Bar Soap Aging

Several samples of commercial and experimental bar soaps containing BHT were analyzed at various time periods in order to monitor the effect of aging on BHT content. As indicated in Table III, bar soap C, initially prepared with 150 ppm of BHT, although showing a fairly steady decrease of antioxidant content with time, still contained 85 ppm of BHT after 18 months aging at ambient temperature. However, because additional aging experiments have indicated that BHT stability is apparently quite dependent upon certain sample composition and storage factors, the monitoring of BHT levels for both formulation and storage studies will be of continuing interest in our laboratory.

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Synergism in Binary Mixtures of Surfactants:

II. Some Experimental Data

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ABSTRACT

The conditions derived previously for three types of synergism in aqueous binary mixtures of surfactants—mixed micelle formation, surface tension reduction efficiency, and surface tension reduction effectiveness—are reviewed and verified by use of experimental data from the chemical literature. They involve the experimentally determined parameters, β and β^M, related to the interaction between the two surfactants in the mixed monolayer at the aqueous solution/air interface and in the mixed micelle, respectively. The experimental data needed to determine whether a binary surfactant system is capable of synergism in these respects are: (a) the surface tension/log concentration curves of the individual surfactants in the vicinity of their critical micelle concentrations (cmc); (b) the cmc of at least one mixture of the two surfactants; and (c) the solution phase concentration of at least one mixture of the two surfactants needed to produce a surface tension attainable by both individual surfactants. From the available data, some tentative generalizations regarding the effect of chemical structure and the molecular environment of the values of β and β^M have been made.

For the past few years, we have been studying the interfacial properties of aqueous solutions containing two surfactants and the degree of molecular interaction between the surface-active components. Recently (1), we have derived equations showing the conditions necessary for synergism in these systems. To date, we have investigated synergism in three areas: (a) mixed micelle formation; (b) surface tension reduction efficiency; and (c) surface tension reduction effectiveness.

The relationships derived all involve a molecular interaction parameter, β, that is determined experimentally. The basic equations for determining the value of β are:

$$\frac{X^2 \ln \dfrac{C_{12}\alpha}{C_1 X}}{(1-X)^2 \ln \dfrac{C_{12}(1-\alpha)}{C_2(1-X)}} = 1 \qquad [1]$$

$$\beta = \frac{\ln \dfrac{C_{12}}{C_1 X}}{(1-X)^2} \qquad [2]$$

where C_1, C_2, and C_{12} are the solution phase concentrations of surfactants 1 and 2 and their mixture, respectively, required to produce a given effect; α is the mole fraction of surfactant 1 in the total mixed surfactant in the solution phase; and X is its mole fraction in the total mixed surfactant in the surface phase. In these equations, the only quantities that must be measured experimentally are C_1, C_2, and C_{12}. Equation 1 is solved numerically for the value of X and the value of β is then obtained from Equation 2.

Synergism in Mixed Micelle Formation

Synergism in this respect is present when the critical micelle concentration (cmc) of any mixture is lower than those of both surfactants in the mixture. Here, the experimental

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values required are the cmc of the two individual surfactants, C_1^M and C_2^M, and the cmc, C_{12}^M, of at least one mixture of the two, all in aqueous medium at the same temperature. From these values, β^M, the parameter related to the degree of molecular interaction between the two surfactants in the mixed micelle, is calculated by equations analogous to Equations 1 and 2, above.

