

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231671594>

# Synergistic Effects in Mixtures of an Anionic and a Cationic Surfactant

ARTICLE *in* LANGMUIR · DECEMBER 2000

Impact Factor: 4.46 · DOI: 10.1021/la000814t

---

CITATIONS

50

---

READS

31

## 1 AUTHOR:

[Magnus Bergstrom](#)

Uppsala University

62 PUBLICATIONS 1,566 CITATIONS

SEE PROFILE

# Synergistic Effects in Mixtures of an Anionic and a Cationic Surfactant

Magnus Bergström<sup>†</sup>

Department of Chemistry, Surface Chemistry, Royal Institute of Technology,  
SE-100 44 Stockholm, Sweden and Institute for Surface Chemistry, P.O. Box 5607,  
SE-114 86 Stockholm, Sweden

Received June 12, 2000. In Final Form: October 24, 2000

Synergistic effects in mixtures of an anionic and a cationic surfactant have been theoretically investigated. We derive an explicit expression for the critical micelle concentration (cmc) as a function of the aggregate composition from the Poisson–Boltzmann mean field theory and, thus, demonstrate that the conspicuously large synergistic effects that have been experimentally observed can be rationalized without the need of invoking any specific interactions between the surfactant headgroups. The simple relation  $\beta = -4\epsilon_{\text{el}}/kT$  is derived, i.e., the “interaction parameter”  $\beta$  is directly related to the electrostatic free energy contribution  $\epsilon_{\text{el}}$  for the pure surfactant, implying, among other things, that the magnitude of  $\beta$  decreases with increasing cmc for the pure surfactant in agreement with experimental observations. We furthermore demonstrate that the aggregate composition is close to equimolar composition ( $x_1 = 0.5$ ) at cmc in almost the entire regime of overall surfactant compositions and that the free monomer concentration of the surfactant in excess is generally much larger than the corresponding quantity for the surfactant in deficit.

## Introduction

It is well-known that surfactants may self-assemble above a certain concentration, the so called critical micelle concentration (cmc), forming dropletlike aggregates (micelles). Since cmc strongly depends on the structure of the surfactant molecule, it is usually a nontrivial function of the surfactant composition in a binary surfactant mixture (e.g., mole fraction  $x_1$  of aggregated Surfactant 1). For a mixture of two only slightly differing surfactants, the cmc has been observed to depend linearly on the composition of the micelles. However, for certain mixtures cmc may deviate appreciably from linear behavior and deviations from such a dependence is usually referred to as *synergistic effects*. For a binary surfactant mixture it is customary to describe the dependence of cmc on the surfactant composition with the following expression

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

where  $\text{cmc}_1$  and  $\text{cmc}_2$  are the cmcs of pure surfactants 1 and 2, respectively, and the synergistic effects are taken into account by the two functions  $f_1(x_1) = \exp[(1 - x_1)^2 \beta]$  and  $f_2(x_1) = \exp[x_1^2 \beta]$ . The surfactant mixture is referred to as behaving ideally when eq 1 becomes a linear function, i.e., when  $\beta = 0$  and, consequently, both  $f_1$  and  $f_2$  equal unity. Accordingly, a negative deviation from the ideal behavior of  $\text{cmc}(x_1)$  corresponds to negative  $\beta$  values and vice versa. It may be noted that eq 1, as well as the concept of synergistic effects as defined in the present paper, presupposes the existence of cmcs for the pure surfactants; i.e.,  $\text{cmc}_1$  and  $\text{cmc}_2$  must assume some finite values, and as a result, eq 1 is only relevant for surfactant mixtures satisfying this requirement.

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 surfactants 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 ( $\beta = 0$ ).<sup>1</sup>

Aqueous mixtures of an anionic and a cationic surfactant have been frequently studied during the past decade or so, and they have been found to exhibit fundamentally different properties than the corresponding solutions of pure ionic surfactant or mixtures of an ionic and a nonionic surfactant.<sup>2–10</sup> The spontaneous formation of rather small unilamellar vesicles has been particularly emphasized, although a number of other structures, such as small globular and large wormlike micelles as well as large lamellar sheets, also have been observed.

The most conspicuous property is, however, the unusually large reduction in cmc when two oppositely charged surfactants are mixed in an aqueous solvent.<sup>11,12</sup> Whereas mixtures of an ionic and a nonionic surfactant normally yield a deviation from ideal behavior corresponding to  $-5$

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

(2) Kamenka, N.; Chorro, M.; Talmon, Y.; Zana, R. *Colloid Surf.* **1992**, *67*, 213.

(3) Kaler, E. W.; Herrington, K. L.; Murthy, A. K.; Zasadzinski, J. A. N. *J. Phys. Chem.* **1992**, *96*, 6698.

(4) Marques, E.; Khan, A.; da Graça Miguel, M.; Lindman, B. *J. Phys. Chem.* **1993**, *97*, 4729.

(5) Yaacob, I. I.; Bose, A. *J. Colloid Interface Sci.* **1996**, *178*, 638.

(6) Yacilla, M. T.; Herrington, K. L.; Brasher, L. L.; Kaler, E. W.; Chiruvolu, S.; Zasadzinski, J. A. N. *J. Phys. Chem.* **1996**, *100*, 5874.

