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# A Theoretical Analysis of Synergistic Effects in Mixed Surfactant Systems

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Synergistic effects in mixed binary surfactant systems have been investigated by analyzing the main contributions to the free energy of forming a mixed surfactant aggregate. We show that a nonlinear behavior of the critical micelle concentration (cmc) with respect to the surfactant composition of the aggregates is determined by a nonlinear behavior of the free energy per aggregated surfactant. It appears that synergistic effects are due mainly to entropic free energy contributions related with the surfactant headgroups. For a mixture of a monovalent ionic and a nonionic surfactant in the absence of added salt we obtain, entirely because of electrostatic reasons, a negative deviation from ideal behavior of the cmc vs the aggregate composition corresponding to an interaction parameter  $\beta \approx -1$ , whereas  $\beta$  values on the order of  $-5$  or even less can arise for mixtures of two ionic surfactants with the same charge number but with different hydrocarbon moieties. Moreover, we introduce a novel expression for the free energy of mixing aggregated surfactant headgroups with surrounding solvent molecules. Accordingly, synergistic effects arise as a result of different headgroup cross-section areas in mixtures of two nonionic surfactants with rigid headgroups. These effects are found to be rather small, with  $0 > \beta > -1$ , when the difference in headgroup size is modest but can become more significant when the size difference is larger. In mixtures of an ionic and a nonionic surfactant with different headgroup cross-section areas the two contributions to synergistic effects always enhance one another and, hence,  $\beta$  values below  $-1$  are obtained. Generally, the synergistic effects tend to increase with increasing asymmetry between the two surfactants.

## Introduction

Above a certain concentration, the critical micelle concentration (cmc), surfactant molecules are known to self-assemble, forming aggregates of various structure, e.g. globular or rod-shaped micelles or different bilayer structures. The process of assembling free surfactant monomers to generate aggregates is, of course, entropically unfavorable as the entropy of mixing surfactant and solvent molecules then decreases. This unfavorable change in entropy of mixing decreases with increasing surfactant concentration  $c_{\text{surf}}$  or, otherwise expressed, the chemical potential of free surfactant monomers increases with increasing  $c_{\text{surf}}$  and, when the chemical potential of the free monomers becomes equal to the corresponding quantity in the surfactant aggregates, the latter start to form. The surfactant concentration where aggregates start to appear is known as the cmc; above this concentration aggregates and free surfactant monomers coexist.

When a surfactant and a cosurfactant are added, mixed aggregates form and the cmc becomes a function of the surfactant composition. For a mixture of two slightly differing surfactants, the cmc has been observed to depend linearly on the composition of the micelles, i.e.

$$\text{cmc}(x_1) = x_1 \text{cmc}_1 + (1 - x_1) \text{cmc}_2 \quad (1)$$

where  $x_1$  denotes the mole fraction of one of the surfactants in the aggregates, and  $\text{cmc}_1$  and  $\text{cmc}_2$  are the cmcs of pure Surfactant 1 and 2, respectively. Surfactant systems for which the cmc is seen to obey eq 1 are often referred to as ideal surfactant mixtures. The overall mole fraction of

Surfactant 1 at the cmc equals  $y_1 \equiv \text{cmc}_1^m / (\text{cmc}_1^m + \text{cmc}_2^m)$ , where  $\text{cmc}_1^m$  and  $\text{cmc}_2^m$  are the free monomer concentrations of Surfactant 1 and 2 at  $\text{cmc}(x_1) = \text{cmc}_1^m + \text{cmc}_2^m$ , since by definition, the amount of surfactant existing as free monomers is much larger than the amount of aggregated surfactant at cmc. As a result, we can also write

$$\frac{1}{\text{cmc}(y_1)} = \frac{y_1}{\text{cmc}_1} + \frac{(1 - y_1)}{\text{cmc}_2} \quad (2)$$

for an ideal surfactant mixture.

However, for a number of surfactant mixtures *synergistic effects* are important which means that the cmc deviates appreciably from the behavior predicted by eq 1. To account for these synergistic effects it is customary to write

$$\text{cmc}(x_1) = x_1 f_1(x_1) \text{cmc}_1 + (1 - x_1) f_2(x_1) \text{cmc}_2 \quad (3)$$

where, in accordance with the theory of regular mixtures, activity factor functions are introduced by setting

$$f_1(x_1) = \exp[(1 - x_1)^2 \beta] \quad (4a)$$

and

$$f_2(x_1) = \exp[x_1^2 \beta] \quad (4b)$$

In analogy with the treatment of regular mixtures,  $\beta$  is mostly referred to as the interaction parameter, and its deviation from zero (and, consequently, the deviation of  $f_1$  and  $f_2$  from unity) is commonly assumed to result from specific interactions between the surfactant headgroups. Thus, a negative deviation from ideal behavior of the

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$\text{cmc}(x_1)$  function, corresponding to negative  $\beta$  values, is believed to result from a net attraction between the two different surfactant molecules.

According to eqs 3 and 4, the magnitude of the synergistic effect can be quantified by means of the  $\beta$  parameter. The  $\beta$  values with the largest magnitude observed experimentally have been found for mixtures of an anionic and a cationic surfactant where  $\beta$  is on the order of  $-20$  or even less.<sup>1,2</sup> For mixtures of a monovalent ionic and a nonionic surfactant the  $\beta$  values are, as a rule, considerably smaller and fall in the range  $-5 < \beta < -1$ .<sup>1,2</sup> However, significant synergistic effects have been observed for mixtures of two ionic surfactants with identical headgroups but different hydrocarbon parts.<sup>3–5</sup> The synergistic effect was observed to increase with increasing difference in aliphatic chain length in mixtures of surfactants with identical TAB (= trimethylammonium bromide) headgroups, and values as large as  $\beta = -11$  was found for the mixture of C<sub>6</sub>TAB and C<sub>16</sub>TAB.<sup>4</sup> On the other hand, for mixtures of two nonionic surfactants,  $\beta$  is usually rather small ( $-1 < \beta < 0$ ), but, occasionally, it may be larger.

Below we perform a rigorous derivation of the function  $\text{cmc}(x_1)$  from basic thermodynamic arguments. We also investigate the relative importance in this context of the various contributions to the free energy of forming a surfactant aggregate. Since these free energy contributions for the most part turn out to be of entropic origin, and can be calculated from mean field theories, we argue that synergistic effects mostly are due to entropy contributions to the aggregation free energy rather than to specific interactions among the surfactant headgroups.

Synergistic effects for various surfactant mixtures have previously been calculated by Blankschtein and co-workers from similar thermodynamic assumptions as those we employ below.<sup>6–9</sup> A similar treatment to that of Blankschtein et al. for mixtures of an anionic and a nonionic surfactant has also been carried out by Reif and Somasundaran.<sup>10</sup> However, we have adopted a different approach than what has been done in previous works and derived a general expression for the  $\text{cmc}(x_1)$  function in terms of the nonlinear behavior of one or more free energy contributions. From this general expression we have been able to derive explicit expressions of  $\text{cmc}(x_1)$  for some cases where the synergistic effects are entirely determined by electrostatics. Moreover, we introduce a novel approach for nonionic surfactants by calculating the headgroup free energy contribution from the entropy of mixing headgroups and solvent molecules in the concentrated range.

