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A Model-Independent Evaluation of Experimental Data, and Comparison with Theory, of Synergistic Effects in Mixtures of an Ionic and a Nonionic Surfactant

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Critical micelle concentrations for mixtures of an anionic (sodium dodecyl sulfate) and a nonionic (decyl β-glucoside) surfactant was obtained from surface tension measurements at different concentrations of added NaCl. The observed synergistic effects were analyzed by means of introducing a novel model-independent synergy parameter. The model-independent evaluation has enabled the comparison of experimental results with a theoretical model based on the Poisson–Boltzmann (PB) mean field theory for spherical, cylindrical, and planar geometries, respectively. We found that best agreement with experimental data was obtained for largely curved structures (spherical and cylindrical micelles) at all [NaCl], which is consistent with the fact that rather small micelles, as a rule, form at the critical micelle concentration. Moreover, the PB theory was found to better describe synergistic behavior of the experimental data than the more conventional regular mixture theory, in particular at low electrolyte concentrations. The magnitude of the observed synergistic effects was found to increase as a small amount of NaCl was added and reach a maximum at [NaCl] = 10 mM, in agreement with the PB theory. As expected, synergism was observed to decrease in magnitude upon further addition of NaCl.

Introduction

The critical micelle concentration (cmc) for several binary surfactant mixtures cannot be accurately accounted for by an ideal linear equation. *Nonideal* behavior may thus be taken into account by writing

$$\text{cmc} = a_1\text{cmc}_1 + a_2\text{cmc}_2 \tag{1}$$

where $a_1 = x\gamma_1$ and $a_2 = (1 - x)\gamma_2$ are the activities of surfactant 1 and surfactant 2, respectively, and γ_1 and γ_2 are the corresponding activity coefficients. Ideal behavior is obtained as a special case of eq 1 when $\gamma_1 = \gamma_2 = 1$. Since, by definition, the amount of surfactant existing as free monomers is much larger than the amount of aggregated surfactant at cmc, the overall mole fraction of surfactant 1 (free + aggregated surfactant) $y = a_1\text{cmc}_1/(a_1\text{cmc}_1 + a_2\text{cmc}_2)$, where the free concentration of either surfactant equals $\text{cmc}_1^m = a_1\text{cmc}_1$ and $\text{cmc}_2^m = a_2\text{cmc}_2$, respectively, at cmc. As a result, cmc as a function of the overall mole fraction y may be written as

$$\frac{1}{\text{cmc}} = \frac{y}{\gamma_1\text{cmc}_1} + \frac{1 - y}{\gamma_2\text{cmc}_2} \tag{2}$$

and the activities may be evaluated from experimental cmc vs y data from the relations $a_1 = y\text{cmc}/\text{cmc}_1$ and $a_2 = (1 - y)\text{cmc}/\text{cmc}_2$.

We have in a recent paper[1] demonstrated that the activity coefficients may be calculated from the free energy per aggregated monomer ϵ, i.e.

$$\gamma_1(x) = \exp\left[\left(\epsilon_{\text{ex}}(x) - \epsilon_{\text{ex}}(x=1) + (1 - x)\frac{d\epsilon_{\text{ex}}}{dx'}\right.\right.$$
$$\left.\left.(x' = x)\right)/kT\right] \tag{3}$$

$$\gamma_2(x) = \exp\left[\left(\epsilon_{\text{ex}}(x) - \epsilon_{\text{ex}}(x=0) - x\frac{d\epsilon_{\text{ex}}}{dx'}(x' = x)\right)/kT\right] \tag{4}$$

where the excess free energy per aggregated surfactant is defined as $\epsilon_{\text{ex}} \equiv \epsilon - kT[x \ln x + (1 - x) \ln(1 - x)]$. x is the mole fraction of surfactant 1 that minimizes ϵ for a certain solution state, i.e., certain values of cmc_1^m and cmc_2^m, whereas x' denotes the not yet minimized mole fraction. k is Boltzmann's constant, and T is the absolute temperature. It is straightforward to show that γ_1 and γ_2 both equal unity if ϵ_{ex} is linear with respect to x, i.e., $\epsilon(x) = x\epsilon_1 + (1 - x)\epsilon_2$, where ϵ_1 and ϵ_2 are constants.

Since originally suggested by Rubingh,[2] nonideal behavior has usually been rationalized by treating the surfactant aggregates as a regular mixture, the molecular free energy of which may be written as

$$\epsilon(x)/kT = x \ln x + (1 - x) \ln(1 - x) + \beta_{\text{int}}x(1 - x) \tag{5}$$

The parameter $\beta_{\text{int}} = w/kT$ is the pairwise interaction energy in kT units between a surfactant 1 and a surfactant 2 molecule in the mixed aggregates subtracted by the corresponding interactions between two surfactant 1 and two surfactant 2 molecules, respectively, i.e., $w = F_{AB} - \frac{1}{2}(F_{AA} + F_{BB})$. By inserting eq 5 in eqs 3 and 4, the following

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

(2) Rubingh, D. N. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; p 337.

expressions for the activity coefficients are obtained

$$\gamma_1 = e^{(1-x)^2 \beta_{\text{int}}} \tag{6}$$

$$\gamma_2 = e^{x^2 \beta_{\text{int}}} \tag{7}$$

In accordance, a negative deviation of cmc from ideal behavior (synergism) is obtained for negative values of the interaction parameter ($\beta_{\text{int}} < 0$) whereas a positive deviation from ideal behavior (antagonism) prevails as $\beta_{\text{int}} > 0$. In accordance with regular mixture (RM) theory, $\beta_{\text{int}} < 0$ means that 1−2 pairwise head group interactions in the mixed micelles are either more attractive or less repulsive than the corresponding 1−1 and 2−2 interactions.