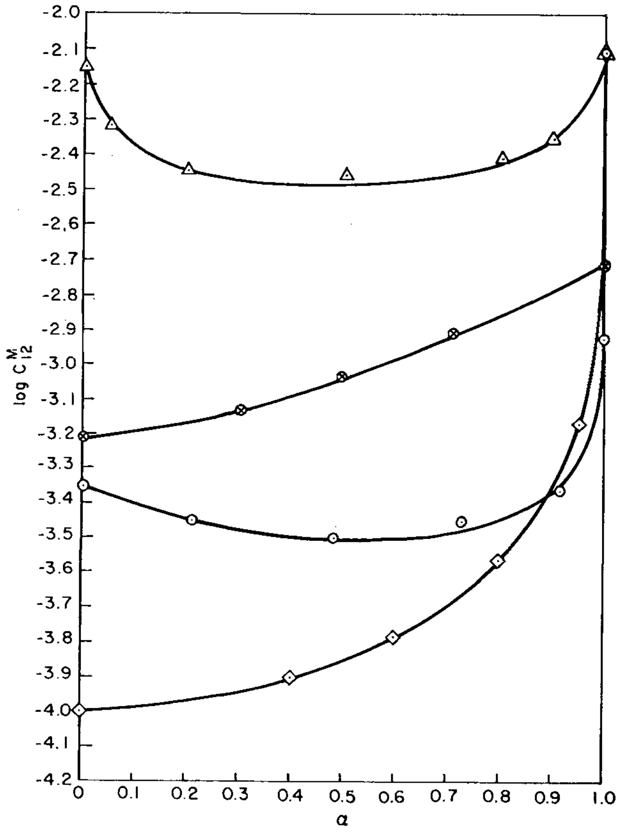

FIG. 1. Synergism in mixed micelle formation. Logarithm of the cmc, C_{12}^M, of the mixture vs α, the mole fraction of surfactant 1 in the total surfactant in the solution phase. △ $C_{12}H_{25}SO_4Na/C_8H_{17}(OC_2H_4)_4OH$ at 25 C. $\beta^M = -3.1$; $|\ln C_1^M/C_2^M| = 0.13$. Data from reference 7. ⊕ $C_{10}H_{21}S(O)CH_3/C_{10}H_{21}(OC_2H_4)_3$ at 25 C. $\beta^M = -0.09$; $|\ln C_1^M/C_2^M| = 1.18$. Data from reference 8. ⊙ $(C_{12}H_{25}SO_4)_2M/C_{12}H_{25}(OC_2H_4)_{49}OH$ at 30 C (M = Zn^{++}, Mn^{++}, Cu^{++}, Mg^{++}. $\beta^M = -3.1$; $|\ln C_1^M/C_1^M| = 1.0$. Data from reference 9. ◈ $C_{12}H_{25}SO_4Na/C_{12}H_{25}(OC_2H_4)_8OH$ at 25 C. $\beta^M = -3.9$; $|\ln C_1^M/C_2^M| = 4.4$. Data from reference 7.

The conditions for synergism in mixed micelle formation are (1): (a) β^M must be negative; and (b) $|\ln (C_1^M/C_2^M)| < |\beta^M|$. Figure 1 shows the cmc as a function of α in a number of binary systems of surfactants. It illustrates the requirement that $|\ln C_1^M/C_2^M|$ must be less than $|\beta^M|$ for synergism to occur.

At the point of maximum synergism in mixed micelle formation, the mole fraction, α_*^M of surfactant 1 in the solution phase equals its mole fraction in the mixed micelle and is given by the relationship:

$$\alpha_*^M = X^M = \frac{\ln (C_1^M/C_2^M) + \beta^M}{2\beta^M} \qquad [3]$$

where X^M is the mole fraction of surfactant 1 in the mixed micelle. The cmc at the point of maximum synergism, i.e., the minimum total mixed surfactant concentration in the solution phase required for mixed micelle formation, $C_{12,\min}^M$, is given by the relationship:

$$C_{12,\min}^M = C_1^M \exp \left[\beta^M \left(\frac{\beta^M - \ln C_1^M/C_2^M}{2\beta^M}\right)^2\right] \qquad [4]$$

Table I lists some data illustrating these relationships.

Synergism in Surface Tension Reduction Efficiency

The efficiency of surface tension reduction by a surfactant has been defined (2) as the solution phase concentration required to produce a given surface tension (reduction). Synergism in this respect is present in a binary mixture of surfactants when a given surface tension (reduction) can be attained at a total mixed surfactant concentration lower than that required of both surfactants in the mixture. We have shown (1) mathematically that the conditions for synergism in this respect are: (a) β must be negative; and (b) $|\ln C_1^\circ/C_2^\circ| < |\beta|$, where C_1° and C_2° are the solution phase concentrations of pure, individual surfactants 1 and 2, respectively, required to attain a given surface tension (reduction). The total mixed surfactant concentration, C_{12}, required to give the same surface tension (reduction) is used together with C_1° and C_2° in Equations 1 and 2 to calculate β, the parameter that is related to molecular interaction in systems showing synergism in this respect. Table III lists some data for the system: $C_{12}H_{25}SO_3K/C_{12}H_{25}N(CH_3)_2O$ (6) in which this type of synergism is present. It also includes data for some hypothetical systems in which the values of C_1^M, C_2^M, A_1°, A_2°, γ_1^M, and γ_2^M (i.e., the cmc, area

