Selection of Surfactant Pairs for Optimization of Interfacial Properties

Milton J. Rosen
Surfactant Research Institute, Brooklyn College of the City University of New York, Brooklyn, New York 11210

Guidelines are provided for the selection of surfactant pairs when synergism in various interfacial properties in aqueous media is desired. To maximize the reduction of the critical micelle concentration, the two surfactants should show strong attractive interaction in the mixed micelle; in order to maximize efficiency in surface tension reduction, strong interaction in the mixed monolayer at the aqueous solution/air interface (large negative β values is needed). The more surface-active material should predominate in the mixture. When interaction is not strong, the two surface-active materials used should have approximately equal surface activities and should be used at equimolar concentration in the aqueous phase. To minimize the surface tension (γ) of the solution, the surfactant-surfactant attractive interaction in the mixed monolayer at the aqueous solution/air interface must exceed that in the mixed micelle. Optimization can be achieved by using two surfactants with approximately equal γ values at their respective critical micelle concentrations (CMC's). When these γ values are not equal, the surfactant with the higher γ value at its CMC should have the smaller area/molecule at the surface. The greater the difference between attractive interaction at the interface and in the micelle, the lower the value of the surface tension.

It is well known that mixtures of surfactants often have interfacial properties that are more pronounced than those of the individual interfacial-active components of the mixture by themselves. When this exists, the mixture is said to exhibit synergism. The selection of the components of the mixture is generally done by trial-and-error. This discussion describes how this selection, for mixtures of two surfactants, can be done in a rational, scientific fashion. The two fundamental properties of solutions of surfactant mixtures are mixed interfacial film formation and mixed micelle formation. Synergism in mixed monolayer and mixed micelle formation has been shown to be related to synergism in various performance properties, such as foaming (1), wetting, emulsification, detergency (2), and flotation separation of minerals (3). This discussion will cover the selection of surfactant pairs for mixed micelle formation in aqueous solution, and for mixed monolayer formation at the aqueuos solution/air interface and its consequent reduction of surface tension.

General considerations. In order for a mixture of two surfactants to exhibit synergism, there must be an attractive interaction between the two surfactants. Attractive interactions between two surfactants can be due either to mutual electrostatic attraction of oppositely-charged hydrophilic head groups, or to Van der Waals attraction of their hydrophobic groups. Electrostatic charges will generally produce the strongest interactions. Thus, interaction in surfactant pairs containing an anionic surfactant decreases in the order: anionic-cationic > anionic-zwitterionic capable of acquiring a proton > anionic-polyoxyethylenated nonionic > anionic-other nonionic surfactant. For surfactant pairs containing a cationic surfactant, the order is: cationic-anionic > cationic-zwitterionic capable of losing a proton > cationic-nonionic surfactant (4). Similarly charged surfactants have only a weak attraction for each other, except under special conditions. Surfactant-surfactant attraction generally increases with an increase in the chain length when both hydrophobic groups are straight chain. Interaction at a planar interface shows a maximum when both chains are of equal length, while interaction in the mixed micelle appears to increase monotonically with an increase in the total number of carbons in the hydrophobic groups.

Interactions between surfactants are measured by the so-called β-parameters: β^σ for interaction in the mixed monolayer at the aqueuos solution/air interface; β^M for interaction in the mixed micelle in the aqueous media; β^σ_{LL} for the Ls mixed monolayer at the liquid/liquid interface; and β^σ_{LS} for the mixed monolayer at the liquid/solid interface. The more negative the value of the β parameter, the stronger the attractive interaction. β^σ and β^M values can be easily determined (see Appendix) from surface tension-concentration curves of the individual surfactants and at least one mixture of them at a fixed molar ratio of the two surfactants; β^σ_{LL}, from interfacial tension-concentration curves; β^σLS from adhesion tension—or surface tension and contact angle—concentration curves. β parameters can also be estimated from a published table (5a) containing values for more than 100 surfactant pairs.

Synergism in mixed micelle formation: Reduction of the critical micelle concentration. When it is desired to reduce the CMC of a surfactant solution, for example, to induce solubilization at a lower surfactant concentration, then a surfactant pair can be chosen that exhibits synergism in this respect. That is, the CMC of a solution of the two surfactants is lower than the CMC of either surfactant in the same medium.

The conditions for this to exist (6) are:

1. β^M must be negative;
2. β^M, as an absolute number, must be greater than ln (C_1^M/C_2^M), as an absolute number, i.e., $/\beta^M >$.

Ln (C_1^M/C_2^M), where β^M is the parameter for mixed micelle formation, obtained from the CMC values, C_1^M, C_2^M, for surfactant 1 and 2, respectively, and at least one mixture of them, C_{12}^M. The first condition means that the two surfactants must attract each other in the mixed micelle; the second condition, that this attraction must be greater than the difference between the natural logs of their CMC values.