Hitherto, experimental cmc vs composition data has most frequently been evaluated by assuming data to follow the RM theory. In accordance, it has in general been found that synergistic effects for mixtures of an ionic and a nonionic surfactant are larger in magnitude as compared to mixtures of two nonionic surfactants with typical values ranging between $-5 > \beta_{\text{int}} > -1$ in the former case.[3] In particular, the common ethylene oxide based surfactants generate, as a rule, β_{int} values in the lower regime ($-1 < \beta_{\text{int}} < -4$) together with a common ionic surfactant[4−6] whereas the synergism observed in mixtures where the nonionic surfactant is a sugar-based alkylglucoside seems to be smaller in magnitude, i.e., $-1 < \beta_{\text{int}} < -3$,[4,7−10] although somewhat lower β_{int} values have been observed in mixtures of sodium dodecyl sulfate and alkyl maltosides.[8,11] Moreover, when a substantial amount of inert salt was added, synergism has been found to decrease in magnitude.[3]

The RM theory is based on the assumption that micelle formation may be described by specific pairwise interactions as the most important free energy contribution. However, the RM theory is contradicted by some common well-established theoretical frameworks dealing with properties of surfactant aggregates. In particular, micelles consisting of ionic surfactants have been successfully accounted for in a quantitative manner by using the Poisson−Boltzmann (PB) mean field theory.[12−14] In the PB theory, specific molecular interactions are completely neglected as the surface charge on the aggregate interfaces is assumed to be smeared-out. As a consequence, the electrostatic micelle free energy is found to be dominated by the entropic penalty of concentrating counterions, treated as point charges, outside the charged interfaces.[15]

To overcome inconsistencies that may appear as a result of assuming the RM theory to well describe experimental data, we have below introduced a novel model-independent procedure to evaluate synergistic effects from experimen-
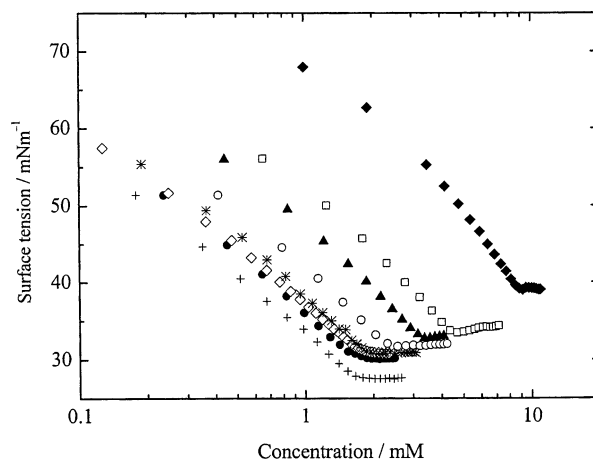

Figure 1. Surface tension for mixtures of SDS and $C_{10}G$ plotted against the overall surfactant concentration for different solution mole fractions y of SDS in the absence of added salt: $y = 0$ (+); $y = 0.1$ (●); $y = 0.2$ (◇); $y = 0.4$ (∗); $y = 0.6$ (○); $y = 0.8$ (▲); $y = 0.9$ (□); $y = 1.0$ (◆).

tally determined cmc values of surfactant mixtures. We also demonstrate that we may rationalize experimental observations of mixtures of an ionic and a nonionic surfactant by using the PB mean field theory rather than the RM theory based on specific interactions.

Materials and Methods

The sodium dodecyl sulfate (SDS) was obtained from Sigma (99% (GC)) and recrystallized in ethanol at least twice prior to use. The *n*-decyl β-D-glucopyranoside ($C_{10}G$, >98% GC) was obtained from Sigma, the sodium chloride (NaCl) was obtained from Merck (suprapur), and both were used as received. The water used in the experiments was obtained from a Millipore RiOs-8 and Milli-Q PLUS 185 purification system and finally filtered through a 0.2 μm Millipak filter.

The surface tension was measured with a Krüss K12 tensiometer, employing the Wilhelmy plate method. The measuring plate was made of platinum and was sand blastend to ensure a contact angle of zero degrees at the three-phase line. The thickness and width of the plate were $L_T = 0.2$ mm and $L_W = 12.5$ mm, respectively. The surface tension is calculated from the relation

$$F = 2(L_T + L_W)\gamma L_V \cos \theta + L_T L_W \Delta \rho g h \tag{8}$$

where F is the force acting on the plate (measured by the balance) and γ_{LV} is the liquid−vapor surface tension, θ is the contact angle at the three-phase line, $\Delta\rho$ is the density difference between the liquid and the vapor phase, g is the gravitational constant, and h is the immersion depth of the plate in the liquid (usually chosen at $h = 0$). The values reported are those obtained after the surface tension remained constant for $t > 60$ s. Equilibrium surface tension was seen to appear after typically a few minutes.

Examples of surface tension isotherms for the case of no added salt are given in Figure 1.