(7) Marques, E. F.; Regev, O.; Khan, A.; da Graça Miguel, M.; Lindman, B. *J. Phys. Chem. B* **1998**, *102*, 6746.

(8) Bergström, M.; Pedersen, J. S. *J. Phys. Chem.* **1999**, *103*, 2250.

(9) Bergström, M.; Pedersen, J. S.; Schurtenberger, P.; Egelhaaf, S. U. *J. Phys. Chem. B* **1999**, *103*, 9888.

(10) Bergström, M.; Pedersen, J. S. *J. Phys. Chem. B* **2000**, *104*, 4155.

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

(12) Villeneuve, M.; Kaneshina, S.; Imae, T.; Aratono, M. *Langmuir* **1999**, *15*, 2029.

<sup>†</sup> Telephone: +46 8 790 99 05. Fax: +46 8 20 89 98. E-mail: magnus.bergstrom@surfchem.kth.se.

$< \beta < -1$ , and synergistic effects in mixtures of two nonionic surfactants are even less, experimentally obtained  $\beta$  values for mixtures of an anionic and a cationic surfactant are usually several magnitudes larger.<sup>11</sup> Moreover, the synergistic effects are observed to increase with increasing length of the surfactant tail. Accordingly,  $\beta$  values for  $C_nSO_4^-Na^+/C_nTA^+Br^-$  (TA = trimethylammonium) mixtures have been found to be  $\beta = -25.5$  for  $n = 12$ ,  $\beta = -18.5$  ( $n = 10$ ), and  $\beta = -10.5$  ( $n = 8$ ).<sup>13–15</sup>

In analogy with the regular mixture theory,  $\beta$  is generally referred to as the interaction parameter and its deviation from zero has frequently been believed to be the result of specific interactions between the surfactant headgroups so that it is different between Surfactant 1 and 2 as compared with between two identical headgroups. According to this interpretation the conspicuously large magnitudes of  $\beta$  found for mixtures of oppositely charged surfactants are due to very strong attractive interactions between the aggregated anionic and cationic headgroups, and it has even been suggested<sup>16</sup> that such interactions may account for the micelle-to-vesicle transition frequently observed in aqueous catanionic surfactant mixtures.

However, in a recent theoretical investigation, we have demonstrated that synergistic effects observed in systems containing ionic surfactants may be rationalized from the Poisson–Boltzmann mean field theory without the need of invoking any specific interactions.<sup>17</sup> According to the theory, the cmc may be written in the form

$$cmc(x_1) = A(x_1)x_1cmc_1 + B(x_1)(1 - x_1)cmc_2 \quad (3)$$

where

$$A(x_1) = \exp \left[ \left( \epsilon_i^m(x_1) - \epsilon_i^m(x_1 = 1) + (1 - x_1) \frac{d\epsilon_i^m(x_1)}{dx_1} \right) / kT \right] \quad (4)$$

and

$$B(x_1) = \exp \left[ \left( \epsilon_i^m(x_1) - \epsilon_i^m(x_1 = 0) - x_1 \frac{d\epsilon_i^m(x_1)}{dx_1} \right) / kT \right] \quad (5)$$

are entirely determined by the behavior of the free energy per aggregated surfactant  $\epsilon_i^m(x_1)$  and  $k$  is the Boltzmann constant and  $T$  the absolute temperature. From eqs 3–5, it follows that a nonlinear  $cmc(x_1)$  function is obtained as a result of a nonlinear behavior of the  $\epsilon_i^m(x_1)$  function and that the ideal form  $cmc(x_1) = x_1cmc_1 + (1 - x_1)cmc_2$  is recovered if  $\epsilon_i^m(x_1)$  is a linear function. It was found that significant synergistic effects mainly are obtained as a result of free energy contributions related to the surfactant headgroups whereas effects due to the packing of the surfactant chains in the hydrocarbon micellar cores usually are negligible.<sup>17</sup>

Hence, in a system where synergistic effects are mainly due to electrostatics, information about the behavior of  $cmc(x_1) = A(x_1)x_1cmc_1 + B(x_1)(1 - x_1)cmc_2$  can be obtained by analyzing the nonlinear electrostatic contribution to

the aggregate free energy. Moreover, the free monomer concentrations for surfactants 1 and 2 for a given value of  $x_1$  may be calculated from eqs 3–5 to  $cmc_1^m(x_1) = A(x_1)x_1cmc_1$  and  $cmc_2^m(x_1) = B(x_1)(1 - x_1)cmc_2$ , respectively.

According to the theory of regular mixtures

$$A(x_1) = e^{(1 - x_1)^2\beta} \quad (6)$$

and

$$B(x_1) = e^{x_1^2\beta} \quad (7)$$

In our recent theoretical analysis it was, however, found that  $A(x_1)$  and  $B(x_1)$  cannot in general be written in this form, and hence, synergistic effects cannot in general be accurately described by a simple  $\beta$  parameter.<sup>17</sup> We were nevertheless able to make a rough estimate of the generated synergistic effects by employing the terminology from the regular solution theory. Accordingly, we found that synergistic effects in mixtures of a monovalent ionic and a nonionic surfactant with otherwise identical headgroups (same size and hydration number etc so that only electrostatic effects differ between the two surfactants) roughly corresponds to  $\beta = -1$  in the absence of added salt and that the synergistic effects become somewhat enhanced if the cross-section areas of the surfactant headgroups are unequal. More pronounced synergistic effects of electrostatic origin, which may fall below  $\beta = -5$  or so, were, however, found for mixtures of two identically charged surfactants having different cmcs.<sup>17</sup>

The purpose of the present paper is to demonstrate that the very large synergistic effects observed in mixtures of an anionic and a cationic surfactant may indeed be rationalized as a result of the increase in the entropy of counterions as the charge is canceled at the aggregate interface, and a pair of counterions released, rather than of specific interactions. In accordance, we below evaluate the reduction of cmc when a monovalent anionic and a monovalent cationic surfactant are mixed in an aqueous solution by deriving explicit expressions for  $A(x_1)$  and  $B(x_1)$  as well as calculating cmc vs the overall surfactant composition  $y_1$ .

