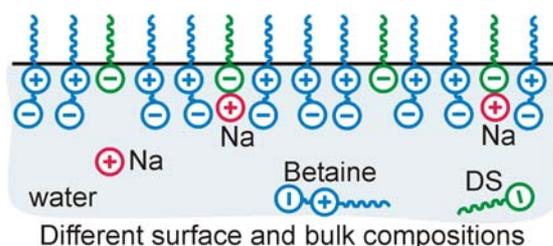


## Mixed Solutions of Anionic and Zwitterionic Surfactant (Betaine): Surface Tension Isotherms, Adsorption and Relaxation Kinetics

Authors: K. D. Danov,<sup>†</sup> S. D. Kralchevska,<sup>†</sup> P. A. Kralchevsky,<sup>†,\*</sup>  
K. P. Ananthapadmanabhan,<sup>§</sup> and A. Lips<sup>§</sup>

<sup>†</sup> *Laboratory of Chemical Physics & Engineering, Faculty of Chemistry, University of Sofia,  
1164 Sofia, Bulgaria*

<sup>§</sup> *Unilever Research US, Edgewater, 45 River Road, New Jersey 07020, USA*



**Abstract.** Here we present experimental surface tension isotherms of mixed solutions of two surfactants, sodium dodecylsulfate (SDS) and cocoamidopropyl betaine (Betaine), measured by means of the Wilhelmy plate method. The kinetics of surface tension relaxation exhibits two characteristic timescales, which have been distinguished to determine correctly the equilibrium surface tension. The transition from the zwitterionic to the cationic form of Betaine is detected by surface tension measurements. The critical micellization concentration (cmc) increases monotonically with the rise of the mole fraction of SDS in the surfactant blend. The experimental surface tension isotherms are fitted by means of the two-component van der Waals model, and an excellent agreement between theory and experiment was achieved. Having determined the parameters of the model, we calculated different properties of the mixed surfactant adsorption layer at various concentrations of SDS, Betaine and salt. Such properties are the adsorptions of the two surfactants; the surface dilatational elasticity, the occupancy of the Stern layer by bound counterions, the surface electric potential, etc. In particular, the addition of a small amount of Betaine to SDS significantly increases the surface elasticity. The results could be further applied to predict the thickness and stability of foam films, or the size of the rodlike micelles in the mixed solutions of SDS and Betaine.

\* To whom correspondence may be addressed: Peter A. Kralchevsky, LCPE, Faculty of Chemistry, Sofia University; 1 J. Bourchier Ave., 1164 Sofia, Bulgaria. Phone: (+359) 2-962 5310. Fax: (+359) 2-962 5643. E-mail: pk@lcpe.uni-sofia.bg

## 1. Introduction

The advance in the theory of adsorption from solutions of ionic surfactants,<sup>1-10</sup> and their blends with nonionic ones,<sup>1-7</sup> allows a detailed analysis and computer modeling of the interfacial properties. The development of electric double layer and adsorption of counterions have been taken into account. For recent reviews – see refs 8–11. The processing of experimental surface tension isotherms by means of an adequate theoretical model can provide useful information for the properties of the surfactant adsorption layer. To achieve that, one has to first determine the adsorption constants as adjustable parameters from the best fit of experimental data. Having these parameter values, with the help of a computer program, one can calculate numerous properties of the system. Thus, for each combination of surfactant and salt concentrations one can calculate the surface tension; the adsorption of every specific component, including the counterions; the surface electric potential; the surface dilatational elasticity,<sup>12,13</sup> the characteristic relaxation time of surfactant adsorption; the thickness of the equilibrium foam and emulsion films formed from the respective solution, and so forth.

Recently, a two-component version of the van der Waals model was developed, which accounts for the binding of counterions.<sup>14</sup> It was successfully applied to investigate the adsorption from mixed solutions of an ionic and a nonionic surfactant: sodium dodecyl sulfate (SDS) and dodecanol,<sup>14</sup> and sodium dodecylbenzene sulfonate and dodecylbenzene.<sup>15</sup> Our aim in the present paper is to apply this model to analyze new experimental data for the surface tension of mixed solutions of SDS and cocoamidopropyl betaine, a zwitterionic surfactant.