Model-Independent Analysis of Synergistic Effects

Synergistic effects observed in experimentally investigated systems have traditionally, as a rule, been analyzed by means of employing the regular mixture (RM) theory and expressing the magnitude of synergism (or antagonism) with the parameter β_{int}. However, such an analysis of experimental data must be dependent on a particular model, namely, the RM theory. Moreover, we have recently demonstrated that the RM approach for many cases is inadequate to describe experimental results accurately.[1,16]

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

(16) Bergström, M. *Langmuir* **2001**, *17*, 993.

Hence, there is an urgent need for a novel model-independent procedure to investigate synergistic effects found from experimental data as well as predicted by different theoretical models.

In accordance with eq 1, a nonideal behavior of cmc is taken into account by letting the activities a_1 and a_2 of surfactant 1 and 2 assume values not equal to unity. As a result, the magnitude of synergism may be quantified using the (model-independent) parameter

$$\beta \equiv 4 \ln(a_1 + a_2) = 4 \ln(x\gamma_1 + (1 - x)\gamma_2) \qquad (9)$$

For an ideal mixture, $a_1 = x$ and $a_2 = 1 - x$ giving $\beta = 0$ in the entire composition range. Moreover, a positive deviation from ideal behavior gives $\beta > 0$ whereas a negative deviation gives $\beta < 0$, in analogy with the interaction parameter β_{int} in the RM theory. Furthermore, we may calculate β for a regular mixture giving

$$\beta = 4 \ln(xe^{(1-x)^2\beta_{int}} + (1 - x)e^{x^2\beta_{int}}) \qquad (10)$$

It is straightforward to show that β as calculated from eq 10 always reaches its minimum value at $x_{min} = 0.5$ where $\beta = \beta_{int}$. As a matter of fact, we have chosen to multiply $\ln(a_1 + a_2)$ by 4 in the definition of β in eq 9 just because we are looking for a parameter that equals β_{int} for the RM theory at optimal synergism, i.e., where β reaches its minimum value ($=\beta_{min}$) at the optimal aggregate mole fraction $x_{min} = 0.5$.

We may finally investigate the special case of two surfactants that do not mix at all. In that case two different kinds of one-component micelles will coexist and, at dilute solutions, the free monomer concentrations at cmc, cmc$_1$, and cmc$_2$ will be independent of composition. As a result, a_1 and a_2 equal unity in the entire composition range and $\beta = 4 \ln 2 \approx 2.77$. For mixtures where two different kinds of aggregates still coexist but the surfactants do partly mix in the micelles, e.g., mixtures of hydrocarbon and fluorocarbon surfactants, antagonistic effects are expected to be present, i.e., $\beta > 0$, with a β value less than $4 \ln 2$.

Synergistic Effects for Mixtures of an Ionic and a Nonionic Surfactant As Calculated from the Poisson−Boltzmann Theory

The electrostatic free energy of surfactant aggregates consisting of ionic surfactants is usually accounted for by employing the Poisson−Boltzmann (PB) mean-field theory. The PB theory takes into account the reduction of entropy as the counterions of the ionic surfactants are concentrated outside the charged micellar interface whereas specific interactions between aggregated surfactant headgroups are neglected insofar the charges located at the micelle interface are assumed to be smeared-out. Accordingly, the electrostatic free energy per aggregated charge to first order in curvature may be written as a function of the reduced charge density $S = \sigma/(8c_t\epsilon_0\epsilon_r RT)^{1/2}$, i.e.[17]

$$\epsilon_{el}/kT = 2\left[\ln(S + (S^2 + 1)^{1/2}) - \frac{(S^2 + 1)^{1/2} - 1}{S}\right] - \frac{4H_{el}}{S\kappa}\ln\left(\frac{1 + (S^2 + 1)^{1/2}}{2}\right) \qquad (11)$$

where $\sigma = e_{el}/a_{ch}$ is the density of the smeared-out charges for a surface with an area a_{ch} per surface charge and e_{el} is the elementary charge. H_{el} is the mean curvature of the aggregate at the surface of charge and $\kappa^{-1} = (\epsilon_0\epsilon_r RT/$

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

$2c_tN_A^2e_{el}^2)^{1/2}$ is the Debye length where c_t denotes the total concentration of electrolyte in the solution, R is the gas constant, N_A is the Avogadro number, and ϵ_0 and ϵ_r are the permittivity in vacuum and the dielectric constant, respectively.

For the case of mixtures of a monovalent ionic and a nonionic surfactant, we may evaluate the nonideal behavior according to the PB theory by inserting the proper expression for the excess free energy per aggregated surfactant

$$\epsilon_{ex}(x) = x\epsilon_{el} \qquad (12)$$

where x is the mole fraction of aggregated ionic surfactant, in eqs 3 and 4 and calculate γ_1 and γ_2. Since $S = xe_{el}/a_{el}(8(a_1cmc_1 + c_s)\epsilon_0\epsilon_r RT)^{1/2}$ is dependent on x, ϵ_{el} is not a constant with respect to x and, as a consequence, cmc behaves nonideally according to the PB theory. a_{el} is the area per aggregated surfactant at the surface of charge, a_1cmc_1 is the concentration of free ionic surfactant at cmc, and c_s is the concentration, if any, of added electrolyte.