### Derivation of $A(x_1)$ and $B(x_1)$ for a Mixture of an Anionic and a Cationic Surfactant with Otherwise Identical Headgroups

Electrostatics give rise to a large and positive contribution to the aggregate free energy which is mainly due to the entropically unfavorable organization of counterions into a diffuse layer located outside the electrically charged surface of each aggregate. The electrostatic potential of a surface with smeared-out surface charge density and pointlike counterions immersed in an electrolyte solution may be calculated from the Poisson equation assuming the concentration of counterions outside the surface to be distributed in accordance with an exponential Boltzmann factor.<sup>18</sup> The rearrangement of counterions when a charged surface is formed in an aqueous solution is taken into account in the derivation of the (nonlinear) Poisson–Boltzmann equation, and hence, the resulting electrostatic potential is frequently referred to as a screened potential distinguishing it from the ordinary (static) Coulomb potential. The free energy of a charged surface, with an adjacent layer of counterions, immersed in an aqueous medium can then be obtained by integrating the potential over all charges of the surface. An exact explicit expression

(13) Zhu, B. Y.; Rosen, M. J. *J. Colloid Interface Sci.* **1984**, *99*, 435.

(14) Corkhill, J. M.; Goodman, J. F.; Ogden, C. P.; Tate, J. R. *Proc. R. Soc. London Ser. A* **1963**, *273*, 84.

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

(16) Salkar, R. A.; Mukesh, D.; Samant, S. D.; Manohar, C. *Langmuir* **1998**, *14*, 3778.

(17) Bergström, M.; Eriksson, J. C. *Langmuir* **2000**, *16*, 7173.

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

for the resulting electrostatic free energy can only be analytically derived for a planar surface. However, approximate expressions for a spherical and cylindrical surface have been evaluated by Evans and Ninham<sup>19</sup> by expanding  $\epsilon_{\text{el}}$  to first order with respect to  $1/\kappa r_{\text{el}}$  and, independently, to second order in  $1/\kappa r_{\text{el}}$  by Lekkerkerker<sup>20</sup> and Mitchell and Ninham<sup>21</sup> where  $r_{\text{el}}$  is the radial distance to the surface of charge and the inverse of the Debye-length is defined as

$$\kappa = \sqrt{\frac{2c_{\text{t}}N_{\text{A}}e_{\text{el}}^2}{\epsilon_0\epsilon_{\text{r}}kT}} \quad (8)$$

$c_{\text{t}}$  denotes the total concentration of electrolyte in the solution,  $N_{\text{A}}$  the Avogadro number, and  $e_{\text{el}}$  the elementary charge, and  $\epsilon_0$  and  $\epsilon_{\text{r}}$  are the permittivity of vacuum and the dielectric constant, respectively.

The resulting free energy per surface charge can be summarized with the following equation:<sup>22</sup>

$$\epsilon_{\text{el}}/kT = h_0 + \frac{2h_1}{\kappa}H + \frac{4h_{21}}{\kappa^2}H^2 + \frac{4h_{22}}{\kappa^2}K \quad (9)$$

The parameters

$$h_0 = 2 \left[ \ln(S + \sqrt{S^2 + 1}) - \frac{\sqrt{S^2 + 1} - 1}{S} \right] \quad (10)$$

$$h_1 = -\frac{4}{S} \ln \left( \frac{1 + \sqrt{S^2 + 1}}{2} \right) \quad (11)$$

$$h_{21} = \frac{1}{2S} - \frac{1}{S^3} + \frac{1}{S^3\sqrt{S^2 + 1}} \quad (12)$$

$$h_{22} = -\frac{1}{2S} D_1 \left( \ln \left( \frac{1 + \sqrt{S^2 + 1}}{2} \right) \right) \quad (13)$$

where

$$D_1(x) = \int_0^x \frac{t}{e^t - 1} dt \quad (14)$$

are all functions of the reduced charge density

$$S \equiv \frac{\sigma}{\sqrt{8c_{\text{t}}\epsilon_0\epsilon_{\text{r}}N_{\text{A}}kT}} \quad (15)$$

where  $\sigma = e_{\text{el}}/a_{\text{el}}$  is the density of the smeared-out charges for a surface with an area  $a_{\text{el}}$  per surface charge. In addition,  $\epsilon_{\text{el}}$  explicitly depends on the mean  $H = 1/2(c_1 + c_2)$  as well as the Gaussian curvature  $K = c_1 \times c_2$ , respectively, where the principal curvatures  $c_1 = c_2 = 1/r_{\text{el}}$  for a spherical surface and  $c_1 = 1/r_{\text{el}}$  and  $c_2 = 0$  for a cylindrical surface. For a noncurved planar surface  $c_1 = c_2 = 0$  so that only the curvature independent part  $h_0$  contributes to the electrostatic free energy, i.e.,  $\epsilon_{\text{el}}/kT = h_0$ .