### Thermodynamics of the Self-Assembly of Mixed Surfactant Aggregates

The work of bringing  $N_1$  and  $N_2$  surfactant molecules present at the chemical potentials  $\mu_1^{\text{free}}$  and  $\mu_2^{\text{free}}$  in the surrounding bulk solution into a surfactant aggregate is

defined by the function

$$E(N_1, N_2, \mu_1^{\text{free}}, \mu_2^{\text{free}}) = G(N_1, N_2) - N_1\mu_1^{\text{free}} - N_2\mu_2^{\text{free}} \quad (5)$$

where  $G(N_1, N_2)$  is the free energy of the aggregate. By minimizing  $E(N_1, N_2, \mu_1^{\text{free}}, \mu_2^{\text{free}})$  with respect to  $N_1$  and  $N_2$  at constant chemical potentials  $\mu_1^{\text{free}}$  and  $\mu_2^{\text{free}}$  the following two equilibrium conditions are obtained

$$\left(\frac{\partial E}{\partial N_1}\right)_{N_2, \mu_1^{\text{free}}, \mu_2^{\text{free}}} = \mu_1^{\text{agg}} - \mu_1^{\text{free}} = 0 \quad (6a)$$

and

$$\left(\frac{\partial E}{\partial N_2}\right)_{N_1, \mu_1^{\text{free}}, \mu_2^{\text{free}}} = \mu_2^{\text{agg}} - \mu_2^{\text{free}} = 0 \quad (6b)$$

where the chemical potentials of aggregated surfactants are defined by  $\mu_{1,2}^{\text{agg}} \equiv (\partial G / \partial N_{1,2})_{N_1, \mu_1^{\text{free}}, \mu_2^{\text{free}}}$ . Hence, the equilibrium values of  $N_1$  and  $N_2$  are obtained from eqs 6a and 6b for given values of  $\mu_1^{\text{free}}$  and  $\mu_2^{\text{free}}$ . Conversely, since the chemical potentials of the free monomers are directly related to the monomer concentrations through  $\mu_{1,2}^{\text{free}} \propto kT \ln c_{1,2}^{\text{free}}$ , one can in principle obtain the free monomer concentrations as functions of  $N_1$  and  $N_2$  from the free energy function  $E(N_1, N_2, \mu_1^{\text{free}}, \mu_2^{\text{free}})$  together with the equilibrium conditions in eqs 6.

Alternatively, we can express the aggregate free energy as a function of the total number of surfactant monomers  $N \equiv N_1 + N_2$ , and the (average) mole fraction of Surfactant 1 in the aggregates  $x \equiv N_1/N$ . Moreover, if we consider the aggregation process at a fixed overall surfactant concentration that corresponds to the cmc, we can write  $E$  as a function of  $N$  and  $x$  as well as of the free monomer concentrations  $\text{cmc}_1^{\text{m}}$  and  $\text{cmc}_2^{\text{m}}$  of Surfactant 1 and 2 at the critical micelle concentration. The number of independent variables may be further reduced by considering the size-independent function  $\epsilon(x, \text{cmc}_1^{\text{m}}, \text{cmc}_2^{\text{m}}) \equiv E_{\bar{N}}(x, \text{cmc}_1^{\text{m}}, \text{cmc}_2^{\text{m}})/\bar{N}$  for a spherical micelle<sup>11</sup> where  $\bar{N}$  is the aggregation number of the equilibrium micelle for which  $E$  reaches a minimum with respect to  $N$ . The aggregate (local) free energy for elongated rods<sup>12</sup> or bilayer vesicles<sup>13</sup> can be written on the form  $E(N) = \alpha + \beta N$ , where  $\alpha \equiv \alpha(x, \text{cmc}_1^{\text{m}}, \text{cmc}_2^{\text{m}})$  is a free energy parameter related to the curvature of the aggregates and  $\beta \equiv \beta(x, \text{cmc}_1^{\text{m}}, \text{cmc}_2^{\text{m}})$  is the free energy per unit area of either an infinitely long cylinder (micelles) or an infinitely large planar bilayer (vesicles). Hence,  $\epsilon \equiv E(N)/N = \beta$  becomes independent of  $N$ , but a function of  $x$ ,  $\text{cmc}_1^{\text{m}}$ , and  $\text{cmc}_2^{\text{m}}$ , in the limit  $N \rightarrow \infty$ .

By minimizing the free energy function  $\epsilon(x, \text{cmc}_1^{\text{m}}, \text{cmc}_2^{\text{m}})$  with respect to the aggregate composition  $x$  we obtain the following equilibrium condition

$$\left(\frac{\partial \epsilon(x = x_1)}{\partial x}\right)_{\text{cmc}_1^{\text{m}}, \text{cmc}_2^{\text{m}}} = 0 \quad (7)$$

where  $x_1$  denotes the equilibrium mole fraction of aggregated Surfactant 1.

(11) Eriksson, J. C.; Ljunggren, S.; Henriksson, U. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 833.

(12) Eriksson, J. C.; Ljunggren, S. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1209.

(13) Bergström, M.; Eriksson, J. C. *Langmuir* **1996**, *12*, 624.

(1) Holland, P. M. In *Mixed Surfactant Systems*, Chapter 2; Holland, P. M., Rubingh, D. N., Eds.; ACS Symposium Series 501; American Chemical Society: Washington, DC, 1992, pp 40.

(2) Jönsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactant and Polymers in Aqueous Solution*; Wiley: Chichester, 1998; Chapter 5.

(3) García-Mateos, I.; Velázquez, M. M.; Rodríguez, L. J. *Langmuir* **1990**, *6*, 1078.

(4) López-Fontán, J. L.; Suárez, M. J.; Mosquera, V.; Sarmiento, F. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3583.

(5) Merta, J.; Stenius, P. Personal communication.

(6) Sarmoria, C.; Puvvada, S.; Blankschtein, D. *Langmuir* **1992**, *8*, 2690.

(7) Shiloach, A.; Blankschtein, D. *Langmuir* **1997**, *13*, 3968.

(8) Shiloach, A.; Blankschtein, D. *Langmuir* **1998**, *14*, 1618.

(9) Shiloach, A.; Blankschtein, D. *Langmuir* **1998**, *14*, 7166.

(10) Reif, I.; Somasundaran, P. *Langmuir* **1999**, *15*, 3411.

Moreover, the magnitude of the minimized free energy is given by a constraint of fixed concentration of aggregated surfactant, i.e.

$$\epsilon(x_1, cmc_1^m, cmc_2^m)/kT = \tilde{a} \quad (8)$$

where  $k$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\tilde{a} = E_N(x = x_1, cmc_1^m, cmc_2^m)/N$  for a spherical micelle and  $\tilde{a} = \beta(x = x_1, cmc_1^m, cmc_2^m)$  for a rod-shaped micelle or a bilayer vesicle.  $\tilde{a}$  is constant with respect to  $x_1$ ,  $cmc_1^m$ , and  $cmc_2^m$  and determined by the overall volume fraction

$$\phi_{tot} \equiv \int_0^N C(N) e^{-E(N)/kT} dN \quad (9)$$

of aggregated surfactant defining the cmc value.

Hence, from the two equations 7 and 8, the two unknown variables  $cmc_1^m$  and  $cmc_2^m$  as well as the total cmc may be calculated for a given composition, i.e.

$$cmc(x_1) \equiv cmc_1^m(x_1) + cmc_2^m(x_1) \quad (10)$$

### Ideal Surfactant Mixtures

Let us consider two surfactants for which all contributions to the free energy per aggregated monomer  $\epsilon$ , except the one which is related to the entropy of mixing the two surfactants ( $= x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)$ ), vary linearly with the aggregate composition  $x_1$ . Then we can write eq 8 as

$$\begin{aligned} \epsilon(x_1)/kT &= x_1 g_1 + (1 - x_1) g_2 - x_1 \ln cmc_1^m - \\ &(1 - x_1) \ln cmc_2^m + x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1) = \tilde{a} \end{aligned} \quad (11)$$

where the constant residual free energies of Surfactant 1 and 2, respectively,  $g_1$  and  $g_2$  are implicitly given by

$$\epsilon(x_1 = 1)/kT = g_1 - \ln cmc_1 = \tilde{a} \quad (12)$$

and

$$\epsilon(x_1 = 0)/kT = g_2 - \ln cmc_2 = \tilde{a} \quad (13)$$

where  $cmc_1 \equiv cmc_1^m(x_1 = 1)$  and  $cmc_2 \equiv cmc_2^m(x_1 = 0)$  are the cmcs of pure Surfactant 1 and 2, respectively.