TABLE I

Synergism in Mixed Micelle Formation[a] at 25 C

$C_{12}SO_4Na/C_{12}(EO)_8$[b] in 0.5 M NaCl $\beta^M = -2.6$			$C_{12}SO_4Na/C_8(EO)_4$[c] $\beta^M = -3.1$		
α	X^M	$C_{12}^M \times 10^5$ (mol dm^{-3})	α	X^M	$C_{12}^M \times 10^3$ (mol dm^{-3})
0	0	6.0	0	0	7.0
0.20	0.17	5.4	0.05	0.21	4.8
0.40	0.26	5.9	0.20	0.35	3.6
0.60	0.34	7.6	0.50	0.49	3.5
0.80	0.44	10.5	0.80	0.62	3.9
0.90	0.53	13.6	0.90	0.70	4.5
1	1	41.0	1	1	8.0
α_*^M(calc.) = 0.13			α_*^M(calc.) = 0.48		
$C_{12,\min}^M$(calc.) = 5.7×10^{-5}			$C_{12,\min}^M$(calc.) = 3.4×10^{-3}		

[a] Data from reference 7.

[b] $CH_3(CH_2)_{11}SO_4Na/C_{12}H_{25}(OC_2H_4)_8OH$

[c] $CH_3(CH_2)_{11}SO_4Na/C_8H_{17}(OC_2H_4)_4OH$

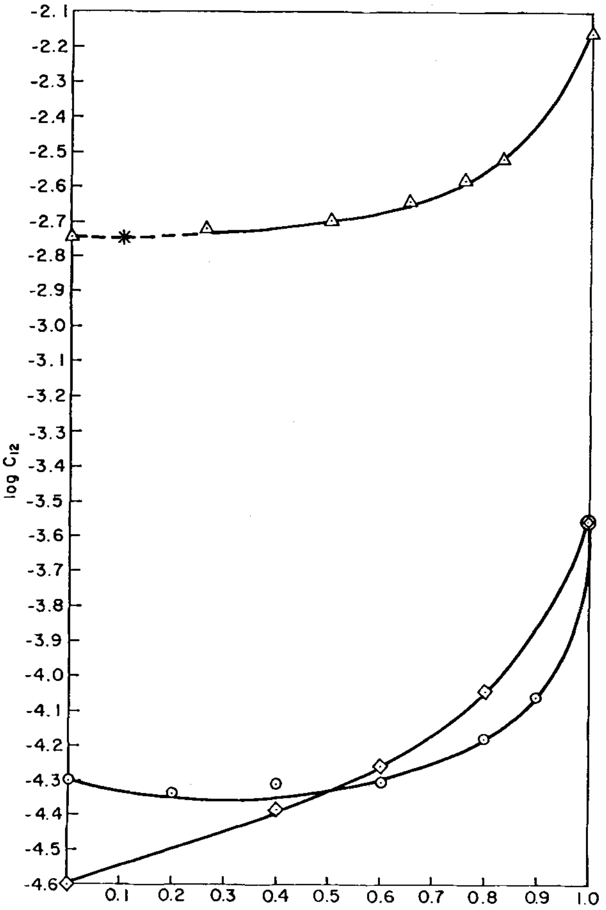

FIG. 2. Synergism in surface tension reduction efficiency. Logarithm of the total surfactant concentration, C_{12}, required to attain a given surface tension vs α, the mole fraction of surfactant 1 in the total surfactant in the solution phase. △ $C_{12}H_{25}SO_4Na/C_8H_{17}OH$ at 23 C to produce γ = 40.3 mN m^{-1} (dyne cm^{-1}). β = -1.7; $|\ln C_1^\circ/C_2^\circ|$ = 1.36. Data from reference 10. ⊙ $C_{12}H_5SO_4Na/C_{12}H_{25}(OC_2H_4)_8OH$ in 0.5 M NaCl at 25 C to produce γ = 36 mN m^{-1}. β = -3.2; $|\ln C_1^\circ/C_2^\circ|$ = 1.7. Data from reference 7. ◈ $C_{12}H_{25}SO_4Na/C_{14}H_{29}SO_4Na$ in 0.5 M NaCl at 25 C to produce γ = 36 mN m^{-1}. β = -0.1; $|\ln C_1^\circ/C_2^\circ|$ = 2.4. Data from reference 7.

the mixed monolayer at the aqueous solution/air interface.

Figure 2 shows the total surfactant concentration required to attain a given surface tension (reduction) as a function of α in a number of binary surfactant systems. It illustrates the requirement that $|\ln C_1^\circ/C_2^\circ|$ must be less than $|\beta|$ for synergism in surface tension reduction efficiency to occur.