For a mixture of two monovalent and oppositely charged surfactants we can write the electrostatic free energy per aggregated surfactant as

$$\epsilon_{\text{el}}^m = |2x_1 - 1|\epsilon_{\text{el}} \quad (16)$$

An approximate expression for  $\epsilon_{\text{el}}^m$  can be obtained by means of considering the case where  $S \gg 1$ . This is a fairly good approximation for electrolyte concentrations  $c_{\text{t}}$  below about 0.2 M, for which  $S \geq 10$ , provided  $x_1$  is not close to equimolar composition. Since the contribution from energetic effects to the electrostatic free energy is negligible in the regime of  $S$  values larger than about unity,<sup>18</sup> we may conclude that the synergistic effects due to electrostatics obtained in our analysis is of an entropic origin (entropy of mixing counterions and solvent molecules).

For a planar aggregate surface we can write

$$\epsilon_{\text{el}}/kT = 2\ln(2S/e) \quad (17)$$

in accordance with the assumption  $S \gg 1$ . Moreover, assuming the electrolyte concentration to follow

$$c_{\text{t}} = |2x_1 - 1|cmc_1 \quad (18)$$

and inserting  $\sigma = |2x_1 - 1|e_{\text{el}}/a$  in eq 15, we obtain from eqs 16–18

$$\epsilon_{\text{el}}^m/kT = |2x_1 - 1|(\ln|2x_1 - 1| + \epsilon_{\text{el}}^1/kT) \quad (x_1 > 0.5) \quad (19a)$$

and

$$\epsilon_{\text{el}}^m/kT = |2x_1 - 1|(\ln|2x_1 - 1| + \epsilon_{\text{el}}^2/kT) \quad (x_1 < 0.5) \quad (19b)$$

where  $\epsilon_{\text{el}}^1/kT = 2\ln(2S_1/e)$  and  $\epsilon_{\text{el}}^2/kT = 2\ln(2S_2/e)$  are electrostatic free energies per monomer for pure surfactants 1 and 2, respectively, and  $S_1$  and  $S_2$  are obtained by inserting  $c_{\text{t}} = cmc_1$  and  $c_{\text{t}} = cmc_2$ , respectively, in eq 15.

By inserting eq 19 in eqs 4 and 5, we obtain for  $x_1 > 0.5$

$$A(x_1) = (2x_1 - 1) \exp[2(1 - x_1)] \quad (20)$$

and

$$B(x_1) = \exp[-2(x_1 + \epsilon_{\text{el}}^1/kT)]/(2x_1 - 1) \quad (21)$$

and for  $x_1 < 0.5$  we arrive at the following expressions

$$A(x_1) = \exp[-2((1 - x_1) + \epsilon_{\text{el}}^2/kT)]/(1 - 2x_1) \quad (22)$$

and

$$B(x_1) = (1 - 2x_1) \exp[2x_1] \quad (23)$$

Eqs 22 and 23 are, of course, symmetrical to eqs 20 and 21 in the sense that the latter are recovered by inserting  $x_1$  and  $1 - x_1$  instead of  $1 - x_1$  and  $x_1$ , respectively, in the former.

We note that for  $S > 10$   $\epsilon_{\text{el}}^1$  is large (at least about  $5kT$ ) and, hence,  $A(x_1) \gg B(x_1)$ , which means that the free monomer concentration of surfactant 1, i.e., the surfactant in excess, at cmc is, except for compositions close to  $y_1 = 0.5$ , much larger than the corresponding concentration of the surfactant in deficit (cf. Figure 1). This behavior of the  $cmc_1^m(x_1)$  and  $cmc_2^m(x_1)$  functions is in agreement with direct measurements of  $[DTA^+]$  with an ion-selective electrode by Kamenka et al.<sup>2</sup> who thus observed a much larger concentration of free monomers of the surfactant in excess in mixtures of  $C_{12}SO_4^-Na^+$  (SDS) and  $C_{12}TA^+Br^-$  (DTAB).

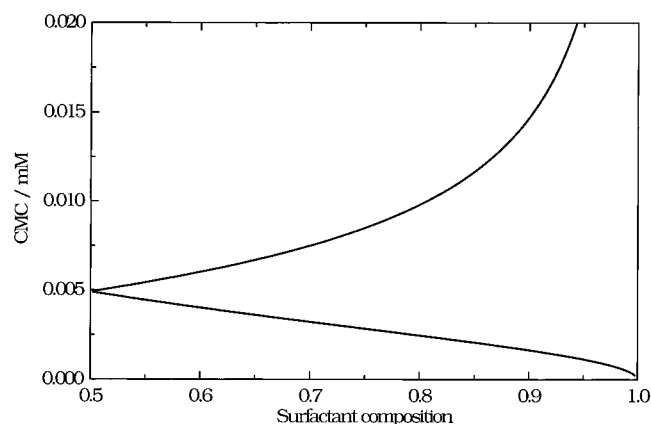
(19) Evans, D. F.; Ninham, B. W. *J. Phys. Chem.* **1983**, *87*, 5025.