From eqs 11–13 we set

$$\begin{aligned} \epsilon(x_1)/kT &= x_1 \ln cmc_1 + (1 - x_1) \ln cmc_2 - \\ &x_1 \ln cmc_1^m - (1 - x_1) \ln cmc_2^m + x_1 \ln x_1 + \\ &(1 - x_1) \ln (1 - x_1) = 0 \end{aligned} \quad (14)$$

Minimizing the free energy in accordance with eq 7 yields

$$\begin{aligned} \frac{d\epsilon(x = x_1)}{dx} &= kT [\ln cmc_1 - \ln cmc_2 - \ln cmc_1^m + \\ &\ln cmc_2^m + \ln x_1 - \ln (1 - x_1)] = 0 \end{aligned} \quad (15)$$

From the above eqs 14 and 15 it follows that

$$cmc_1^m = x_1 cmc_1 \quad (16)$$

and, furthermore,

$$cmc_2^m = (1 - x_1) cmc_2 \quad (17)$$

and, hence, the  $cmc \equiv cmc_1^m + cmc_2^m$  is predicted to be a linear function with respect to  $x_1$ , i.e., the simple expression  $cmc(x_1) = x_1 cmc_1 + (1 - x_1) cmc_2$  is recovered.

### Nonideal Surfactant Mixtures

For a mixture of two surfactants for which at least one contribution to  $\epsilon$  has a nonlinear dependence on  $x_1$ , eq 8 can be written as follows

$$\begin{aligned} \epsilon(x_1)/kT &= x_1 g_1 + (1 - x_1) g_2 - x_1 \ln cmc_1^m - \\ &(1 - x_1) \ln cmc_2^m + x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1) + \\ &\epsilon_i^m(x_1)/kT = \tilde{a} \end{aligned} \quad (18)$$

where  $\epsilon_i^m(x_1)$  is the nonlinear contribution to the free energy per aggregated surfactant or, if more than one free energy contribution is nonlinear with respect to  $x_1$ , the sum of these contributions. As before  $g_1$  and  $g_2$  are the sum of the residual linear contributions to  $\epsilon$  at  $x_1 = 1$  and  $x_1 = 0$ , respectively.

Hence, for the pure surfactants we can write

$$\epsilon(x_1 = 1)/kT = g_1 + \epsilon_i^m(x_1 = 1)/kT - \ln cmc_1 = \tilde{a} \quad (19)$$

and

$$\epsilon(x_1 = 0)/kT = g_2 + \epsilon_i^m(x_1 = 0)/kT - \ln cmc_2 = \tilde{a} \quad (20)$$

and, as a consequence, eqs 18–20 give

$$\begin{aligned} \epsilon(x_1)/kT &= x_1 [\ln cmc_1 - \epsilon_i^m(x_1 = 1)/kT] + \\ &(1 - x_1) [\ln cmc_2 - \epsilon_i^m(x_1 = 0)/kT] - x_1 \ln cmc_1^m - \\ &(1 - x_1) \ln cmc_2^m + x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1) = 0 \end{aligned} \quad (21)$$

In accordance with the minimization in eq 7 we can write

$$\begin{aligned} \frac{d\epsilon(x = x_1)}{dx} &= kT [\ln cmc_1 - \ln cmc_2 - \ln cmc_1^m + \\ &\ln cmc_2^m + \ln x_1 - \ln (1 - x_1)] + \epsilon_i^m(x_1 = 0) - \\ &\epsilon_i^m(x_1 = 1) + \frac{d\epsilon_i^m(x = x_1)}{dx} = 0 \end{aligned} \quad (22)$$

from which, together with eq 21, we obtain the following expression for the free monomer concentrations of each surfactant at the cmc:

$$cmc = A(x_1) x_1 cmc_1 + B(x_1) (1 - x_1) cmc_2 \quad (23)$$

where

$$\begin{aligned} A(x_1) &= \exp \left[ \left( \epsilon_i^m(x_1) - \epsilon_i^m(x_1 = 1) + \right. \right. \\ &\left. \left. (1 - x_1) \frac{d\epsilon_i^m(x = x_1)}{dx} \right) / kT \right] \end{aligned} \quad (24)$$

and

$$B(x_1) = \exp \left[ \left( \epsilon_i^m(x_1) - \epsilon_i^m(x_1 = 0) - x_1 \frac{d\epsilon_i^m(x = x_1)}{dx} \right) / kT \right] \quad (25)$$

For the sake of simplicity we will in the remaining of this



paper use the denotation  $d\epsilon_i^m(x_1)/dx_1$  instead of  $d\epsilon_i^m(x = x_1)/dx$ . We further note that  $cmc_1^m(x_1) = A(x_1)x_1cmc_1$  and  $cmc_2^m(x_1) = B(x_1)(1 - x_1)cmc_2$ .

Hence, by analyzing the free energy function  $\epsilon_i^m(x_1)$  we can determine  $A(x_1)$  and  $B(x_1)$  and thus obtain information about the behavior of  $cmc(x_1) = A(x_1)x_1cmc_1 + B(x_1)(1 - x_1)cmc_2$ . It may be noted that both  $A(x_1)$  and  $B(x_1)$  become equal to unity for the case where  $\epsilon_i^m(x_1)$  is a linear function and, in accordance with the derivation in the previous section, we recover expression 1 valid for an ideal surfactant mixture.

According to the theory of regular mixtures we have

$$A(x_1) = \exp[(1 - x_1)^2\beta] \quad (26)$$

and

$$B(x_1) = \exp[x_1^2\beta] \quad (27)$$

However, as will be evident below,  $A(x_1)$  and  $B(x_1)$  cannot generally be written in this form and, as a rule, synergistic effects cannot be accurately described by means of a simple  $\beta$  parameter defined by eqs 3 and 4.

In mathematical terms, the cmc depends linearly on  $x_1$  if, and only if,

$$\frac{d^2cmc}{dx_1^2} = 0 \quad (28)$$

is valid for all values of the micellar surfactant composition, i.e.  $0 \leq x_1 \leq 1$ . Similarly,  $cmc(x_1)$  has a positive deviation from linear behavior if

$$\frac{d^2cmc}{dx_1^2} < 0 \quad (29)$$

and a negative deviation when

$$\frac{d^2cmc}{dx_1^2} > 0 \quad (30)$$

If there exists a local maximum value for a positively deviating  $cmc(x_1)$  function or a local minimum value for a negatively deviating  $cmc(x_1)$  function in the range  $0 < x_1 < 1$ , i.e., if

$$\frac{dcmc}{dx_1}[x_1 = x_1^{opt}] = 0 \quad (31)$$

we can derive the following second derivative expression from eqs 23, 24, and 25

$$\frac{d^2cmc}{dx_1^2}[x_1 = x_1^{opt}] = cmc_1A(x_1) \left[ x_1(1 - x_1) \left( \frac{d^2\epsilon_i^m/kT}{dx_1^2} \right)^2 + \frac{d^2\epsilon_i^m/kT}{dx_1^2} \right] \quad (32)$$

where, according to eq 31,  $cmc_1A(x_1) = cmc_2B(x_1)$ .

From eq 32 we realize that  $cmc(x_1)$  has a negative deviation from linearity (that is its second derivative at the minimum is larger than zero) if

$$\frac{d^2\epsilon_i^m/kT}{dx_1^2}[x_1 = x_1^{opt}] > 0 \quad (33)$$

A negative deviation of  $cmc(x_1)$  is also obtained as

$$\frac{d^2\epsilon_i^m/kT}{dx_1^2}[x_1 = x_1^{opt}] < [x_1(1 - x_1)]^{-1} \quad (34)$$

whereas  $cmc(x_1)$  deviates positively for intermediate values, i.e.,  $[x_1(1 - x_1)]^{-1} < d^2[\epsilon_i^m(x_1 = x_1^{opt})/kT]/dx_1^2 < 0$ .

