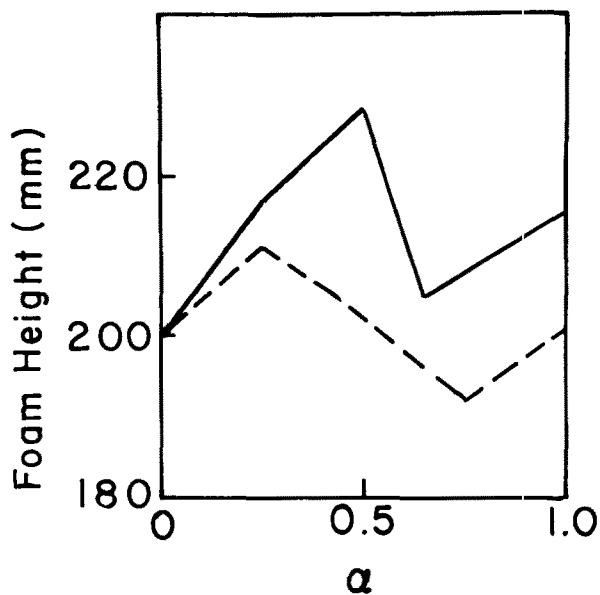


FIG. 2. Initial foam height at 60 C vs α for mixtures of: —, LAS- $C_{11}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$; ---, LAS- $C_{11}CONH(CH_2)_3N^+(CH_3)_2O^-$ at 0.25% conc.

zwitterionics by itself.) For the systems investigated, the data at 60 C parallel those at 25 C, and the same types of synergism (or absence thereof) are shown at both temperatures.

Foam effectiveness. Figures 1-3 are plots of initial foam height vs α , the mole fraction of the non-anionic component of the mixture, for 0.25% solutions of the individual surfactants and their mixtures in 0.1N aqueous NaCl, using the Ross-Miles technique. From the plots, it is apparent that synergism in foaming effectiveness (i.e., when the mixture can attain an initial foam height greater than that shown by either surfactant of the mixture by itself) exists in some of these systems. The existence of synergism in γ reduction or in mixed micelle formation is determined by comparing

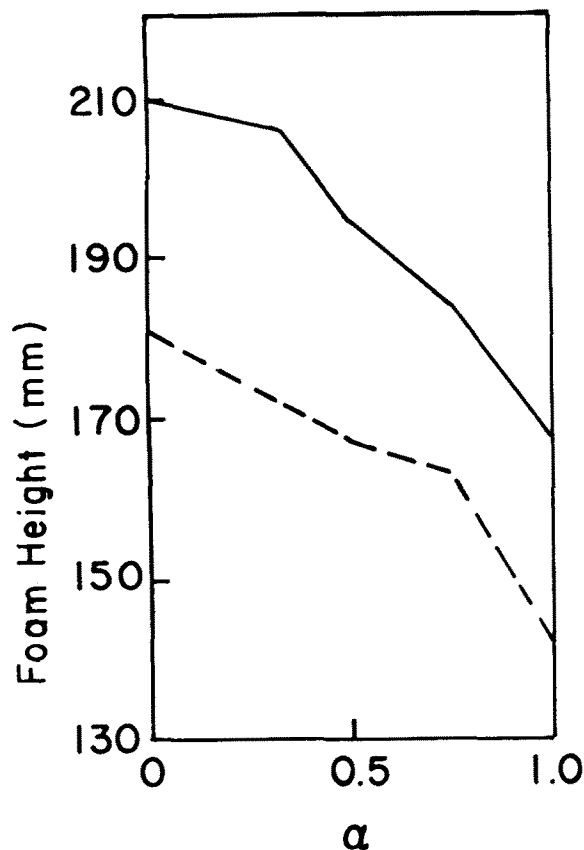


FIG. 3. Initial foam height vs α for $C_{12}(EO)_2SO_4Na - C_{12}EO_{10}$ mixtures (0.25% conc). —, 60 C; ---, 25 C.

the synergism parameters listed in Table 1 with the conditions for synergism listed above. The existence of synergism in foaming effectiveness is determined from plots of initial foam height vs α .

Systems 1-7, Table 1, all showed synergism in γ reduction efficiency and in mixed micelle formation. However, only systems 1-5 showed synergism in γ reduction effectiveness. The other two systems (6 and 7) showed no synergism in γ reduction effectiveness and no synergism in foaming effectiveness.

It therefore appears that synergism in foaming effectiveness correlates only with synergism in γ reduction effectiveness, not with synergism in mixed micelle formation or in γ reduction efficiency. This is reasonable, in view of our previous data using this foaming technique (7) that show that initial foam height increases as γ is reduced. Therefore, if the mixture can reach a lower value of γ than attainable with its component surfactants by themselves (i.e., it shows synergism in γ reduction effectiveness), it should produce a greater initial foam height than its component surfactants.