At the point of maximum synergism, the mole fraction, α_*, of surfactant 1 in the solution phase equals its mole fraction in the mixed monolayer at the aqueous solution/air interface, and is given by the relationship:

$$\alpha_* = X = \frac{\ln (C_1^\circ/C_2^\circ) + \beta}{2\beta} \qquad [5]$$

where X is the mole fraction of surfactant 1 in the mixed monolayer. The minimum surfactant concentration in the solution phase, $C_{12,\min}$, required to attain a given surface tension (reduction) is given by the expression:

$$C_{12,\min} = C_1^\circ \exp \left[\beta\left(\frac{\beta - \ln C_1^\circ/C_2^\circ}{2\beta}\right)^2\right] \qquad [6]$$

Table II lists some data illustrating these relationships.

TABLE II

Synergism in Surface Tension Reduction Efficiency at 25 C

	$C_{12}SO_4Na/C_{12}(EO)_8$[a] in 0.5 M NaCl β = -3.2; γ = 36 mN m^{-1}	
α	X	$C_{12} \times 10^5$ (mol dm^{-3})
0	0	5.0
0.20	0.22	4.6
0.40	0.30	4.9
0.60	0.38	5.0
0.80	0.47	6.5
0.90	0.55	8.7
1	1	28

α_*(calc.) = 0.23
$C_{12,\min}$(calc.) = 4.2 × 10^{-5}

[a] Data from reference 7.

TABLE III

Synergism in Surface Tension Reduction Effectiveness[a]

α	$f_{1,c}X_c$	$f_1^MX^M$	$\gamma_{12,c}$ (mN m^{-1}) (calc)	Synergism
System: $C_{12}H_{25}SO_3K/C_{12}H_{25}N(CH_3)_2O$; β^M = -16.5; β = -21.6				
0.1	0.0012	0.0060	21.2	yes
0.5	0.00375	0.0176	21.6	yes
0.9	0.0184	0.0447	22.3 (23.6, exptl)	yes
System: hypothetical; β^M = -16.5; β = -18.0				
0.1	0.0041	0.0060	31.6	yes
0.5	0.0120	0.0176	31.6	yes
0.9	0.0311	0.0447	31.7	yes
System: hypothetical; β^M = -16.5; β = -16.5				
0.1	0.0068	0.0060	35.9	no
0.5	0.0195	0.0176	35.7	no
0.9	0.0489	0.0447	35.6	no

[a] Data from reference 6; γ_1^M = 34.8 mN m^{-1}; γ_2^M = 37.9 mN m^{-1}.

Synergism in Surface Tension Reduction Effectiveness

The effectiveness of surface tension reduction has been defined (3) as the surface tension reduction attained at the cmc. Synergism in this respect is present when any mixture at its cmc reaches a surface tension that is lower than that attained at the cmc of the individual surfactants. We have shown mathematically (1) that the condition for synergism in this respect is:

$$f_{1,c} \cdot X_c < f_1^M \cdot X^M, \qquad [7]$$

where $f_{1,c}$ and f_1^M are the activity coefficients of surfactant 1 in the mixed monolayer and in the mixed micelle, and X_c and X^M its respective mole fractions there, all at the cmc of the mixture. The activity coefficients are calculated by the relationships (4,5):

$$f_{1,c} = \exp \beta(1-X_c)^2 \qquad [8]$$

$$f_1^M = \exp \beta^M(1-X^M)^2 \qquad [9]$$

from which we obtain:

$$\beta < \beta^M\left[\frac{(1-X^M)^2}{(1-X_c)^2}\right] + \frac{\ln \frac{X^M}{X_c}}{(1-X_c)^2} \qquad [10]$$

When $X_c \geq X^M$, β must be < β^M for synergism of this type to occur.

Currently, there are almost no data in the literature from which calculations of β, β^M, X_c, and X^M can be made on