The right hand side of eq 34 is always less or equal to  $-4$  which means that  $\epsilon_i^m(x_1)$  must have a rather sharp maximum. Normally the  $\epsilon_i^m(x_1)$  function does not behave in such a manner and for those expressions of  $\epsilon_i^m(x_1)$  that will be presented below negative values of  $d^2[\epsilon_i^m(x_1 = x_1^{opt})/kT]/dx_1^2$  at  $x_1 = x_1^{opt}$  correspond to a positive deviation of  $cmc(x_1)$ .

In the following sections we will analyze synergistic effects in mixed surfactant systems by means of investigating the function  $\epsilon_i^m(x_1)$  for different mixtures containing ionic as well as nonionic surfactants.

### Contributions to the Free Energy of Forming a Surfactant Aggregate

As already indicated above, the free energy of forming a surfactant aggregate can be written as a sum of several contributions:<sup>11,14</sup> (i) the reduction of contact area between hydrocarbon and water, (ii) conformational entropy due to packing restrictions of the hydrocarbon chains, (iii) electrostatics for a charged aggregate surface and its diffuse layer of counterions, (iv) additional contributions related to the headgroups, and (v) entropy of mixing the two surfactants in the aggregates.

(i) The driving force for the otherwise entropically unfavorable self-assembly of surfactant molecules is the hydrophobic effect, i.e., the reduction of hydrocarbon/water interfacial area as the hydrocarbon tails of the surfactants form the liquidlike cores of the aggregates.<sup>15</sup> This contribution can be calculated as the work of bringing  $N_1$  and  $N_2$  surfactants to a hydrocarbon bulk phase<sup>15</sup> plus the hydrocarbon/water interfacial tension times the area per aggregated surfactant at the hydrocarbon/water interface ( $\gamma_{hc/w} \times a$ ). This free energy contribution is constant with respect to the composition of an aggregate of given structure for a particular aggregated surfactant and, as a result, the corresponding function  $\epsilon_{hc/w}^m(x_1)$  is a linear function and no synergistic effects are obtained due to this contribution as far as the structural change of the aggregates with  $x_1$  is small.

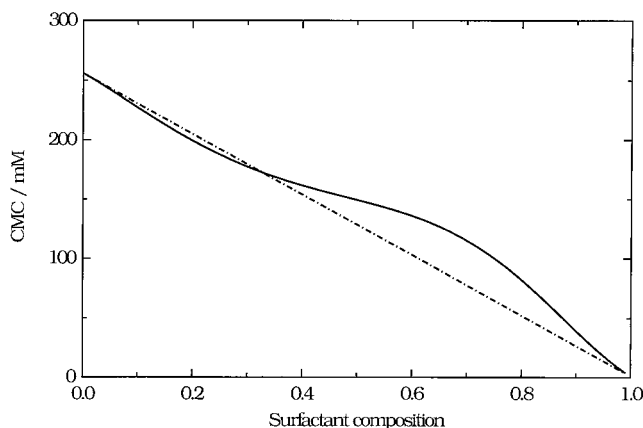
In the calculations presented in this paper we have assumed a constant (planar) structure of the aggregates with respect to surfactant composition as the influence on  $cmc(x_1)$  due to a changing curvature of the aggregates is found to be small.

(ii) Restrictions in chain conformations in the hydrocarbon part of a surfactant aggregate as compared with an alkane bulk phase gives rise to a rather small but important contribution to the aggregate free energy. In particular, this contribution significantly influences the equilibrium radial thickness of a spherical,<sup>11</sup> cylindrical<sup>12</sup> or planar<sup>16</sup> geometrical part of a surfactant aggregate. It has been quantitatively estimated using mean field approaches by Gruen and de Lacey<sup>17</sup> as well as Szleifer et al.<sup>18</sup> We have performed a calculation of  $cmc(x_1)$  from

(14) Ljunggren, S.; Eriksson, J. C. *Prog. Colloid Polym. Sci.* **1987**, *74*, 38.

(15) Tanford, C. *The hydrophobic effect*; Wiley: New York, 1980; Chapter 7.

(16) Ljunggren, S.; Eriksson, J. C. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 913.



**Figure 1.** The cmc for a mixture of two nonionic surfactants with a  $C_8$  and a  $C_{16}$  aliphatic hydrocarbon chain, respectively, and identical headgroups plotted against the mole fraction of the long-chain surfactant in the aggregates ( $x_1$ ) (solid line). The hydrocarbon chain conformational entropy, which is the only nonlinear contribution to  $\epsilon(x_1)/kT$  for this particular system, was calculated from an expression given in ref 19. The deviation from ideality approximately corresponds to  $\beta = 0.4$ . The corresponding curve for an ideal surfactant mixture as obtained from eq 1 is also given (dashed-dotted line). The cmcs for the pure surfactants are set to  $cmc_1 = 1$  mM and  $cmc_2 = 256$  mM corresponding to a decrease of cmc with a factor two for each methylene group ( $-\text{CH}_2-$ ) in an aliphatic hydrocarbon chain.<sup>20</sup>

the chain conformational free energy contribution for a mixture of surfactants with  $C_8$  and  $C_{16}$  aliphatic chains using explicit polynomial expressions given by Yuet and Blankschtein<sup>19</sup> which they obtained from calculations according to the procedure set up by Szleifer et al. The resulting behavior of  $cmc(x_1)$  [cf. Figure 1] deviates rather slightly (and positively!) from linearity and, since this deviation from linear behavior is expected to decrease with decreasing difference in chain length between the two surfactants, the contribution from chain conformational entropy to any synergistic effects can for most cases be regarded as negligible.

(iii) Electrostatics yields a large positive contribution to the aggregate free energy for mixtures consisting of at least one ionic surfactant. According to the Poisson–Boltzmann (mean field) description, this contribution is mainly due to the entropically unfavorable organization of the counterions into a diffuse layer located outside the electrically charged surface of an aggregate, whereas the purely energetic effects usually are much smaller.

For aggregates encompassing monovalent surfactants the electrostatic free energy per unit charge can be rather accurately calculated from the Poisson–Boltzmann theory, which for planar geometry gives a free energy per charge equal to

$$\epsilon_{el}/kT = 2 \left[ \ln(S + \sqrt{S^2 + 1}) - \frac{\sqrt{S^2 + 1} - 1}{S} \right] \quad (35)$$

Hence, the electrostatic free energy becomes a function of the reduced charge density,  $S$ , which is defined as

$$S = \frac{\sigma}{\sqrt{8c_t\epsilon_0\epsilon_r N_A kT}} \quad (36)$$

where  $\sigma = e_{el}/a_{ch}$  is the surface charge density,  $e_{el}$  the elementary charge and  $a_{ch}$  the area per charge at the aggregate surface.  $\epsilon_0$  and  $\epsilon_r$  are the electric permeability in a vacuum and the relative permeability, respectively, and  $N_A$  is the Avogadro constant. Curvature-dependent terms can be added to eq 35 to account for significantly curved structures such as micelles.<sup>21,22</sup> However, as already stated above we have in the present work treated all aggregates as planar structures since curvature effects on the cmc is found to be negligible in a first approximation.

Normally  $S$  is a rather strong function of the surfactant composition and, as a consequence, eq 35 is not a constant but depends on the aggregate composition. In accordance, the electrostatic free energy contribution gives rise to significant synergistic effects which will be treated in detail further below. In physical terms, these synergistic effects arise as a consequence of the dilution of counterions, and the subsequent increase in entropy of mixing counterions and water molecules, when e.g. a nonionic surfactant is admixed to an ionic surfactant solution.