The LAS- $C_{15}COO-Na^+$ system (8, Table 1) shows negative synergism in foaming effectiveness (Fig. 4), i.e., the mixture at certain α values produces a foam height lower than that of either surfactant by itself at the same concentration. This system also shows negative synergism in γ reduction effectiveness, i.e., the minimum γ value for the LAS- $C_{15}COO-Na^+$ mix-

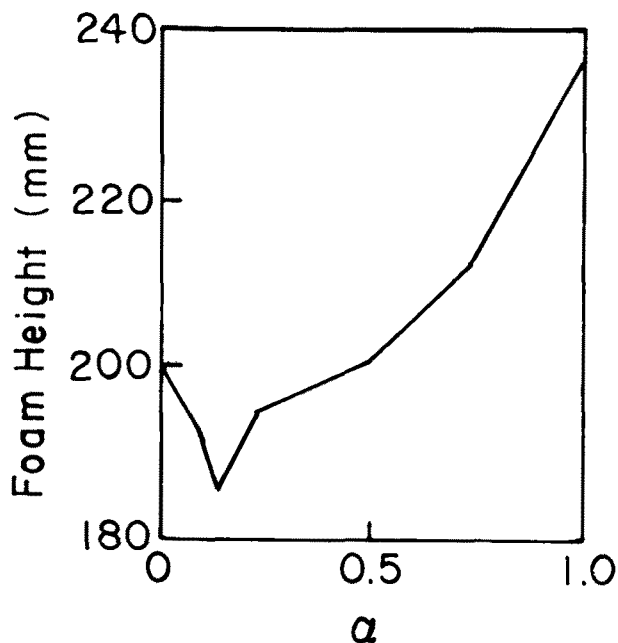


FIG. 4. Initial foam height at 60 C vs $\alpha(\text{C}_{15}\text{COO}^-\text{Na}^+)$ for LAS- $\text{C}_{15}\text{COO}^-\text{Na}^+$ mixtures (0.25% conc).

tures at $\alpha = 0.15$ ($\text{C}_{15}\text{COO}^-\text{Na}^+$) is greater than that for either surfactant of the mixture by itself.

This is consistent with the data for other systems investigated that show that (positive) synergism in foaming effectiveness is related to (positive) synergism in γ effectiveness.

Although it is commonly believed that the use of soap as a foam depressant in laundry detergents is due to the formation of foam-breaking calcium soap as a result of the reaction of the soap with Ca^{2+} in the water, our results indicate that this foam depression can be obtained even in the absence of Ca^{2+} and that it is associated with an increase in the surface tension of the solution.

In order to determine whether this increase in the surface tension and decrease in foaming might be due to the presence of some free fatty acid in the interfacial film as a result of partial hydrolysis of the soap there, one mg of free fatty acid was added to one l of the 0.25% LAS solution at a pH of 6.28. Foaming and surface tension measurements showed no significant decrease in either the initial foam height or the foam stability and no increase in the surface tension of the solution.

From our previous investigation of synergism in γ reduction effectiveness (4), the conditions for negative synergism in γ reduction effectiveness are: (i) $\beta^o - \beta^M$ must be positive; (ii) $\beta^o - \beta^M > |(\gamma^o \text{CMC}^o - \gamma^M \text{CMC}^M)/S|$. Examination of the synergism parameters for the LAS- $\text{C}_{15}\text{COO}^-\text{Na}^+$ system listed in Table 1 shows that this system does indeed meet these conditions. This phenomenon of negative synergism is being investigated further.