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

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

(22) Ljunggren, S. Personal communication.





**Figure 1.** Critical micelle concentrations of an anionic surfactant ( $cmc_1^m$ ) and of a cationic surfactant ( $cmc_2^m$ ) plotted against the anionic rich part of the overall surfactant composition  $y_1$ . The diagram is symmetrical with respect to the equimolar composition, and hence, the concentration of free monomers of the surfactant in excess is larger than the corresponding quantity for the surfactant in deficit except at  $x_1 = y_1 = 0.5$  where they are equal. The cmc for the pure surfactant is set equal to  $cmc_1 = 10$  mM.

A consequence of the fact that the free monomer concentration of the surfactant in excess is generally much larger than the concentration of the surfactant in deficit is that the aggregate composition slightly above the cmc changes with overall surfactant concentration at a fixed overall surfactant composition. The reason for this is that the fraction of free monomers, which is almost exclusively the surfactant in excess, increases with decreasing overall surfactant concentration and, as a result, the composition in the aggregates must subsequently approach equimolarity. As a matter of fact, a change toward equimolar composition in mixed SDeS/DeTAB ( $C_{10}SO_4^-Na^+/C_{10}TAB$ ) aggregates with decreasing overall surfactant concentration ( $=[SDeS] + [DeTAB]$ ) at constant molar ratio ( $=[SDeS]:[DeTAB]$ ) has been directly observed by Villeneuve et al. in recent surface tension measurements.<sup>12</sup> Moreover, Bergström and Pedersen<sup>8,9,23</sup> arrived at the same conclusion from small-angle neutron scattering (SANS) studies by observing, for both SDS-rich and DTAB-rich aggregates, an increasing micellar size, and a subsequent transition to vesicles, as  $[SDS] + [DTAB]$  was decreasing at a fixed molar ratio  $[SDS]:[DTAB]$ .

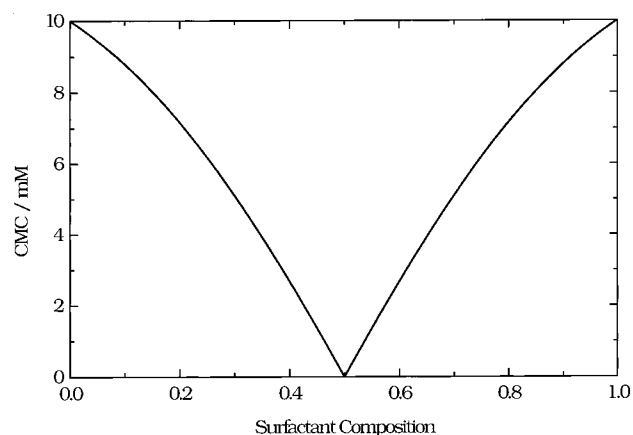
Hence, according to eqs 20–23, the cmc for a mixture of a (monovalent) anionic and a (monovalent) cationic surfactant is given by

$$cmc(x_1) = x_1(2x_1 - 1) \exp[2(1 - x_1)]cmc_1 \quad (x_1 > 0.5) \quad (24)$$

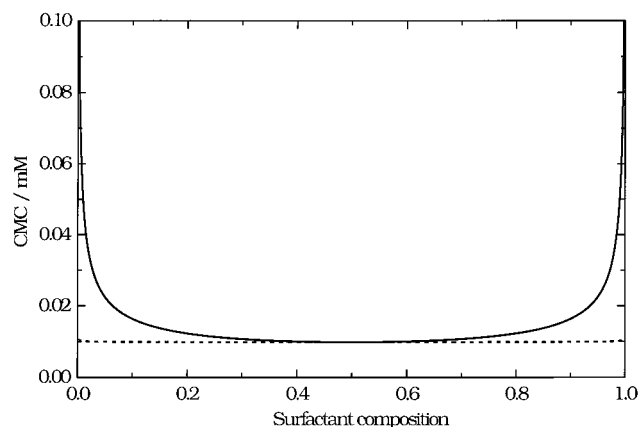
and

$$cmc(x_1) = (1 - x_1)(1 - 2x_1) \exp[2x_1]cmc_2 \quad (x_1 < 0.5) \quad (25)$$

Equations 24 and 25 are shown in Figure 2 and it is seen that  $cmc(x_1)$  to a rather good approximation behaves as  $(2x_1 - 1)cmc_1$  ( $x_1 > 0.5$ ) and  $(1 - 2x_1)cmc_2$  ( $x_1 < 0.5$ ) as assumed for the electrolyte concentration  $c_i$  in eq 18. Moreover, the appearance of the cmc vs  $x_1$  curve shown in Figure 2 is not influenced by the fact that the assumption  $S \gg 1$  breaks down at  $x_1 \approx 0.5$ . Accordingly, the cmc at  $x_1 = 0.5$  is much lower than  $cmc_1$  and  $cmc_2$  but not exactly zero as implied by eqs 24 and 25 due to the assumption  $S \gg 1$ .



**Figure 2.** Cmc for a mixture of a monovalent anionic and an otherwise identical monovalent cationic surfactant plotted against the mole fraction of the anionic surfactant in the aggregates  $x_1$  in accordance with eqs 20–23. The cmcs for the pure surfactants are set equal to  $cmc_1 = cmc_2 = 10$  mM. The aggregates are assumed to have a planar geometry.