The resulting activity coefficients as functions of x may be expressed in terms of three dimensionless parameters λ, λ_0, and B, i.e.

$$\gamma_1 = \frac{\lambda_0}{\lambda}\left(\frac{x + (x^2 + \lambda)^{1/2}}{1 + (1 + \lambda_0)^{1/2}}\right)^2\left(\frac{1 + (1 + x^2/\lambda)^{1/2}}{1 + (1 + 1/\lambda_0)^{1/2}}\right)^{-B}$$
$$\exp\left[2((1 + \lambda_0)^{1/2} - \lambda_0^{1/2} - (x^2 + \lambda)^{1/2} + \lambda^{1/2}) - \frac{Bx(1 - x)}{x^2 + \lambda + (\lambda(x^2 + \lambda))^{1/2}}\right] \qquad (13)$$

$$\gamma_2 = \left(\frac{1 + (1 + x^2/\lambda)^{1/2}}{2}\right)^{-B}\exp\left[\frac{Bx^2}{x^2 + \lambda + (\lambda(x^2 + \lambda))^{1/2}} - 2((x^2 + \lambda)^{1/2} - \lambda^{1/2})\right] \qquad (14)$$

where

$$\lambda \equiv \frac{2a_{el}^2}{\pi l_B}N_A(\gamma_1 x_1 cmc_1 + c_s) \qquad (15)$$

$$\lambda_0 \equiv \frac{2a_{el}^2}{\pi l_B}N_A(cmc_1 + c_s) \qquad (16)$$

$$B \equiv \frac{4H_{el}}{S\kappa} = \frac{2a_{el}H_{el}}{\pi l_B} \qquad (17)$$

Hence, λ and λ_0 depend on the area per aggregated surfactant at the surface of charge a_{el}, whereas B also depends on the mean curvature H_{el}. $H_{el} = 1/R_{el}$ for spherical geometry and $H_{el} = 1/2R_{el}$ for cylindrical geometry where R_{el} is the radius of curvature at the surface of charge. The Bjerrum length $l_B \equiv e_{el}^2/4\pi\epsilon_0\epsilon_r kT$ equals 7.15 Å for an aqueous medium at 25 °C. We may note that the activity coefficient $\gamma_1 = a_1/x$ of the charged species is present both on the left-hand side and on the right-hand side of eq 13 and must therefore be calculated iteratively.

Equations 13 and 14 may be simplified for two limiting cases: (i) in the absence of added salt and (ii) when the concentration of added salt is much larger than the concentration of free ionic surfactant (excess salt).

Absence of Salt. For the special case of no added salt ($c_s = 0$) the electrolyte concentration is generally low which
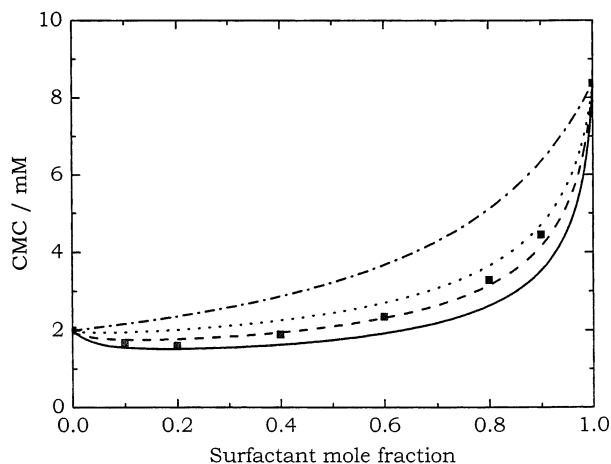
Figure 2. cmc for mixtures of SDS and $C_{10}G$ plotted against the overall mole fraction y of SDS in the absence of added salt. Symbols represent experimental data. Solid line represents calculations of the activities from the Poisson–Boltzmann (PB) model using eqs 20 and 21 assuming spherical geometry with radius of curvature $R_{el} = 20$ Å and area per aggregated surfactant at the surface of charge $a_{el} = 85$ Å^2. cmc as obtained by calculating the activity coefficients from the PB model assuming cylindrical geometry (dashed line, $R_{el} = 18$ Å and $a_{el} = 58$ Å^2) and planar geometry (dotted line, $a_{el} = 32$ Å^2) are also included. The dashed–dotted line shows ideal behavior of cmc.

means that λ and λ_0 both are $\ll 1$. As a result, eqs 13 and 14 may be simplified so as to give

$$\gamma_1 = \left(\frac{\lambda_0}{\lambda}\right)^{1-B/2} x^2 \exp\left[2(1-x) - \frac{Bx(1-x)}{x^2 + 2\lambda}\right] \quad (18)$$

$$\gamma_2 = \left(\frac{1 + (1 + x^2/\lambda)^{1/2}}{2}\right)^{-B} \exp\left[\frac{Bx^2}{x^2 + 2\lambda} - 2x\right] \quad (19)$$

Considering that $\lambda/\lambda_0 = a_1$ when $c_s = 0$ and replacing λ with λ_0 in the exponent in eq 18, we may derive an explicit expression for the activity of the ionic surfactant

$$\gamma_1 = x^{(2-B)/(4-B)} \exp\left[\frac{2(1-x)(2x^2 + 4\lambda_0 - Bx)}{(4-B)(x^2 + 2\lambda_0)}\right] \quad (20)$$

Likewise, λ may approximately be replaced with λ_0 in eq 19 giving

$$\gamma_2 = \left(1 + \frac{x}{\lambda_0^{1/2}}\right)^{-B} \exp\left[\frac{Bx^2 - 2x(x^2 + 2\lambda_0)}{x^2 + 2\lambda_0}\right] \quad (21)$$

where $\lambda_0 \equiv 2a_{el}^2 N_A cmc_1/\pi l_B$ in the absence of added salt. As a matter of fact, the latter approximation gives a more realistic behavior of cmc $= a_1 cmc_1 + a_2 cmc_2$ as calculated from eqs 20 and 21 at low mole fractions of the ionic surfactant (cf. Figure 2). The reason for this is that the approximation to first order in curvature of ϵ_{el} in eq 11 breaks down at low electrolyte concentrations, when the Debye-length κ^{-1} is large, which results in unrealistically low cmc values, as calculated from eq 13, at very low electrolyte concentrations.