(iv) The most important contribution associated with nonionic surfactant headgroups is due to the entropy of mixing headgroups and solvent molecules. For a rather concentrated mixture of particles with a circular cross-section the following expression may be used

$$\epsilon_{hg}^m(x_1) = \ln \eta + \frac{\eta(20 - \eta)}{15(1 - \eta)} - \frac{2}{3} \ln(1 - \eta) \quad (37)$$

where the area fraction of headgroups at the aggregate surface equals  $\eta(x_1) = [x_1 a_1^{hg} + (1 - x_1) a_2^{hg}]/a$ .  $a_1^{hg}$  and  $a_2^{hg}$  are the cross section areas of the headgroups of Surfactant 1 and 2, respectively, and  $a$  the area per aggregated surfactant. The derivation of eq 37, which is given in detail in the Appendix, is based on the two-dimensional equation of state obtained by a Padé approximation from the known virial coefficients up to  $B_6$ .<sup>23</sup> It is evident that eq 37 is nonlinear with respect to  $x_1$  and we will treat the resulting synergistic effects in more detail below. We may note that the last two higher order terms in eq 37 vanishes as  $\eta \rightarrow 0$ .

The expression in eq 37 is valid for *rigid* surfactant headgroups with a circular cross section. For *flexible* headgroups the higher order second and third terms in the expression, which become important for area fractions above about  $\eta = 0.2$ , are expected to be different. In particular, the flexibility of the headgroups will result in larger repulsive excluded volume effects as compared with rigid headgroups. However, to our knowledge there are no available quantitative expressions for an equation of state of rather concentrated flexible particles.

An additional, rather large and negative, contribution to the headgroup free energy is due to the shielding of the hydrocarbon/water interface from the headgroups. However, this contribution is constant for a particular surfactant headgroup and, hence, the corresponding contribution to  $\epsilon_{hg}^m(x_1)$  is linear implying that it does not give rise to any synergistic effects.

Other free energy contributions related to the surfactant headgroups, including specific interactions between different headgroups, are difficult to estimate quantitatively

(17) Gruen, D. W. R.; Lacey, E. H. B. In *Surfactants in solution*; Mittal, K., Lindman, B., Eds.; Plenum: New York, 1984; Vol. I, pp 279.

(18) Szleifer, I.; Kramer, D.; Ben-Shaul, A. *J. Chem. Phys.* **1990**, *92*, 6800.

(19) Yuet, P. K.; Blankschtein, D. *Langmuir* **1996**, *12*, 3802.

(20) Israelachvili, J. N. *Intermolecular and Surface Forces* 2nd ed.; Academic press: London, 1991; Chapter 16.

(21) Lekkerkerker, H. N. W. *Physica A* **1989**, *159*, 319.

(22) Mitchell, D. J.; Ninham, B. W. *Langmuir* **1989**, *5*, 1121.

(23) Nilsson, U.; Jönsson, B.; Wennerström, H. *J. Phys. Chem.* **1993**, *97*, 5654.

but are probably small. However, we cannot exclude that specific interactions may occasionally contribute non-negligibly to any observed synergistic effects.

(v) The entropy of mixing different surfactants in the aggregates is, of course, always present in mixed surfactant systems but, in accordance with the above given derivation of the ideal  $cmc(x_1)$  curve, this contribution does not give rise to any synergistic effects.

In summary, the most important contributions to synergistic effects in mixed surfactant systems are due to the largely entropic electrostatic free energy contribution as well as the entropy of mixing headgroups and solvent molecules. In the following sections we will investigate and quantitatively estimate these synergistic effects for some different cases.

### Mixture of an Ionic and a Nonionic Surfactant in the Absence of Added Salt

For mixtures consisting of a monovalent ionic surfactant and a nonionic surfactant with an otherwise similar headgroup (same size and hydration number etc so that only electrostatic effects differ between the two surfactants), the electrostatic free energy per aggregated surfactant can be written as follows

$$\epsilon_{el}^m = x_1 \epsilon_{el} \quad (38)$$

where the free energy per charge  $\epsilon_{el}$  is approximately given by eq 35 which is strictly valid for planar geometry. An approximate expression for  $\epsilon_{el}^m$  can be obtained by means of considering the case where  $S \gg 1$ . This is a fairly good approximation for electrolyte concentrations  $c_t$  below about 0.2 M, for which  $S \geq 10$ , provided  $x_1$  assumes values not too far from unity. Moreover, the contribution from energetic effects to the electrostatic free energy is negligible in the regime of  $S$  values larger than about unity.<sup>24</sup> Hence, we may conclude that the synergistic effects due to electrostatics obtained in our analysis is entirely of an entropic origin (entropy of mixing counterions and solvent molecules).

In accordance with the assumption  $S \gg 1$ , we can write eq 35 simply as

$$\epsilon_{el}/kT = 2 \ln(2S/e) \quad (39)$$

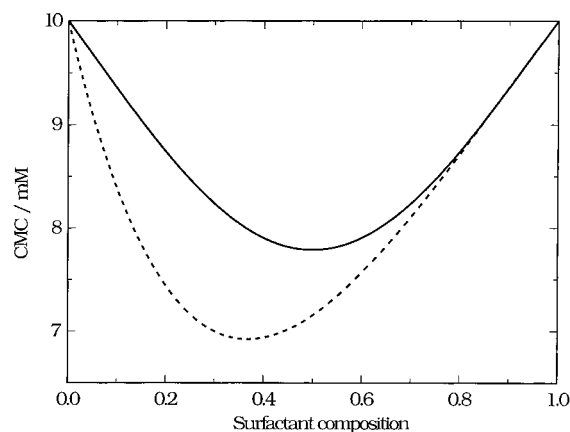
Assuming a linear behavior of the electrolyte concentration

$$c_t = x_1 cmc_1 \quad (40)$$

for the case of no added salt, and inserting  $\sigma = N_{el}e_{el}/Na = x_1 e_{el}/a$  in eq 36, where  $N_{el}$  is the number of charges per aggregate, we obtain from eqs 38 and 39

$$\epsilon_{el}^m = x_1 (\ln x_1 + \epsilon_{el}^1) \quad (41)$$

where  $\epsilon_{el}^1 = 2 \ln(2S_1/e)$  is the (constant) free energy per aggregated pure ionic surfactant and  $S_1$  is obtained by inserting  $c_t = cmc_1$  in eq 36.



**Figure 2.** The cmc for a mixture of a monovalent ionic and an otherwise similar nonionic surfactant plotted against the mole fraction of the ionic surfactant in the aggregates ( $x_1$ ) according to eq 42 (dashed line) and  $cmc(x_1) = cmc_1 x_1 \exp[-(1-x_1)^2] + cmc_2(1-x_1) \exp(-x_1^2)$  (solid line). The former approximately corresponds to  $\beta = -1.5$  whereas the latter gives  $\beta = -1$  exactly. The cmcs for the pure surfactants are set to  $cmc_1 = cmc_2 = 10$  mM.

Upon inserting eq 41 in eqs 24 and 25 we obtain  $A(x_1) = x_1 \exp(1-x_1)$  and  $B(x_1) = \exp(-x_1)$ , implying that

$$cmc(x_1) = x_1^2 \exp(1-x_1) cmc_1 + (1-x_1) \exp(-x_1) cmc_2 \quad (42)$$

The cmc as given by eq 42 is plotted against  $x_1$  in Figure 2 and the function is seen to be skewed, exhibiting a negative deviation from ideal behavior approximately corresponding to a  $\beta$  value of  $-1.5$ .