**Figure 3.** Cmc for a mixture of a monovalent anionic and an otherwise identical monovalent cationic surfactant plotted against the overall mole fraction of the anionic surfactant  $y_1$  (solid line). The cmcs for the pure surfactant are set equal to  $cmc_1 = cmc_2 = 10$  mM which correspond to  $\epsilon_{el} = 7kT$  according to eq 9. As a result, the cmc curve according to eq 1 with  $\beta = -4\epsilon_{el}/kT = -28$  (dashed line) coincides with the former curve near  $y_1 = 0.5$ . The aggregates are assumed to have a planar geometry.

### The Cmc as a Function of the Overall Surfactant Composition $y_1$

In Figure 3 we have plotted cmc as a function of the overall surfactant concentration  $y_1 \equiv cmc_1^m(x_1)/(cmc_1^m(x_1) + cmc_2^m(x_1))$  for the case of planar aggregate geometry. This curve  $[cmc(y_1)]$  appears very different from the one plotted in Figure 2  $[cmc(x_1)]$  because the composition in the aggregates reaches values very close to equimolar composition even if the overall composition  $y_1$  deviates appreciably from 0.5. As a matter of fact, overall surfactant compositions in the range  $0.002 < y_1 < 0.998$  (shown in Figure 3) corresponds to compositions in the aggregates of  $0.497 < x_1 < 0.503$ . The reason for this is the enormous reduction of the unfavorable electrostatic free energy as the charges of two oppositely charged surfactants cancel in the aggregates. As a result, values close to  $x_1 = 0.5$  are obtained when minimizing the aggregate free energy with respect to the composition at cmc. As a matter of fact, aggregation compositions very close to equimolar composition in almost the entire range of overall compositions  $y_1$  was observed in recent surface tension measurements by Villeneuve et al.<sup>12</sup>

(23) Bergström, M.; Pedersen, J. S. *J. Phys. Chem. B* **1999**, *103*, 8502.

For compositions close to  $x_1 = 0.5$  the approximation  $S \gg 1$  is no longer valid and, hence, we have used  $\epsilon_{\text{el}}/kT = h_0$  (cf. eq 10) rather than eq 17 when calculating  $\epsilon_{\text{el}}^m(x_1)$  from eq 16. In accordance, the derivative of  $\epsilon_{\text{el}}^m$  with respect to  $x_1$  equals

$$\frac{d\epsilon_{\text{el}}^m/kT}{dx_1} = 4\ln(S + \sqrt{S^2 + 1}) - \frac{2\sqrt{S^2 + 1} - 1}{S} \quad (26)$$

for planar geometry which becomes zero in the limit of  $x_1 \rightarrow 0.5$  corresponding to  $S \rightarrow 0$ . As a result

$$\lim_{x_1 \rightarrow 0.5} A(x_1) = e^{-\epsilon_{\text{el}}^1/kT} \quad (27)$$

and

$$\lim_{x_1 \rightarrow 0.5} B(x_1) = e^{-\epsilon_{\text{el}}^2/kT} \quad (28)$$

are obtained from eqs 4 and 5. Equations 27 and 28 are valid for an arbitrary aggregate geometry since the inclusion of curvature-dependent terms in the expression for  $\epsilon_{\text{el}}$  does not change the fact that  $\epsilon_{\text{el}}^m(x_1) = d\epsilon_{\text{el}}^m(x_1)/dx_1 = 0$  in the limit  $x_1 \rightarrow 0.5$ . Hence, in the special case  $\epsilon_{\text{el}}^1 = \epsilon_{\text{el}}^2$  the simple expression

$$\beta = -4\epsilon_{\text{el}}^1/kT = -4\epsilon_{\text{el}}^2/kT \quad (29)$$

is obtained from eqs 27 and 28 by inserting  $x_1 = 0.5$  in eqs 6 and 7 and, as a consequence, a plot of cmc against  $y_1$  according to eqs 6 and 7 with  $\beta = -4\epsilon_{\text{el}}^1/kT$  coincides with the calculated  $\text{cmc}(y_1)$  curve at  $y_1 = 0.5$  (cf. Figure 3). Most interestingly, according to eq 29, the electrostatic contribution to synergistic effects in mixtures of an anionic and a cationic surfactant only depend on the electrostatic free energy for the pure surfactant aggregates but not on the structure of the mixed aggregates. The reason for this is that the physical origin of the synergistic effects is the elimination of the unfavorable electrostatic free energy as oppositely charged surfactants aggregate giving an aggregate mole fraction  $x_1 = 0.5$  in virtually the entire overall composition range  $y_1$ . As is evident from Figure 3, the cmc is brought down enormously in catanionic mixtures (a factor  $\sim 10^4$  for the example shown in Figure 3) when  $y_1$  approaches 0.5.