We may calculate the synergism parameter $\beta \equiv 4 \ln(a_1 + a_2)$ from eqs 20 and 21. Inserting typical values of $a_{el} = 85$ Å^2 and $R_{el} = 20$ Å for spherical micelles and cmc$_1 = 8.4$ mM valid for SDS gives $\lambda_0 = 3.24 \times 10^{-3}$ and $B = 0.38$, the values of which imply a β with a minimum $\beta_{min} = -2.7$ at $x_{min} = 0.28$ (cf. Figure 3).
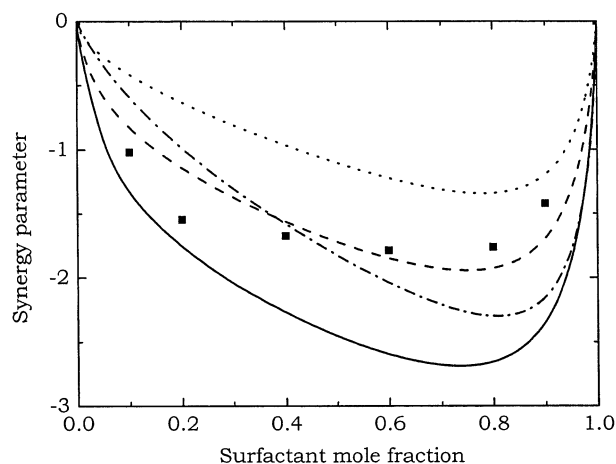

Figure 3. The synergy parameter β as defined in eq 9 plotted against the overall mole fraction y of SDS for mixtures of SDS and $C_{10}G$ in the absence of added salt. Symbols represent experimental data. Solid line represents calculations of the activities from the Poisson–Boltzmann (PB) model using eqs 20 and 21 assuming spherical geometry. β calculated from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also given. R_{el} and a_{el} were set to the same values for the different geometries as given in Figure 2. The dashed–dotted line represents the best available fit of β according to the regular mixture theory (eqs 6 and 7 with $\beta_{int} = -2.4$).

For planar geometry $B = 0$ implying that $a_1 = x^3/2 e^{(1-x)}$ and $a_2 = (1-x)e^{-2x}$ and

$$cmc = x^{3/2} e^{(1-x)} cmc_1 + (1-x) e^{-2x} cmc_2 \quad (22)$$

giving a β function with a minimum value $\beta_{min} = -1.34$ at $x_{min} = 0.298$. Hence, the magnitude of synergistic effects increases with increasing curvature of surfactant aggregates in the absence of added salt (cf. Figure 3).

We may note that the expression in eq 22 is somewhat different than that previously suggested by us[1] since in ref 1 we overlooked the minimization of the aggregate free energy ϵ, in eqs 3 and 4, with respect to aggregate composition x *at constant chemical potentials*, i.e., at constant cmc$_1^m = a_1 cmc_1$ and cmc$_2^m = a_2 cmc_2$.

Excess Salt. For the case of large concentrations of added salt, λ is no longer much smaller than unity. However, we may take into account that $c_s \gg a_1 cmc_1$, which means that $\lambda = \lambda_0 \equiv \lambda_s = 2a_{el}^2 N_A c_s/\pi l_B$, and we may rewrite γ_1 and γ_2 in eqs 13 and 14 so as to give

$$\gamma_1 = \left(\frac{x + (x^2 + \lambda_s)^{1/2}}{1 + (1 + \lambda_s)^{1/2}}\right)^2 \left(\frac{1 + (1 + x^2/\lambda_s)^{1/2}}{1 + (1 + 1/\lambda_s)^{1/2}}\right)^{-B} \exp\left[2((1 + \lambda_s)^{1/2} - (x^2 + \lambda_s)^{1/2}) - \frac{Bx(1-x)}{x^2 + \lambda_s + (\lambda_s(x^2 + \lambda_s))^{1/2}}\right] \quad (23)$$

$$\gamma_2 = \left(\frac{1 + (1 + x^2/\lambda_s)^{1/2}}{2}\right)^{-B} \exp$$

$$\left[\frac{Bx^2}{x^2 + \lambda_s + (\lambda_s(x^2 + \lambda_s))^{1/2}} - 2((x^2 + \lambda_s)^{1/2} - \lambda_s^{1/2})\right] \quad (24)$$

For very large salt concentrations, i.e., $\lambda_s \gg 1$, we note that $\gamma_1 = \gamma_2 = 1$ and ideal behavior is recovered.