However, in the derivation of eq 42 we have assumed a linear behavior of the electrolyte (i.e., the ionic free monomer) concentration in eq 40. Hence, the result in eq 42 can be improved if the electrolyte concentration is set equal to  $c_t = cmc_1^m = x_1^2 \exp(1-x_1) cmc_1$  in expression 36 for  $S$ . As a result we obtain

$$A(x_1) = \exp[-(1-x_1)^2] \quad (43)$$

and

$$B(x_1) = \exp(-x_1^2) \quad (44)$$

which, incidentally, exactly corresponds to the expressions 26 and 27, valid for the theory of regular mixtures, with  $\beta$  equal to  $-1$ . The curve showing cmc vs  $x_1$  obtained from eqs 43 and 44 is given as well in Figure 2. As the electrolyte concentration  $c_t = x_1^2 \exp(1-x_1) cmc_1$  is lower than what is obtained from the corresponding linear expression 40, the chemical potential of the charged surfactant becomes somewhat higher and the deviation of cmc from linearity lower in the former case.

The procedure can be repeated in an iterative manner using  $c_t = x_1 \exp[-(1-x_1)^2]$  to calculate a new expression for  $S$ ,  $\epsilon_{el}^m$ , and  $cmc(x_1)$ , etc. This results in the addition of higher order terms in the exponents of  $A(x_1)$  and  $B(x_1)$ . However, only slight improvements are thus obtained and the resulting synergistic effects appear to converge where the deviation of  $cmc(x_1)$  from linearity approximately corresponds to  $\beta = -1$ .

Finally, it may be noted that electrostatics is a strong function of the electrolyte concentration and, hence,  $\epsilon_{el}$  eventually vanishes as  $S \rightarrow 0$  when a large and increasing amount of an additional salt is added to the surfactant

(24) Evans, D. F.; Wennerström, H. *The Colloidal Domain*; VCH: New York, 1994; Chapter 3.



solution. This trend has been observed, for instance, in  $C_{12}PyrCl/C_{12}E_8$  mixtures for which  $\beta = -2.7$  (pure water),  $\beta = -1.4$  (0.1 M NaCl), and  $\beta = -1.0$  (0.5 M NaCl).<sup>25</sup>

### Mixtures of Two Ionic Surfactants with Identical Headgroups but Different Hydrocarbon Tails

Mixtures of two (monovalent) ionic surfactants with identical headgroups can in fact give rise to synergistic effects provided the hydrocarbon parts of the surfactants differ in such a way that the cmcs of the pure surfactants are unequal. We can write the electrostatic free energy as

$$\epsilon_{el}^m = \epsilon_{el} \quad (45)$$

and assuming a linear dependence of the electrolyte concentration

$$c_t = x_1 cmc_1 + (1 - x_1) cmc_2 \quad (46)$$

when calculating  $S$  from eq 36 for the case where no extra electrolyte is added to the solution. From eqs 45, 24, and 25 we thus obtain

$$A(x_1) = \frac{\exp[-(1 - x_1)(1 - \lambda)/(x_1 + \lambda(1 - x_1))]}{x_1 + \lambda(1 - x_1)} \quad (47)$$

and

$$B(x_1) = \frac{\lambda \exp[x_1(1 - \lambda)/(x_1 + \lambda(1 - x_1))]}{x_1 + \lambda(1 - x_1)} \quad (48)$$

Hence, the synergistic effects only depend on the quotient  $\lambda \equiv cmc_2/cmc_1$  of the cmcs of the pure surfactants and not on the absolute values of  $cmc_1$  and  $cmc_2$ .

In Figure 3 we have plotted the resulting cmc

$$cmc(x_1) = x_1 \frac{\exp[-(1 - x_1)(1 - \lambda)/(x_1 + \lambda(1 - x_1))]}{x_1 + \lambda(1 - x_1)} cmc_1 + (1 - x_1) \frac{\lambda \exp[x_1(1 - \lambda)/(x_1 + \lambda(1 - x_1))]}{x_1 + \lambda(1 - x_1)} cmc_2 \quad (49)$$

for three different values of  $\lambda$ . It is evident that the synergistic effects increases as  $\lambda$  recedes unity.

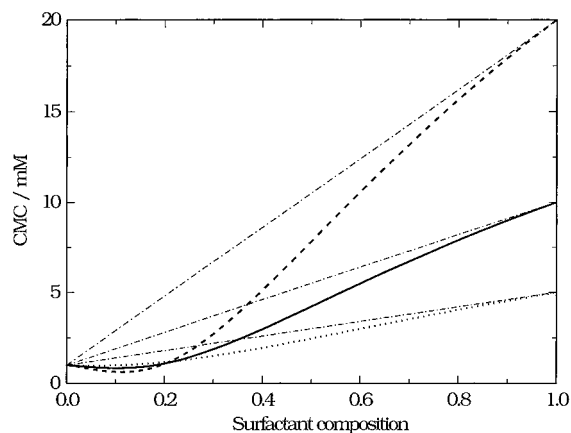
If a certain amount of extra electrolyte  $c_{salt}$  is added to the solutions we obtain

$$A(x_1) = \left(1 + \frac{c_{salt}}{cmc_1}\right) \times \frac{\exp[-(1 - x_1)(1 - \lambda)/(x_1 + \lambda(1 - x_1) + c_{salt}/cmc_1)]}{x_1 + \lambda(1 - x_1) + c_{salt}/cmc_1} \quad (50)$$

and

$$B(x_1) = \left(\lambda + \frac{c_{salt}}{cmc_1}\right) \times \frac{\exp[x_1(1 - \lambda)/(x_1 + \lambda(1 - x_1) + c_{salt}/cmc_1)]}{x_1 + \lambda(1 - x_1) + c_{salt}/cmc_1} \quad (51)$$

Note that if  $c_{salt} \gg cmc_1 \approx cmc_2$ ,  $A(x_1) = B(x_1) = 1$  and the



**Figure 3.** The cmc for mixtures of two monovalent ionic surfactants with identical headgroups but with different cmc values ( $cmc_1 > cmc_2$ ) plotted against the mole fraction of Surfactant 1 in the aggregates ( $x_1$ ) according to eq 49.  $cmc_2$  was fixed to 1 mM for the three cases whereas  $\lambda \equiv cmc_2/cmc_1$  was set to 0.1 (solid line), 0.05 (dashed line) and 0.2 (dotted line). The corresponding curves for the ideal surfactant mixtures as obtained from eq 1 are indicated as dashed-dotted lines. The synergistic effects are most pronounced when the mixture is rich of the surfactant with the lowest value of the cmc ( $cmc_2$ ) where distinct minima in the cmc vs  $x_1$  curves are obtained. The synergistic effects increase with decreasing  $\lambda$  and at the minima they approximately correspond to  $\beta = -2$  (dotted line),  $\beta = -4$  (solid line) and  $\beta = -6$  (dashed line).

ideal behavior of eq 1 is recovered. For  $c_{salt} \ll cmc_1$  eqs 47 and 48 are of course recovered.

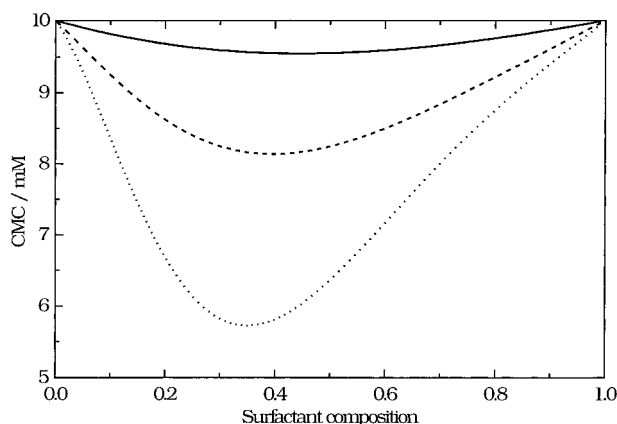
In the derivation of eq 49, we have assumed the electrolyte concentration in eq 46 to depend linearly on  $cmc_1$  and  $cmc_2$ . It is, however, difficult to improve this assumption by means of using eq 49 to calculate  $c_t$  in a similar way as was done for the case of a mixture of an ionic and a nonionic surfactant since the obtained  $cmc(x_1)$  curve does not converge in the iterative procedure. We may nevertheless assume that, in analogy with the case of a mixture of an ionic and a nonionic surfactant, the real synergistic effects are somewhat lower than what is obtained from eq 49.