The ratio of the two surfactants that will yield the minimum CMC for this system is obtained from the relationship:

$$\alpha^{*,M} = \frac{\text{Ln}\,(C_1^M/C_2^M)+\beta^M}{2\beta^M} \qquad [1]$$

where $\alpha^{*,M}$ is the mole fraction of the surfactant 1, in the total mixed surfactant in the aqueous phase (at the point of maximum synergism in mixed micelle formation, $\alpha^{*,M}$ also equals the mole fraction, $X^{*,M}$, of surfactant 1 in the mixed micelle). The minimum CMC of the mixed system, $C^M_{12,\min}$, is given by the equation:

$$C^M_{12,\min} = C_1^M \exp\left[\beta^M\left(\frac{\beta^M - \mathrm{Ln}\,(C_1^M/C_2^M)}{2\beta^M}\right)^2\right] \qquad [2]$$

Note that all these relationships require knowledge of the CMC values of the two individual surfactants and the value of β^M only. Therefore, for maximizing synergism in mixed micelle formation, a surfactant pair should be chosen with strong (electrostatic)interaction between them (large negative β^M value), if possible. From equation [1], since β^M is negative, $\alpha^{*,M}$ decreases with an increase in $\mathrm{Ln}(C_1^M/C_2^M)$, meaning that the surfactant with the larger CMC value must always be used in smaller molar quantity than the surfactant with the smaller CMC value in order to achieve maximum synergism. However, the larger the (negative) value of β^M is relative to Ln (C_1^M/C_2^M), the closer will the molar ratio to achieve maximum synergism approach equimolar ($\alpha^{*,M} = 0.5$). As can be derived from equation [2], the larger the difference between β^M and Ln (C_1^M/C_2^M), the smaller will be the CMC at the point of maximum snyergism.

When interaction between the two surfactants is weak, a pair with approximately equal CMC values ($C_1^M \approx C_2^M$) should be chosen (condition 2) if possible, since under this condition Ln $(C_1^M/C_2^M) \approx 0$ and any negative β^M value will produce synergism. When $C_1^M \approx C_2^M$, then $\alpha^{*,M} \approx 0.5$ (equation [1]), meaning that the two surfactants should be mixed in equimolar amounts to achieve maximum synergism. When $C_1^M \approx C_2^M$, then C^M_{12} min $\approx C_1^M \exp \beta^M/4$. Here, the more negative the value of β^M, the smaller the minimum CMC of the system.

Synergism in mixed monolayer formation: Efficiency in surface tension reduction. When it is desired to use less surfactant to achieve a given surface tension reduction of the solvent (e.g., water), this can be achieved by use of a surfactant mixture that shows synergism in surface tension reduction efficiency. That is, the surfactant mixture produces a lower surface tension than is attainable by either surfactant by itself. The conditions for this to exist are (6):

1. β^σ must be negative;
2. $|\beta^\sigma| > |\,\mathrm{Ln}\, C_1^o/C_2^o)|$.

C_1^0, C_2^0 are the molar concentrations of individual surfactants 1 and 2, respectively, in the solution phase that is needed to produce the same desired surface tension. The values are determined from the γ vs ln (or log) molar concentration curves of the two surfactants, as shown in Figure 1. The first condition means that the two surfactants must have an attraction for each other; the second that this attraction must be stronger than the natural logarithm of the ratio of the concentrations needed to produce the same surface tension (reduction) of the solvent. Therefore, to maximize this type of synergism, two materials with strong (electrostatic) attraction for each other (large negative β^σ value) should be used. If one of the surfactants (surfactant 1) in the composition is fixed, surfactant 2 should, if possible, have a C_2^0 value lower than C_1^0 (if synergism is exhibited, the total mixed surfactant concentration, C_{12}, to attain the desired γ value will always be less than C_2^0).

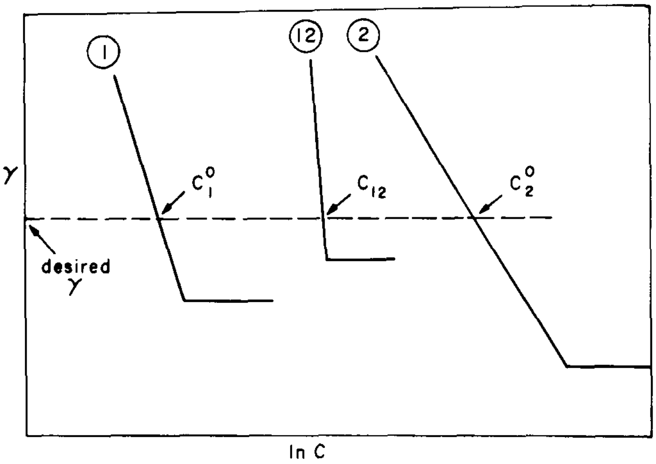

FIG. 1. Evaluation of C_1°, C_2° for surfactants (1) and (2), and $C_{1,2}$ for their mixture (1,2) at some fixed α value.