TABLE IV

Values of the Molecular Interaction Parameters, β^M and β, at 25 C

Surfactant pair	Medium	β^M	β	Reference
$C_{12}SO_4/C_8(EO)_4$	H_2O	-3.1	–	7
$C_{12}SO_4/C_8(EO)_6$	H_2O	-3.4	–	7
$C_{12}SO_4/C_8(EO)_{12}$	H_2O	-4.1	–	7
$C_{12}SO_4/C_{12}(EO)_5$	H_2O	-2.6	–	11
$C_{12}SO_4/C_{12}(EO)_8$	H_2O	-3.9	–	7
$C_{12}SO_4/C_{12}(EO)_8$	0.5 M NaCl	-2.6	-3.2	7
$C_{18}N(CH_3)_2Cl/C_{12}(EO)_8$	0.0024 N NaCl	-3.1	–	7
$C_{20}N(CH_3)_2Cl/C_{12}(EO)_8$	H_2O	-4.4	–	7
$C_{16}N(CH_3)_2Cl/C_{12}(EO)_8$	0.1 N NaCl	-0.83	–	7
$C_{12}PyrBr$[a]$/C_{12}(EO)_8$	H_2O	-0.85	-1.0	12
$C_{12}(EO)_3/C_{12}(EO)_8$	H_2O	-0.41	-0.17	4
$C_{10}SO_4Na/C_8(EO)_{12}$	0.25 N NaCl	-2.0	–	7
$C_{15}SO_4Na/C_{10}(EO)_6$	H_2O	-4.4	–	7
$C_{10}SO_4Na/C_{10}N(CH_3)_3Br$	H_2O	-18.5	–	5,13
$C_{12}SO_3K/C_{12}N(CH_3)_2O$	H_2O	-16.5	-21.6	6
$C_{12}SO_3Na/C_{12}(EO)_8$	H_2O	–	-1.6	12
$C_{12}SO_3Na/C_{12}(EO)_8$	0.1 M NaBr	–	-2.5	4
$C_{12}PyrBr$[a]$/C_{12}(EO)_8$	0.1 M NaBr	–	-0.79	4
$C_{12}SO_4/C_8H_{17}OH$	H_2O	–	-1.7[b]	10
$C_{10}S(O)CH_3/C_{10}(EO)_3$	H_2O	-0.09	-0.15	8

[a] N-dodecylpyridinium bromide

[b] 23 C

per molecule and surface tension at the cmc for the individual surfactants) and the value of β^M are identical with those in the real system, while the value of β is changed.

Values of $f_{1,c}X_c$, $f_1^M X^M$, and $\gamma_{12,c}$ (the surface tension of the mixture at its cmc), at various values of α in Table III are obtained by a procedure described elsewhere (1). The necessary experimental data are: (a) the surface tension/log concentration curves for the two individual surfactants in the vicinity of their cmc, including the portion of each for some distance below the cmc, (b) the cmc, C_{12}^M, of at least one mixture of the two surfactants, and (c) the concentration, C_{12}, of at least one mixture of the two surfactants required to produce a given surface tension attained by both individual surfactants.

From the data in Table II, it is apparent that $f_{1,c}X_c$ must be $< f_1^M X^M$ for synergism in surface tension effectiveness to occur. As the negative value of β becomes closer to that of β^M, the synergistic effect becomes smaller and eventually disappears.

Effect of Surfactant Chemical Structure on Synergism

Since the synergistic relationships all involve the molecular interaction parameters, β or β^M, it is to be expected that changes in the chemical structures of the two surfactants involved will affect the extent of the synergistic relationship between them. Thus, from Equations 4 and 6, we obtain the respective ratios:

$$\frac{C_{12,\min}^M}{C_1^M} = \exp\left[\beta^M\left(\frac{\beta^M - \ln C_1^M/C_2^M}{2\beta^M}\right)^2\right]$$

and

$$\frac{C_{12,\min}}{C_1^\circ} = \exp\left[\beta\left(\frac{\beta - \ln C_1^\circ/C_2^\circ}{2\beta}\right)^2\right]$$

When the subscript 1 refers to the more surface-active surfactant (i.e., with the lower C_1^M or C_1° value), the above relationships indicate the extent of synergism in mixed micelle formation and in surface tension reduction efficiency, respectively. The lower the ratio, the greater the synergistic effect. We can see from these relationships that: (a) the more negative the value of β or β^M and (b) the smaller the absolute value of $\ln C_1^M/C_2^M$ or $\ln C_1^\circ/C_2^\circ$, the greater will be the extent of synergism. For a given value of β or β^M, maximum synergism will occur when $\ln C_1^M/C_2^M$ or $\ln C_1^\circ/C_2^\circ = 0$, that is, when both surfactants have the same cmc or surface tension reducing efficiency.

Currently, there is only a limited amount of data available from which the values of β or β^M can be calculated, mainly data on mixed micelle formation. As a result, very few generalizations regarding the effect of changes in the chemical structure of the surfactants on the values of β and β^M can currently be made. Table IV lists some values of β and β^M from the available data.

Based on the values listed in Table IV, the following tentative generalizations can be made:

(a) For anionic-polyoxyethylenated nonionic pairs, the value of β^M becomes more negative as the number of oxyethylene units in the nonionic increases.

(b) For ionic-polyoxyethylenated nonionic pairs, the value of β^M becomes less negative with increase in the electrotype content of the solution.

(c) For the following pairs with similar hydrophobic groups, the values of β and β^M become more negative in the order: polyoxyethylenated nonionic–polyoxyethylenated nonionic < polyoxyethylenated nonionic–cationic < polyoxyethylenated nonionic–anionic << anionic–cationic.

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