Results and Discussion

In Figure 2 we have plotted the experimentally obtained cmc's for mixtures of $C_{10}G$ and SDS in the absence of added
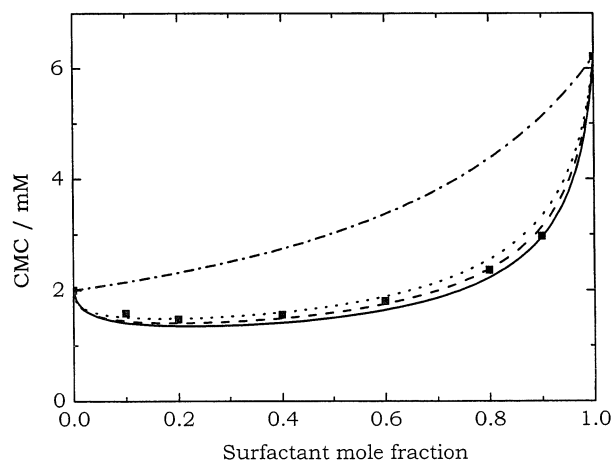
Figure 4. cmc for mixtures of SDS and $C_{10}G$ plotted against the overall mole fraction y of SDS at [NaCl] = 10 mM. Symbols represent experimental data. Solid line represents calculations of the activity coefficients from the Poisson–Boltzmann (PB) model using eqs 13 and 14 assuming spherical geometry. The activity coefficients as calculated from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also included. R_{el} and a_{el} were set to the same values for the different geometries as given in Figure 2. The dashed–dotted line shows ideal behavior of cmc.
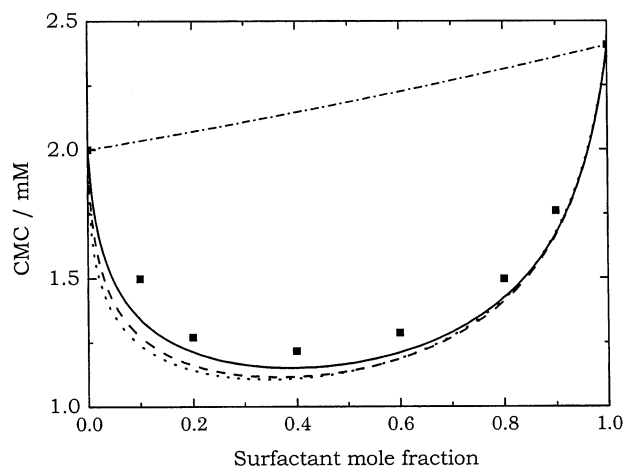

Figure 5. cmc for mixtures of SDS and $C_{10}G$ plotted against the overall mole fraction y of SDS at [NaCl] = 50 mM. Symbols represent experimental data. Solid line represents calculations of the activity coefficients from the Poisson–Boltzmann (PB) model using eqs 13 and 14 assuming spherical geometry. cmc values as obtained by calculating the activity coefficients from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also included. R_{el} and a_{el} were set to the same values for the different geometries as given in Figure 2. The dashed–dotted line shows ideal behavior of cmc.

salt as a function of the overall surfactant mole fraction y of SDS. We have also included cmc vs y according to eq 2 with the activity coefficients γ_1 and γ_2 as calculated from the PB model in eqs 20 and 21 for spherical, cylindrical, and planar geometries, respectively. In Figures 4–6 the corresponding data at concentrations of added salt [NaCl] = 10, 50, and 300 mM are given together with the PB model for different geometries according to eqs 13 and 14. The radius of curvature and the area per aggregated surfactant at the surface of charge was always set to $R_{el} = 20$ Å and $a_{el} = 85$ Å^2 for a spherical micelle roughly corresponding to what was obtained from detailed model calculations of spherical micelles formed from an ionic surfactant with a C_{12} hydrocarbon chain.[12] Likewise, we have set $R_{el} = 18$ Å and $a_{el} = 58$ Å^2 for cylindrical
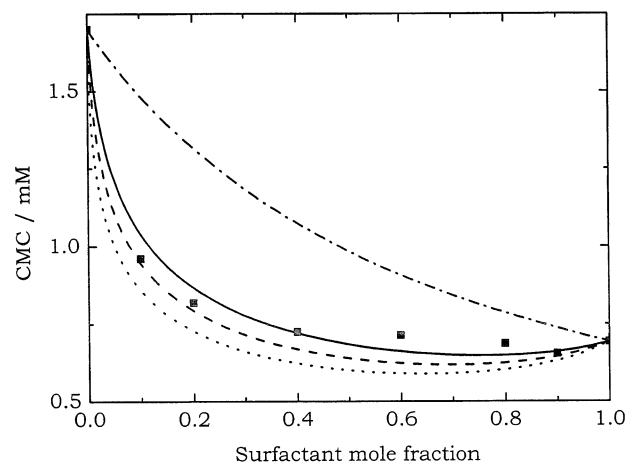

Figure 6. cmc for mixtures of SDS and $C_{10}G$ plotted against the overall mole fraction y of SDS at [NaCl] = 300 mM. Symbols represent experimental data. Solid line represents calculations of the activity coefficients from the Poisson–Boltzmann (PB) model using eqs 13 and 14 assuming spherical geometry. cmc values as obtained by calculating the activity coefficients from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also included. R_{el} and a_{el} were set to the same values for the different geometries as given in Figure 2. The dashed–dotted line shows ideal behavior of cmc.

micelles[18] and $a_{el} = 32$ Å^2 for planar geometry.[19,20] We note that better agreement between data and PB model is obtained for curved aggregate structures, in the absence as well as in the presence of added salt. This is consistent with the fact that rather small micelles are favored at low surfactant concentrations. The micelles are expected to grow rapidly with increasing surfactant concentration.