The  $\text{cmc}(y_1)$  curve in Figure 3 is calculated assuming the aggregates to have a planar geometry. However, since the magnitude of  $\beta$ , according to eq 29, only depends on the electrostatic free energy of the pure surfactant, and highly curved almost spherical micelles are usually formed by a pure ionic surfactant, the synergistic effects may be estimated more accurately by taking into account the curvature dependent terms in eq 9 when calculating  $\epsilon_{\text{el}}^1$  and  $\epsilon_{\text{el}}^2$ . The corresponding  $\beta$ -values are given in Table 1 for a number of catanionic surfactant mixtures with different cmcs. In the calculations of  $\epsilon_{\text{el}}$  we have assumed the cmc to be 10 mM for a mixture of two surfactants with identical  $\text{C}_{12}$  hydrocarbon chains and increasing with a factor of 4 for each ethylene group ( $-\text{CH}_2-\text{CH}_2$ ) that are removed from the aliphatic chain of an ionic surfactant.<sup>24</sup> We have furthermore assumed the pure micelles to be spherically shaped with a radius to the surface of charge  $r_{\text{el}}$  equal to 20 Å for the  $\text{C}_{12}$  surfactant case<sup>25,26</sup> as well as  $r_{\text{el}}$  to be proportional to the number  $n$  of carbon atoms in

**Table 1. Calculated  $\beta$  Values for a Mixture of a Monovalent Anionic and a Monovalent Cationic Surfactant with Identical Cmcs for the Pure Cases<sup>a</sup>**

$n$	cmc/mM	$\epsilon_{\text{el}}/kT$	$\beta = -4\epsilon_{\text{el}}/kT$
16	0.625	8.79	-35.2
14	2.5	7.42	-29.7
12	10	6.07	-24.3
10	40	4.76	-19.0
8	160	3.51	-14.0
6	640	2.39	-9.5

<sup>a</sup> The free energy per aggregated charge for the pure surfactant aggregate  $\epsilon_{\text{el}}$  was calculated from eq 9 assuming the micelles to be spherically shaped with a radius to the surface of charge  $r_{\text{el}} = 20$  Å for the case where the number of carbons in the aliphatic chain  $n = 12$ . For the residual cases  $r_{\text{el}}$  was assumed to be proportional to  $n$ . The area per aggregated surfactant at the surface of charge was set to  $a_{\text{el}} = 50 \text{ Å}^2$ .

an aliphatic hydrocarbon chain. The area per aggregated surfactant at the surface of charge was set equal to  $a_{\text{el}} = 50 \text{ Å}^2$  for all cases in accordance with the fact that  $a_{\text{el}} = 3v_s/r_{\text{el}}$  where  $r_{\text{el}}$  is proportional to the volume  $v_s$  of a surfactant molecule. A clear trend of decreasing magnitude of the synergistic effects with increasing cmc for the pure surfactants is seen. The calculated synergistic effects are in good agreement with the experimental results  $\beta = -25.5$  for  $\text{C}_{12}\text{SO}_4^- \text{Na}^+/\text{C}_{12}\text{TA}^+\text{Br}^-$  with  $n = 12$  (cmc = 8 mM/15 mM),<sup>13</sup>  $\beta = -18.5$  ( $n = 10$ , cmc = 33 mM/66 mM)<sup>14</sup> and  $\beta = -10.5$  ( $n = 8$ , cmc = 130 mM/does not form micelles).<sup>15</sup> It may be noted that for mixtures of oppositely charged surfactants with different cmcs the  $\text{cmc}(y_1)$  function becomes unsymmetrical, and hence, experimentally obtained  $\beta$  values must be different in the anionic-rich and cationic-rich side of the cmc vs  $y_1$  plot.

Since the synergism in mixtures of oppositely charged surfactants is more or less entirely determined by the electrolyte concentration for the pure surfactants, addition of an inert salt is predicted to largely influence  $\epsilon_{\text{el}}$  and, thus,  $\beta$  so that the magnitude of  $\beta$  rapidly decreases with an increasing salt concentration. As a result,  $\beta$  has been observed to increase from  $-18.5$  to  $-13.2$  as 0.05 M NaBr is added to a  $\text{C}_{10}\text{SO}_4^- \text{Na}^+/\text{C}_{10}\text{TA}^+\text{Br}^-$  mixture.<sup>27</sup> These experimental results may be compared with our theoretical estimates using the expression  $\beta = -4\epsilon_{\text{el}}/kT$ , which increases from  $-18.2$  to  $-15.7$  as the electrolyte concentration is increased from 50 to 100 mM.

### Mixtures of Surfactants with Headgroups with Different Cross Section Areas

In our recent analysis, we found that the electrostatic synergistic effects become somewhat enhanced in a mixture of an ionic and a nonionic surfactant with different headgroup cross-section areas.<sup>17</sup> These additional effects are the result of the entropy of mixing headgroups and water molecules, the free energy contribution of which may be written as<sup>17</sup>

$$\epsilon_{\text{hg}}^m(x_1) = \ln \eta + \frac{\eta(20 - \eta)}{15(1 - \eta)} - \frac{2}{3} \ln(1 - \eta) \quad (30)$$

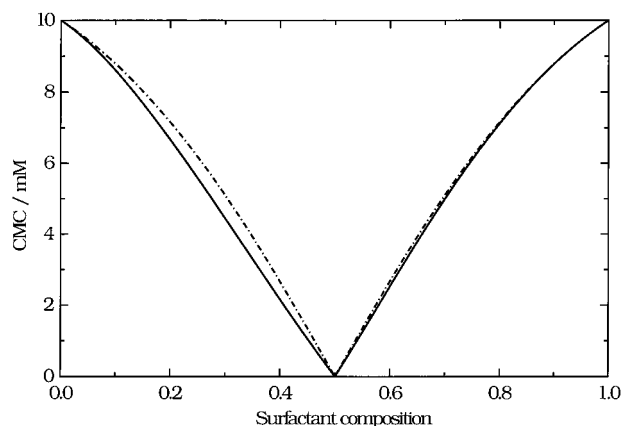
where the area fraction of headgroups at the aggregate surface equals  $\eta(x_1) = [x_1 a_1^{\text{hg}} + (1 - x_1) a_2^{\text{hg}}]/a$ .  $a_1^{\text{hg}}$  and  $a_2^{\text{hg}}$  are the cross-section areas of the headgroups of surfactants 1 and 2, respectively, and  $a$  is the area per aggregated surfactant. In a similar way, it is possible to show that the

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

(26) Eriksson, J. C.; Ljunggren, S. *Langmuir* **1990**, *6*, 895.