On the other hand, if it is not possible to use two surfactants with strong attraction for each other, then surfactant 2 should be selected with a C_2^0 value approximately equal to C_1^0. Under this condition, Ln $C_1^0/C_2^0 \approx 0$, and any negative β^σ value will produce synergism.

At the point of maximum synergism, the mole fraction, α^*, of surfactant 1 in the total surfactant used in the solution phase is given by the expression (6):

$$\alpha^* = \frac{\mathrm{Ln}\,(C_1^0/C_2^0)+\beta^\sigma}{2\beta^\sigma} \qquad [3]$$

This is also the value of X^*, the mole fraction of surfactant 1 in the total surfactant in the mixed monolayer at the interface at the point of maximum synergism. When $C_1^0 \approx C_2^0$, then α^* is ≈ 0.5, meaning that equimolar amounts of the two surfactants should be mixed to give maximum synergism. When $C_1^0 \neq C_2^0$, α^* decreases with Ln (C_1^0/C_2^0), meaning that the less surface-active surfactant (with the larger value of C^o) must be used in smaller amounts to get maximum synergism.

When attractive interaction between the two surfactants is strong, and β^σ is much larger than Ln (C_1^o/C_2^0), then $\alpha^* \approx 0.5$ and equimolar amounts will give maximum synergism, irrespective of the (C_1^0/C_2^0) ratio.

The minimum surfactant in the solution phase required to produce a given surface tension value is given by the expression:

$$C_{12,\min} = C_1^0 \exp\left[\beta^\sigma\left(\frac{\beta^\sigma - \mathrm{Ln}\,(C_1^0/C_2^0)}{2\beta^\sigma}\right)^2\right] \qquad [4]$$

The larger the difference between β^σ and Ln (C_1^0/C_2^0) for a given value of β^σ, the smaller will be $C_{12,\min}$. When $C_1^0 = C_2^0$, then $C_{12,\min} = C_1^0 \exp \beta^\sigma/4$. In this case, the larger the negative value of β^σ, the smaller will be $C_{12\min}$.

In summary: For maximizing synergism in both critical micelle concentration reduction and surface tension reduction efficiency, choose a surfactant pair with strong electrostatic interaction between their hydrophilic head groups, and use more of the more surface-active than of the less surface-active material. The greater the difference between the surfactant-surfactant attractive interaction (negative β^σ of β^M value) and the surface activity difference between the two surfactants (Ln C_1^0/C_2^0 or Ln C_1^M/C_2^M value), the greater the synergistic effect. If their attractive interaction is much greater than their surface activity difference, then use them in equimolar amounts. If surfactant-surfactant interaction is weak, use two surfactants of approximately equal surface activity in approximately equimolar amounts.

Synergism in surface tension reduction effectiveness. When it is desired to reduce the surface tension of an aqueous solution of a surfactant below the value attainable with a particular surfactant, then a second surfactant can be added to produce a mixture showing synergism in surface tension reduction effectiveness. This exists when the mixture can reach a surface tension value lower than that attainable with either surfactant by itself. (note, however, that hydrocarbon-chain surfactant mixtures cannot reduce the surface tension of water below about 22 dynes/cm at 25°C).

The first condition for this to exist is (5b,7):

1. that β^σ - β^M must be negative. This means that the two surfactants must have greater attraction for each other in the mixed monolayer at the interface than in the mixed micelle in the solution phase. This is generally the case when the two surfactants are oppositely charged and have equal hydrophobic chain lengths.
2. $|\beta^\sigma - \beta^M|$ must be greater than $|\ln (C^o/C^M)|$, where C^o and C^M are molar concentrations for the surfactant with the higher γ value at its CMC (C^M); C^o is obtained by linear extension of the γ vs ln C curve of that surfactant (Fig. 2) to a γ value equal to that of the second surfactant at its CMC.

From Figure 2 it is evident that ln (C^o/C^M) equals 0 when both surfactants have the same γ value at their respective CMCs. Under this condition, any negative value of $(\beta^\sigma - \beta^M)$ will yield synergism in this respect. From Figure 2, it is also apparent that the steeper the slope of the surfactant with the higher surface tension at its CMC, the smaller the value of ln (C^o/C^M) will be. Since a steeper slope in such a plot means a smaller area per molecule at the aqueous solution/air interface, in a surfactant pair chosen for this purpose, the surfactant with the higher value of γ at its CMC should be the one with the smaller area/molecule at the interface.