In Figure 3 we have plotted the synergism parameter β as a function of total mole fraction y of SDS in the absence of added salt. In addition to the behavior of the β parameter as predicted by the PB model for spherical, cylindrical, and planar geometries, we have also in Figure 3 included the RM theory with a β_{int} that best represents data. It is seen that spherical and cylindrical geometries agree better with experimental data than planar geometry. Moreover, the RM theory systematically overestimates synergism at high SDS fractions whereas it underestimates synergism at low fractions despite the fact that β_{int} has been optimized to give the best possible agreement with data. Similar tendencies can be observed in the presence of added salt although the RM theory is becoming more similar to the PB theory at higher electrolyte concentrations (cf. Figures 7–9). The reason for this is that optimum synergism according to the PB model is found to approach $x = 0.5$, i.e., the same value predicted by the RM theory, when the concentration of added salt increases (cf. Figure 10).

Comparing the PB model for different geometries, we note that synergism increases with increasing aggregate curvature at low concentrations of added salt whereas it decreases with increasing aggregate curvature at higher concentrations of added salt. The reason for this behavior is that β largely depends on H_{el} (or, equivalently, B) at low electrolyte concentrations whereas it is rather insensitive to a_{el} or S. The magnitude of synergistic effects increases with increasing aggregate curvature (H_{el}). On the contrary, at high electrolyte concentrations β is largely influenced

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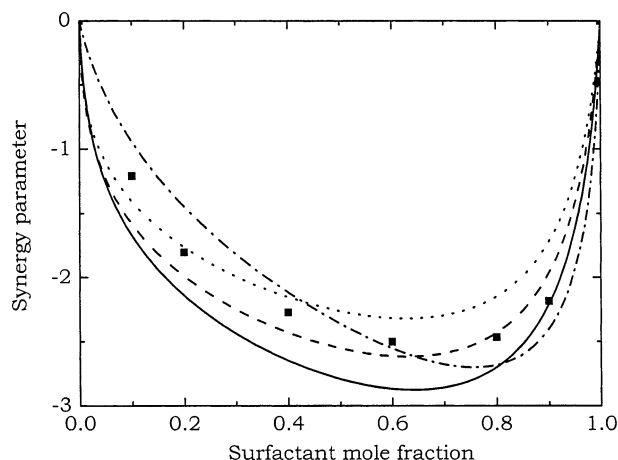
Figure 7. The synergy parameter β as defined in eq 9 plotted against the overall mole fraction y of SDS for mixtures of SDS and $C_{10}G$ at [NaCl] = 10 mM. Symbols represent experimental data. Solid line represents calculations of the activity coefficients from the Poisson−Boltzmann (PB) model using eqs 13 and 14 assuming spherical geometry. β as calculated from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also included. R_{el} and a_{el} were set to same values for the different geometries as given in Figure 2. The dashed−dotted line represents the best available fit of β according to the regular mixture theory (eqs 6 and 7 with β_{int} = −2.7).
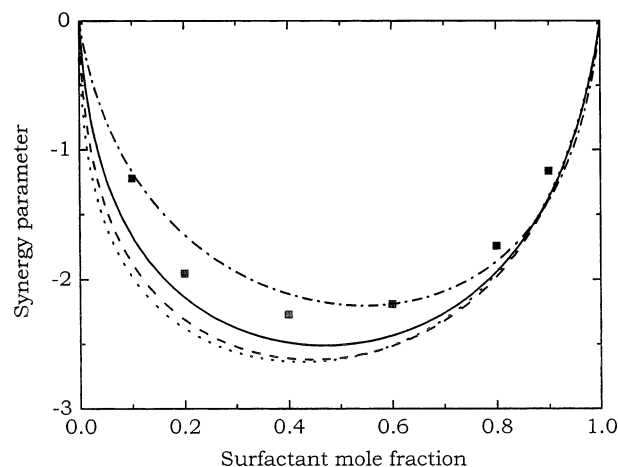

Figure 8. The synergy parameter β as defined in eq 9 plotted against the overall mole fraction y of SDS for mixtures of SDS and $C_{10}G$ at [NaCl] = 50 mM. Symbols represent experimental data. Solid line represents calculations of the activity coefficients from the Poisson−Boltzmann (PB) model using eqs 13 and 14 assuming spherical geometry. β as calculated from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also included. R_{el} and a_{el} were set to same values for the different geometries as given in Figure 2. The dashed−dotted line represents the best available fit of β according to the regular mixture theory (eqs 6 and 7 with β_{int} = −2.2).

by a_{el} but is insensitive to H_{el}. The magnitude of synergism decreases with increasing a_{el}, where an increasing aggregate curvature implies an increasing area per surfactant a_{el} for a given aggregate composition.

In Figure 11 we have plotted the minimum value of β with respect to composition as a function of concentration of added salt. Both experiment and PB model for spheres show an increase of synergism (i.e., a decrease of β_{min}) when salt is added up to 10 mM followed by a decreasing magnitude of the synergistic effects upon further addition of salt. A similar trend has been reported for mixtures of an anionic ($C_{12}SO_3Na$) and a nonionic ethylene oxide based
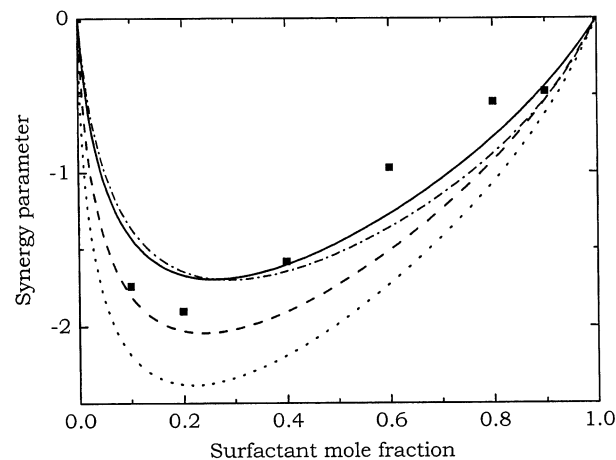