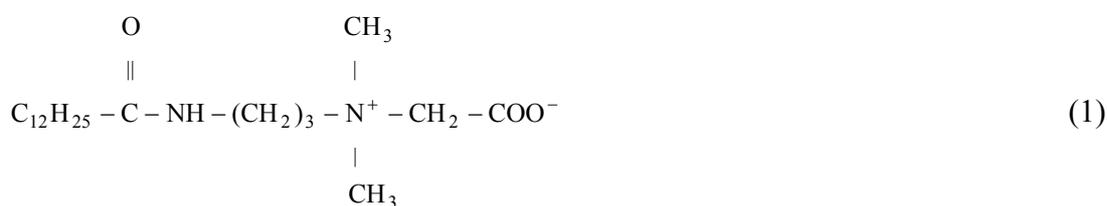
Betaines are widely used as foam boosters thanks to their property to stabilize foams against the antifoaming action of oil droplets contained in the commercial shampoos and hair-conditioners.<sup>16,17</sup> Moreover, the betaines are known to reduce the irritation action of the surfactant solutions on the eye and skin.<sup>18</sup> Previous studies indicate strong synergistic effects of the mixed solutions of SDS and C<sub>12</sub>Betaine.<sup>19,20</sup> Synergistic formation of large rodlike micelles was reported in the mixed solutions of SDS and cocoamidopropyl betaine, at a relatively low total surfactant concentration.<sup>21</sup>

The paper is organized as follows. In section 2 we report surface-tension data for the mixed solutions of cocoamidopropyl betaine (briefly, Betaine), obtained by the Wilhelmy plate method. The transition cationic-zwitterionic Betaine is detected by means of surface tension measurements. The systematic variation of the molar fraction of the mixture SDS-Betaine is carried out at the natural pH = 5.5 (zwitterionic Betaine). In section 3, the experimental data are fitted by means of the two-component van der Waals model, and the obtained parameter values are discussed. Having determined the parameters, in section 4 we present the predictions of the model for the concentration dependencies of the SDS and Betaine adsorptions, binding of Na<sup>+</sup> ions, surface electric potential, surface dilatational elasticity and the effect of NaCl on the composition of the adsorption layer. Finally, in section 5 we discuss the special surface-tension kinetics of the Betaine-containing solutions.

## 2. Experimental Section

**2.1. Materials.** The anionic surfactant used in our experiments was sodium dodecyl sulfate (SDS); Acros Organics, Pittsburgh, PA. Applying the approach from ref 14, we estimated that the mole fraction of dodecanol admixture is only  $(5.3 \pm 2.3) \times 10^{-4}$ , relative to SDS. Hence, this SDS sample is of high purity.

As already mentioned, the used amphoteric surfactant was cocoamidopropyl betaine (briefly, Betaine), commercial name “Tego Betaine F50”; Goldschmidt Chemical Co., McDonald, PA. The structure of its molecule is:



According to the supplier specification, the sample contains 39 wt% active substance (Betaine). To determine how large is the admixture of NaCl in the used Betaine sample, we measured the electroconductivity of the solutions as a function of the Betaine concentration by means of a conductivity meter, model 30 (Denver Instruments, USA). The procedure is analogous to that used in ref 15, section 2.2 therein. From the slope of the obtained straight line we established that the relative weight fraction of NaCl, relative to Betaine, is 0.225 in the used sample; pH = 5.5. (At pH = 5.5 the Betaine is in its zwitterionic form; see section 2.3 below) To have a well-defined ionic strength, our working solutions contain 10 mM NaCl added. The latter concentration is much greater than the ionic strength due to the electrolyte admixture in the Betaine sample, insofar as the highest Betaine concentration in our experiments (restricted to the region below the cmc) is  $\leq 0.8$  mM.

**2.2. Surface Tension Measurements.** The surface tension of the investigated solutions was measured by means of the Wilhelmy plate technique at temperature 25°C and at the natural pH of the solutions, pH = 5.5. Only in one set of experiments (section 2.3 below) the pH was lowered by addition of HCl to investigate how the transition from zwitterionic to cationic Betaine affects the solutions’ surface tension. In all experiments, we used a Krüss tensiometer with a platinum plate, which is connected to a computer to record the relaxation of surface tension,  $\sigma(t)$ , ( $\sigma$  – surface tension;  $t$  – time).