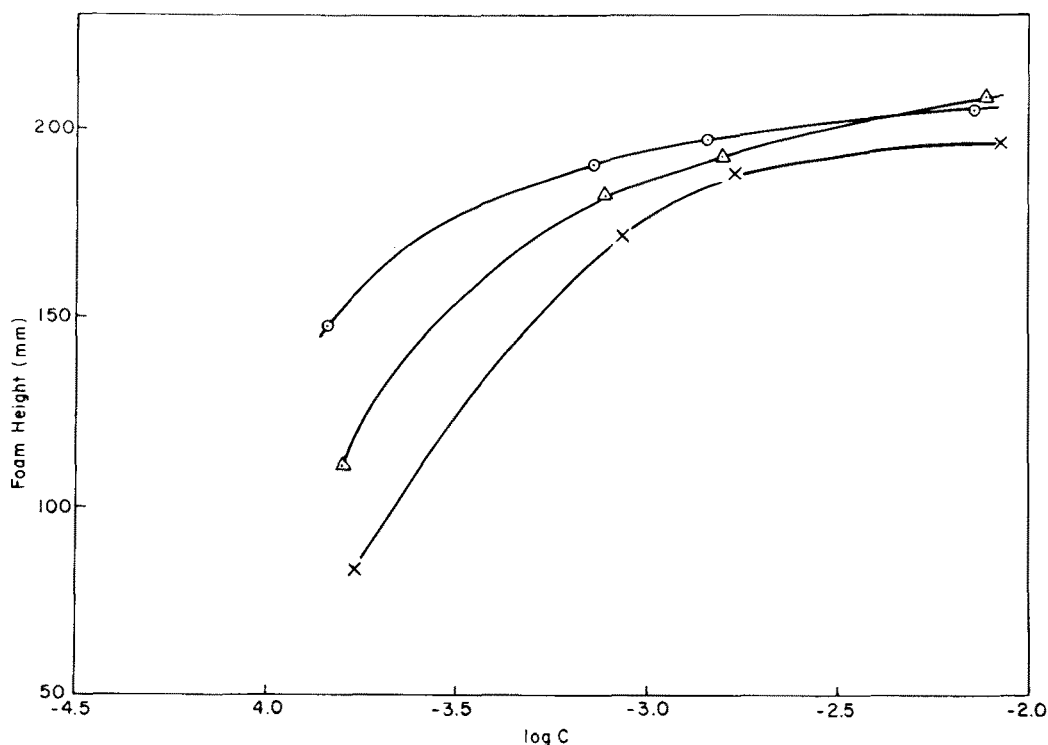


FIG. 5. Initial foam height vs total surfactant concentration for LAS, $\text{C}_{12}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$, and their mixtures at $\alpha = 0.5$ (in 0.1N NaCl, pH 9.3, 60 C). O, LAS; X, $\text{C}_{12}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$; Δ , LAS- $\text{C}_{12}\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$ mixture; $\alpha = 0.5$.

SYNERGISM IN FOAMING

TABLE 2

Average Area/Surfactant Molecule at the Aqueous Solution/Air Interface and Foam Stability (in 0.1N NaCl)

System	α^a	A/mol (\AA^2)		Foam stability	
		25 C	60 C	25 C	60 C
LAS-C ₁₂ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻ (pH = 5.8)	0	46			0.95
	0.5	36			0.98
	1.0	41			0.15
LAS-C ₁₂ N ⁺ (CH ₃) ₂ CH ₂ COO ⁻ (pH = 9.3)	0	46			0.94
	0.5	36			0.98
	1.0	45			0.17
LAS-C ₁₁ CONH(CH ₂) ₃ N ⁺ (CH ₃) ₂ COO ⁻ (pH = 5.8)	0	46			0.95
	0.5	31			0.89
	1.0	34			0.96
LAS-C ₁₁ CONH(CH ₂) ₃ N ⁺ (CH ₃) ₂ O ⁻ (pH = 5.8)	0	46	59		0.95
	0.4	—	40		0.98
	0.5	36	—		0.96
	1.0	31	39		0.99
LAS-C ₁₁ CON(C ₂ H ₄ OH) ₂ (pH = 5.8)	0	46	59		0.98
	0.5	38	41		0.98
	1.0	34	42		0.60
LAS-C ₁₂ EO ₁₀ (pH = 5.8)	0	46		0.97	0.95
	0.24	47		0.94	0.47
	0.76	53		0.98	0.20
	1.0	47		0.97	0.15
C ₁₂ (EO) ₂ SO ₄ ⁻ Na ⁺ -C ₁₂ EO ₁₀ (pH = 5.8)	0	42		0.97	0.99
	0.75	51		0.98	0.38
	1.0	47		0.97	0.15
LAS-C ₁₅ COO ⁻ Na ⁺ (pH = 10.6-10.7)	0		59		0.95
	0.15		58		0.29
	1.0		31		0.98

^aMole fraction of the surfactant listed second in the system.

Foaming efficiency. There appears to be no firm correlation between synergism in γ reduction efficiency (or in mixed micelle formation) and synergism in foaming efficiency (when the mixture can attain a given initial foam height at a concentration lower than that of either surfactant of the mixture by itself). This is shown in Figure 5, where initial foam height is plotted as a function of the total surfactant concentration in the aqueous phase for the LAS-C₁₂N⁺(CH₃)₂CH₂COO⁻ system at pH 9.3. Although this system shows synergism in γ reduction efficiency (and in mixed micelle formation) with maximum synergism in both these respects at $\alpha \approx 0.5$, and this (1:1) mixture shows at about 10^{-4} total molar surfactant concentration a γ value lower than that of either surfactant by itself, the plots in Figure 5 show that LAS by itself is more efficient than the 1:1 mixture until a concentration of about 50×10^{-4} molar is reached.

Foam stability. There appears to be no unambiguous relationship between foam stability, as measured by the ratio of the five-min to the initial foam height, and the packing of the surfactant molecules at the aqueous solution/air interface, either at 25 or 60 C. This is apparent from the data listed in Table 2. In the cases where foam stability is poor (<0.80), it appears to be due not to loose packing of the surfactant molecules at the interface, but to limited solubility of one of the

surfactants of the mixture. Thus, the poor foam stability of C₁₁CON(C₂H₄OH)₂, by itself, in 0.1N aqueous NaCl solution at 60 C is probably due to its insolubility, as evidenced by the cloudiness of the solution. Foaming data at 25 C were, consequently, in most cases unreliable as a means of correlating foaming performance with fundamental surface properties, because some of the products formed by the interaction between the two surfactants in the mixture had limited solubility at 25 C. This was evidenced by the formation of opalescent, cloudy, or viscous solutions at some values of α . Generally, these solutions showed greatly reduced foam heights.

On the other hand, both anionic - C₁₂EO₁₀ systems showed good foam stability at 25 C but very poor foam stability at 60 C, which may reflect the approach, at the higher temperature, to the 76 C cloud point of C₁₂EO₁₀.

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