Figure 9. The synergy parameter β as defined in eq 9 plotted against the overall mole fraction y of SDS for mixtures of SDS and $C_{10}G$ at [NaCl] = 300 mM. Symbols represent experimental data. Solid line represents calculations of the activity coefficients from the Poisson−Boltzmann (PB) model using eqs 13 and 14 assuming spherical geometry. β as calculated from the PB model assuming cylindrical geometry (dashed line) and planar geometry (dotted line) are also included. R_{el} and a_{el} were set to same values for the different geometries as given in Figure 2. The dashed−dotted line represents the best available fit of β according to the regular mixture theory (eqs 6 and 7 with β_{int} = −1.7).
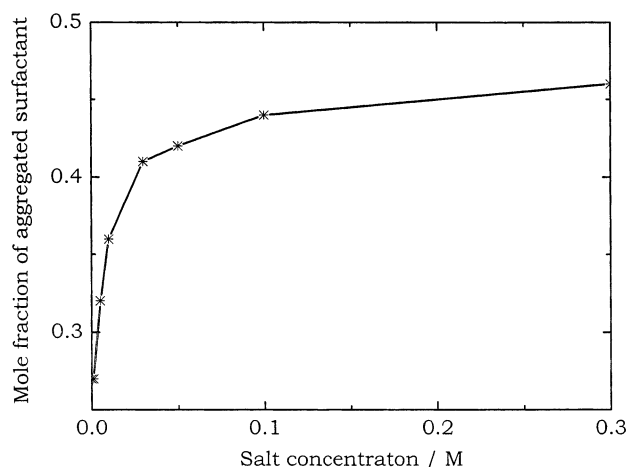

Figure 10. The minimum value of β with respect to composition according to the Poisson−Boltzmann model assuming spherical geometry plotted against concentration of added NaCl. Radius of curvature and area per aggregated surfactant at the surface of charge were set to R_{el} = 20 Å and a_{el} = 85 Å² for all [NaCl].

surfactant ($C_{12}EO_7$) where a maximum in synergism was found at [NaCl] = 0.1 M.[5] We also note that the experimentally obtained β_{min} values are generally higher than those predicted by the PB model. This may be caused by several effects, e.g., specific interactions between nonionic surfactant headgroups (breaking of hydrogen bond upon mixing) or between ionic headgroups not taken into account by the PB mean field model.

Conclusions

We have analyzed cmc determined from surface tension data of mixtures of SDS and $C_{10}G$ at different concentrations of NaCl by means of introducing a model independent parameter β that assumes negative values for mixtures that have a negative deviation from ideal behavior (synergism) and positive values for mixtures that show a
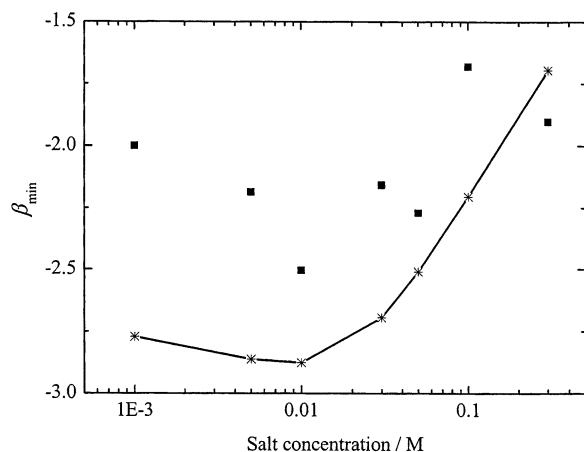
Figure 11. Mole fraction of aggregated SDS (x) where β reaches its minimum, as calculated from the spherical Poisson–Boltzmann model, plotted against the concentration of added NaCl. Radius of curvature and area per aggregated surfactant at the surface of charge were set to $R_{el} = 20$ Å and $a_{el} = 85$ Å² for all [NaCl]. Symbols represent β values minimized with respect to composition as obtained from the model-independent evaluation of experimental data.

positive deviation from ideal behavior (antagonism). Our analysis shows that synergism, defined as the magnitude of the optimum β value, first increases upon adding a small amount of electrolyte, reaches a maximum at [NaCl] = 10 mM corresponding to a minimum value of β equaling −2.5, and then decreases in magnitude at higher concentrations.

Our experimentally obtained cmc and β values were compared with expressions derived from the Poisson–Boltzmann (PB) mean field theory for planar, cylindrical and spherical geometries, respectively. For all NaCl concentrations, the best agreement with data was obtained for curved aggregate interfaces (spherical and cylindrical geometry). Moreover, the PB theory shows a better agreement with data than the conventional regular mixture theory in the sense that the latter systematically underestimates synergism at low fractions and overestimates synergism at high fractions of the ionic surfactant. However, the behavior of β as a function of surfactant composition y as calculated from the PB and RM theories, respectively, are becoming more similar as [NaCl] increases. Moreover, β_{min} as calculated from the spherical PB theory has a minimum at [NaCl] = 10 mM, in agreement with experiments, although the calculated β_{min} is somewhat lower than obtained from experiments at all salt concentrations except the highest one.