It is seen in Figure 3 that the synergistic effects are most pronounced at compositions rich of the surfactant with the lowest cmc which normally is the surfactant with the bulkiest hydrocarbon part or longest chain. This can be rationalized as the short-chain surfactant will have a smaller tendency to assemble in the aggregates which, hence, almost exclusively consist of long-chain surfactants. As a result, the addition of an ionic surfactant with shorter chain will mainly have the effect of increasing the electrolyte concentration and, hence, reducing the chemical potential of aggregated surfactant which means a reduction of the cmc.

Since the synergistic effect is a strong function of the composition it is rather difficult to describe it, as is usually done, simply by a  $\beta$  value. Nevertheless, our calculations agree well with what has been obtained from measurements on mixtures of sodium alkylcarboxylates by Merta and Stenius<sup>5</sup> as well as for mixtures of various  $C_n$ TAB surfactants with different chain lengths by García-Mateos et al.<sup>3</sup> and López-Fontán et al.<sup>4</sup> The former observed a strong dependence of the measured  $\beta$  parameter with surfactant composition so that  $\beta$  increases with increasing fraction of the short-chain surfactant in agreement with the predictions of our theory. In the latter case  $\beta$  was seen to vary from  $-1.3$  for a mixture of  $n = 6/n = 8$  to  $\beta = -11.2$  for a  $n = 6/n = 16$  mixture. Hence, the synergistic effects were seen to increase with increasing difference in cmcs

(25) Rosen, M. J. In *Phenomena in Mixed Surfactant Systems*; Scaemhorn, J. F., Ed.; ACS Symposium Series 311; American Chemical Society: Washington, DC, 1986; pp 144.



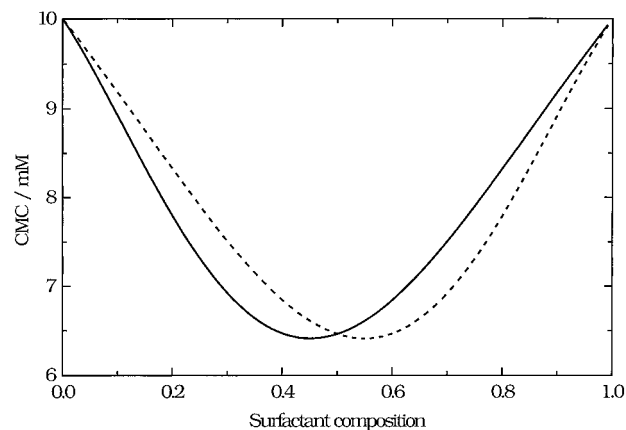


**Figure 4.** The cmc for mixtures of two nonionic surfactants with rigid circular headgroups of different size, as calculated using expression 37, plotted against the mole fraction of Surfactant 1 in the aggregates ( $x_1$ ). For all three curves the area per aggregated surfactant was set to a constant value of  $a = 32 \text{ \AA}^2$  and the sum of the cross-section areas of the two headgroups to  $a_1^{\text{hg}} + a_2^{\text{hg}} = 30 \text{ \AA}^2$ . The difference in headgroup cross-section area is  $\Delta a_{\text{hg}} \equiv a_2^{\text{hg}} - a_1^{\text{hg}} = 5 \text{ \AA}^2$  (solid line, approximately corresponding to  $\beta = -0.2$ ),  $\Delta a_{\text{hg}} \equiv a_2^{\text{hg}} - a_1^{\text{hg}} = 10 \text{ \AA}^2$  (dashed line,  $\beta = -0.8$ ) and  $\Delta a_{\text{hg}} \equiv a_2^{\text{hg}} - a_1^{\text{hg}} = 20 \text{ \AA}^2$  (dotted line,  $\beta = -2.2$ ). The minima of the curves are located at compositions where the surfactant with the bulkiest headgroup is in excess.

between the two surfactants as generated from our theory (cf. Figure 3). The trend of increasing synergistic effects with increasing difference in surfactant chain length was also obtained from model calculations by Shiloach and Blankshtein<sup>8</sup> on different mixtures of two  $C_n\text{TAB}$  surfactants. However, these authors mistakenly claim that the generated synergistic effects are due to the packing of surfactant tails in the micellar cores rather than by electrostatics as we have demonstrated here. As a matter of fact, we have shown above [cf. Figure 1] that the contribution from packing hydrocarbon chains to any synergistic effects is usually very small by using the very same expression for hydrocarbon chain conformational entropy as employed by Shiloach and Blankshtein.

#### Mixtures Containing Nonionic Surfactants with Rigid Headgroups

The most important contribution to the aggregate free energy associated with the headgroups of nonionic surfactants is due to the free energy of mixing the headgroups with solvent molecules. For a rather dense mixture of rigid headgroups we can use eq 37 to calculate the corresponding free energy contribution. It immediately appears that this equation is nonlinear with respect to  $x_1$  and, hence, the mixing of headgroups gives rise to synergistic effects and a nonlinear behavior of cmc. The synergistic effects are highly dependent on the cross-section areas of both headgroups as well as of the area per aggregated surfactant  $a$  and increases with increasing  $a_1^{\text{hg}}$  and  $a_2^{\text{hg}}$  and decreasing  $a$ , i.e., with increasing  $\eta$ . The deviation from linear behavior increases with increasing difference between the headgroup cross-section areas  $a_1^{\text{hg}}$  and  $a_2^{\text{hg}}$  or, in other words, with increasing asymmetry between Surfactant 1 and 2. Examples of  $\text{cmc}(x_1)$  as calculated from eq 37 for different values of  $a_1^{\text{hg}}$  and  $a_2^{\text{hg}}$  at fixed values of  $(a_1^{\text{hg}} + a_2^{\text{hg}})$  and  $a$  are given in Figure 4. The latter was given a constant value of  $32 \text{ \AA}^2$  approximately corresponding to what has been obtained from detailed model calculations of a mixture of two surfactants



**Figure 5.** The cmc for mixtures of an ionic and a nonionic surfactant with rigid circular headgroups of different size plotted against the mole fraction of the ionic surfactant in the aggregates ( $x_1$ ). The curves were calculated from  $\epsilon_1^{\text{m}}(x_1)$  as given by the sums of eqs 37 and 38, respectively. The area per aggregated surfactant was set to a constant value of  $a = 32 \text{ \AA}^2$  and the sum of the cross-section areas of the two headgroups to  $a_1^{\text{hg}} + a_2^{\text{hg}} = 30 \text{ \AA}^2$ . The difference in headgroup cross section area is  $\Delta a_{\text{hg}} \equiv a_1^{\text{hg}} - a_2^{\text{hg}} = 10 \text{ \AA}^2$  (solid line) and  $\Delta a_{\text{hg}} \equiv a_1^{\text{hg}} - a_2^{\text{hg}} = -10 \text{ \AA}^2$  (dashed line). The synergistic effects approximately correspond to  $\beta = -1.8$  for both cases which is the sum of what is obtained for a mixture of an ionic and a nonionic surfactant with identical headgroups (Figure 2) and the corresponding mixture of two nonionic surfactants with different headgroup cross-section areas (Figure 4). The minima of the curves are located at the side of equimolar composition which is rich of the surfactant with the bulkiest headgroup.

with identical  $C_{12}$  hydrocarbon chains in a planar bilayer.<sup>13</sup> From these calculations it appears that  $a$  varies only slightly with surfactant composition, mostly because it is largely determined by the chain conformational free energy contribution. Moreover, for planar geometry  $a$  is virtually independent of the length of an aliphatic hydrocarbon chain.