(27) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984.

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



**Figure 4.** Cmc for mixtures of a anionic and a cationic surfactant with rigid circular headgroups with different cross-section areas plotted against the mole fraction of Surfactant 1 in the aggregates ( $x_1$ ). The area per aggregated surfactant was set equal 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 set to  $\Delta a_{\text{hg}} \equiv a_2^{\text{hg}} - a_1^{\text{hg}} = 10 \text{ \AA}^2$  (solid line). The corresponding curve for two surfactants with headgroups of equal size is also included (dashed-dotted line). The cmc is mostly brought down at compositions rich of the surfactant with the larger headgroup (i.e., Surfactant 2).

cmc( $x_1$ ) curve shown in Figure 2 is slightly brought down if the two surfactants have headgroups with unequal cross-section areas (cf. Figure 4).

Since the overall free energy can be written as a sum of different contributions, we may separate the exponential functions  $A(x_1)$  and  $B(x_1)$  into one electrostatic and one residual headgroup factor, i.e.

$$\text{cmc}(x_1) = A_{\text{el}}(x_1)A_{\text{hg}}(x_1)x_1\text{cmc}_1 + B_{\text{el}}(x_1)B_{\text{hg}}(x_1)(1 - x_1)\text{cmc}_2 \quad (31)$$

where  $A_{\text{el}}(x_1)$  is given by eq 27 for a mixture of an anionic and a cationic surfactant and  $A_{\text{hg}}(x_1)$  is strictly given by eq 4 with  $\epsilon_i^m \equiv \epsilon_{\text{hg}}^m$ . However, as a first approximation we may assume the headgroup contribution to follow the regular solution expression in eq 6, i.e.

$$A_{\text{hg}}(x_1) = e^{(1-x_1)^2\beta_{\text{hg}}} \quad (32)$$

Hence, by taking into account that the composition in the aggregates is  $x_1 = 0.5$  in almost the entire range of  $y_1$  values we obtain from eqs 27 and 32,  $\beta = \beta_{\text{el}} + \beta_{\text{hg}}$  where  $\beta_{\text{el}} = -4\epsilon_{\text{el}}/kT$ . In other words, the synergistic effects from the two free energy contributions are additive in a first approximation. However, the residual headgroup contribution to synergism is usually rather small, i.e.,  $0 > \beta_{\text{hg}}$

$> -1$ ,<sup>17</sup> and can for most cases be neglected when compared with the large electrostatic synergistic effects found in mixtures of an anionic and a cationic surfactant.

## Conclusions

Synergistic effects in mixtures of an anionic and a cationic surfactant have been observed to be several orders of magnitude larger than for related systems such as mixtures of an ionic and a nonionic surfactant. We have recently shown that for the latter case  $\beta = -1$  in the absence of added salt for two surfactants that are otherwise identical and that  $\beta$  becomes slightly reduced (that is more negative) if the cross-section areas of the headgroups are different.<sup>17</sup> On the other hand,  $\beta$  may assume values well below  $-20$  for the corresponding surfactant mixture of two oppositely charged surfactants and the magnitude of  $\beta$  increases with increasing surfactant tail length equivalent to a decreasing cmc for the pure surfactant.

In the present paper, we have rationalized the conspicuously large synergistic effects observed in mixtures of an anionic and a cationic surfactant using the Poisson–Boltzmann mean field theory. The order of magnitude of the observed  $\beta$  values could thus be generated and so could the trend of increasing magnitude of  $\beta$  with increasing surfactant tail length. In accordance, we may conclude that the considerable reduction in cmc in catanionic systems is due to the elimination of the unfavorable electrostatic free energy, and the subsequent reduction of the surfactant aggregate chemical potential, when two oppositely charged surfactants are aggregated. Since the fairly large electrostatic free energy is mainly due to the unfavorable entropy of concentrating counterions in a diffuse layer outside a charged surface, the corresponding synergistic effects are for all practical purposes a result of an increase in entropy as a pair of counterions are released from the spatially restricted diffuse layer to the bulk solution. This is in contrast to the case of mixing an ionic and a nonionic surfactant where the synergistic effects are mainly due to the dilution of counterions in the diffuse layer as a nonionic surfactant is admixed to a charged surfactant layer. However, in neither case is it necessary to invoke any specific interactions between the surfactant headgroups, as frequently done in the past, to rationalize synergistic effects in mixtures containing ionic surfactants.

**Acknowledgment.** M.B. was financed by the Swedish National Board for Industrial and Technical Development (NUTEK) and a company consortia through the Competence Center for Surfactants Based on Natural Products (SNAP).

LA000814T