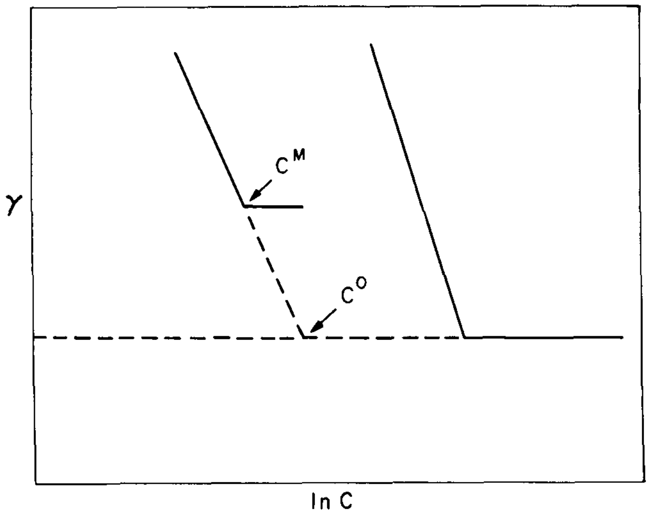

FIG. 2. Evaluation of ln (C^o/C^M) by extension of linear portion of γ vs ln C plot of surfactant with higher γ value at its CMC.

The minimum surface tension, γ^*_{cmc}, of the surfactant mixture at its CMC is given by the expression (7):

$$\gamma^*_{cmc} = \gamma^o_{cmc} - K\,(\beta^\sigma - \beta^M)(1 - X^*)^2 \qquad [5]$$

where γ_{cmc} is the surface tension of either surfactant at its CMC, K the slope of its γ vs ln C plot and X^* its molar ratio in the total surfactant at the interface. From equation [5], the greater the (negative) value of $\beta^\sigma - \beta^M$, the smaller will be the minimum surface tension of the system.

When the two surfactants interact strongly with each other (have large negative β^σ or β^M values), then approximately equimolar quantities of them may be present at the interface or in the mixed micelle at the point of maximum synergism, i.e., $X_1^* \approx 0.5$. Under this condition, the ratio of the two surfactants to be mixed for minimum surface tension value may be estimated (see Appendix) from the relationships:

$$\alpha = \frac{C_1^0}{C_1^0 + C_2^0} \qquad [6]$$

or

$$\alpha^M = \frac{C_1^M}{C_1^M + C_2^M} \qquad [7]$$

APPENDIX

The basic equation for mixed monolayer formation is (4):

$$\frac{X_1^2 \ln (\alpha\, C_{12}/X_1 C_1^0)}{(1 - X_1)^2 \ln [(1 - \alpha)\, C_{12}/(1 - X_1) C_2^0)]} = 1 \qquad [8]$$

and for mixed micelle formation:

$$\frac{(X_1^M)^2 \ln (\alpha\, C_{12}^M/X_1^M C_1^M)}{(1 - X_1^M)^2 \ln [(1 - \alpha) C_{12}^M/(1 - X_1^M) C_2^M]} = 1 \qquad [9]$$

where X_1, X_1^M are the mole fractions of surfactant 1 in the total mixed monolayer and mixed micelle, respectively; α is the mole fraction of surfactant 1 in the total mixed surfactant in the solution phase; C_1^0, C_2^0, and C_{12} are the molar concentrations in the solution phase of surfactant 1, surfactant 2, and their mixture at mole ratio, α, required to produce a given γ value; C_1^M, C_2^M, and C^M_{12} are their respective CMC values.

For evaluation of β^σ, equation [8] is solved numerically for X_1, which is then substituted in equation [10]:

$$\beta^\sigma = \frac{\ln (\alpha\, C_{12}/X_1 C_1^0)}{(1 - X_1)^2} \qquad [10]$$

To evaluate β^M, equation [9] is solved numerically for X_1^M, which is then substituted in equation [11].

$$\beta^M = \frac{\ln (\alpha C^M{}_{12}/X_1{}^M C_1{}^M)}{(1 - X_1{}^M)^2} \qquad [11]$$

Calculation of α for equimolar concentrations of both surfactants at the interface or in the mixed micelle. It is convenient to evaluate β^σ (or β^M) when X_1 (or $X_1{}^M$) equals 0.5, since interactions are frequently at their maximum at that mole fraction. Substituting $X_1 = 0.5 = (1 - X_1)$ in equation [8],

$$\alpha = \frac{C_1^0}{C_1^0 + C_2^0} \qquad [6]$$

Similarly, substituting $X_1{}^M = 0.5 = (1 - X_1{}^M)$ in equation [9],

$$\alpha^M = \frac{C_1{}^M}{C_1{}^M + C_2{}^M} \qquad [7]$$

Thus, the ratio of the two surfactants to be mixed for obtaining equimolar amounts of the two materials in the mixed monolayer or in the mixed micelle is easily calculated from γ vs log C (or ln C) data for the individual surfactants.

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