For moderate differences in headgroup size the synergistic effects correspond to  $\beta$  values of rather small magnitude, i.e., less than unity. However, large differences in headgroup size may result in comparatively large synergistic effects as is seen from the example in Figure 4 where the headgroup areas  $a_1^{\text{hg}} = 5 \text{ \AA}^2$  and  $a_2^{\text{hg}} = 25 \text{ \AA}^2$  for which the reduction of cmc approximately corresponds to  $\beta = -2.2$ . We may, however, note that eq 37 is derived for a monodisperse mixture of particles and, hence, it is expected to become decreasingly accurate as the difference in headgroup size increases.

The equation of state in eq 37 is derived for uncharged particles and is not expected to be valid for ionic surfactant headgroups as well. However, as a first approximation we can use it to study the trend of synergistic effects as an ionic surfactant is mixed with a nonionic surfactant with a different headgroup cross-section area. Examples of  $\text{cmc}(x_1)$  curves as obtained by using eqs 35 and 37 are given in Figure 5. It appears that the resulting synergistic effects approximately equal the sum of what is obtained for an ionic/nonionic surfactant mixture where the size of the surfactant headgroups are same and for a mixture of two nonionic surfactants with different headgroup sizes. Interestingly, the asymmetry with respect to headgroup cross-section area enhances the synergistic effects due to electrostatics irrespective of whether the ionic or the nonionic surfactant has the largest headgroup. Only the location of the minimum on either side of equimolar composition ( $x_1 = 0.5$ ) differs between the two cases (cf. Figure 5). As a result, we may conclude that  $\beta = -1$  makes

a maximum value for mixtures of a monovalent ionic and a nonionic surfactant and  $\beta$  is predicted to be somewhat lower (i.e., more negative) for mixtures where the surfactant headgroups have different cross-section areas.

Hence, our theoretical results agree very well with the general experimental observation that synergistic effects in mixtures of two nonionic surfactants are for most cases studied small, i.e.,  $0 > \beta > -1$  for the various systems given in refs 1 and 2, whereas  $\beta$  is always somewhat lower than  $-1$  ( $-1 > \beta > -5$  for the systems given in refs 1 and 2) for mixtures of a monovalent ionic and a nonionic surfactant.<sup>1,2,26</sup> However, a systematic experimental study of the effect of surfactant asymmetry with respect to headgroup cross-section area on the magnitude of synergistic effects remains to be carried out.

## Conclusions

Synergistic effects in mixed surfactant systems can be rationalized by investigating the composition dependence of the various contributions to the free energy per aggregated monomer of forming a surfactant aggregate. When all of the various free energy contributions, except the one related to the entropy of mixing the two surfactants in the aggregates ( $= x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)$ ), are linear with respect to the composition of aggregates  $x_1$ , the cmc will depend linearly on the composition. However, the inclusion of one (or more) additional nonlinear free energy contribution will give rise to synergistic effects. By determining the nonlinear free energy contribution per aggregated monomer ( $\epsilon_1^m(x_1)$ ) the nonlinear function  $\text{cmc}(x_1)$  can be calculated. It is found that if  $\epsilon_1^m(x_1)$  has a positive deviation from linear behavior, i.e.,  $\beta > 0$ , so does  $\text{cmc}(x_1)$  and vice versa.

Out of the various free energy contributions those related with the surfactant headgroups are mainly responsible for generating synergistic effects. For mixtures of a monovalent ionic surfactant and an otherwise similar nonionic surfactant in the absence of added salt, the electrostatic free energy gives rise to synergistic effects approximately corresponding to  $\beta = -1$ . However, more pronounced synergistic effects arise from the same free energy contribution for mixtures of two identically charged surfactants having different cmcs. The conspicuously large synergistic effects found for mixtures of an anionic and a cationic surfactant will be treated separately in a forthcoming paper.

For mixtures of two nonionic surfactants with rigid headgroups of different size, a negative deviation from linear behavior arises from the entropy of mixing the rather concentrated headgroups with surrounding water molecules at the aggregate surface. This contribution is fairly small, i.e.,  $0 > \beta > -1$ , for moderate differences between the two headgroups but may be much larger if the two headgroups become sufficiently different from each other or if they are densely concentrated. For mixtures containing at least one ionic surfactant, and where the two surfactant headgroups have different cross-section areas, these two contributions to  $\beta$  are found, to a first approximation, to be additive irrespective of which of the surfactants having the bigger headgroup.

The electrostatic free energy is largely determined from the entropy penalty of concentrating counterions in a diffuse layer outside a charged aggregate surface. The mixing of headgroups and water molecules at the aggregate surface yields an additional nonlinear entropy

factor of significant magnitude. Hence, we may conclude that various entropy effects related to the surfactant headgroups, rather than specific interactions between them, are mostly responsible for generating synergistic effects in mixed surfactant systems. It also appears that the magnitude of the synergistic effects increases with increasing asymmetry between two surfactants, i.e., increasing difference in tail length or in headgroup cross-section area of the mixed surfactants.

**Acknowledgment.** We acknowledge Professor Per Stenius and Juha Merta at Helsinki University of Technology for pointing out the large synergistic effects observed in mixtures of two ionic surfactants with identical sodium carboxylate headgroups but different hydrocarbon tails, thus inspiring our work for this particular case. M.B. was financed by the Swedish National Board for Industrial and Technical Development (NUTEK) through the Competence Center for Surfactants Based on Natural Products (SNAP).

## Appendix

The equation of state for a collection of two-dimensional hard disks as estimated using a  $P(3,3)$  Padé approximation on the virial coefficients up to  $B_6$  can be written as follows:<sup>23</sup>

$$\frac{pA}{kT} = \frac{15 + 3\alpha^2 + \alpha^3}{15(1 - \alpha)^2} \quad (\text{A1})$$

where  $p$  is the hard disk pressure,  $A$  is the total area available to the disks and  $\alpha$  is the (variable) area fraction of disks. The difference in free energy between two states is then obtained by integrating over the pressure from the initial to the final state at constant temperature:

$$\Delta g/kT = \int_{A_0/kT}^{\infty} \frac{p}{A} dA = \int_0^{\eta} \frac{15 + 3\alpha^2 + \alpha^3}{15\alpha(1 - \alpha)^2} d\alpha \quad (\text{A2})$$

Using  $\alpha = 0$  as a reference state and integrating to the area fraction  $\eta$  we obtain

$$\Delta g/kT = \ln \eta + \frac{\eta(20 - \eta)}{15(1 - \eta)} - \frac{2}{3} \ln(1 - \eta) - \ln \eta_{\eta=0} \quad (\text{A3})$$

The free energy we are looking for is the work of bringing headgroups at the concentration of surfactants in the bulk solution to concentration  $\eta$  at the aggregate surface. In this process, the contribution from the reference state in the last term of eq A3 will be replaced by the free monomer concentration. However, this term (or rather these terms for a mixed system which is the case we consider in the present paper) is already included in the overall aggregate free energy as given in eq 18 (terms including  $\text{cmc}_1^m$  and  $\text{cmc}_2^m$ ). Hence, the free energy per aggregated surfactant equals

$$\epsilon_{\text{hg}}^m(x_1) = \ln \eta + \frac{\eta(20 - \eta)}{15(1 - \eta)} - \frac{2}{3} \ln(1 - \eta) \quad (\text{A4})$$

which is the expression given in eq 37.

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(26) Liljekvist, P.; Kronberg, B. *J. Colloid Interface Sci.* **2000**, *222*, 159.