Some nontrivial aspects of the surface tension measurements for Betaine solutions deserve a special attention. For sufficiently long times, the adsorption usually happens under diffusion control; adsorption barriers (if any) affect only the earlier stages of the process.<sup>22</sup> Then, at the long adsorption times we expect to have:<sup>23</sup>

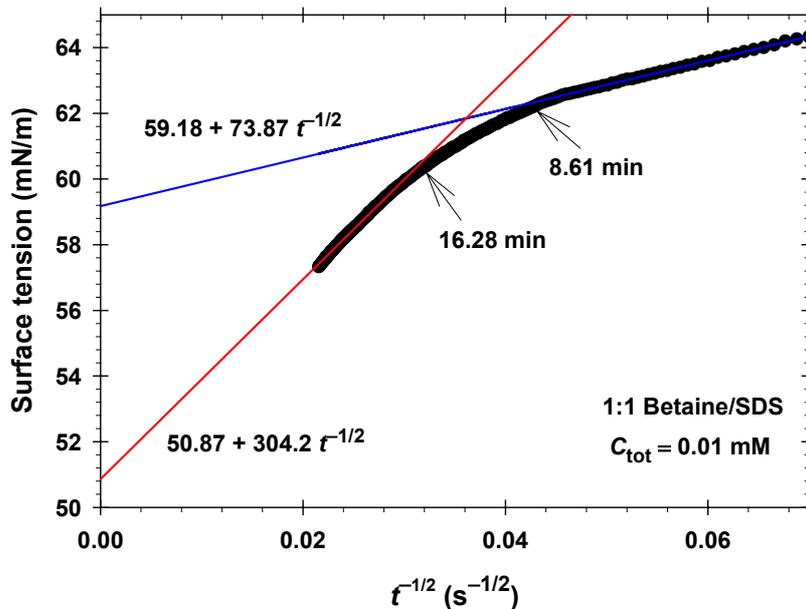
$$\sigma(t) \propto t^{-1/2} \quad (2)$$

The standard procedure to find the equilibrium surface tension is to plot  $\sigma$  vs.  $t^{-1/2}$ , and to extrapolate the linear portion of the experimental curve to  $t^{-1/2} \rightarrow 0$ .<sup>23</sup> This procedure works perfectly for the solutions of SDS, without Betaine. However, if Betaine is present, the experimental curve shows two linear portions, as illustrated in Figure 1.

The data in Figure 1 corresponds to total surfactant concentration  $C_{\text{tot}} = 0.01$  mM at equal molar fractions of Betaine and SDS. The parameters of the two linear regressions, drawn in Figure 1, are listed in Table 1.

**Table 1.** Parameters of the two linear regressions in Figure 1.

Straight line	Intercept (mN.m <sup>-1</sup> )	Slope (mN.m <sup>-1</sup> .s <sup>1/2</sup> )	Regression coefficient
Short-time	59.18 ± 0.015	73.87 ± 0.27	0.9998
Long-time	50.87 ± 0.03	304.2 ± 1.2	0.9992



**Figure 1.** Plot of surface tension,  $\sigma$ , vs.  $t^{-1/2}$  – data for the surface-tension relaxation obtained by the Wilhelmy-plate method for a solution of Betaine + SDS at 1:1 molar ratio; the total surfactant concentration is  $C_{\text{tot}} = 0.01$  mM; 10 mM added NaCl; pH = 5.5. The data for  $t < 8.61$  min and for  $t > 16.28$  min obey different linear dependencies.

The intercept gives the equilibrium surface tension,  $\sigma_{\text{eq}}$ . For this specific example, if the measurement is carried out for less than 8 min, one will determine  $\sigma_{\text{eq}} = 59.18$  mN/m. However, if the measurement continues longer than, say, 30 min, one would obtain  $\sigma_{\text{eq}} = 50.87$  mN/m (Figure 1 and Table 1).

Let us give another example. We checked how long could continue the surface tension relaxation, as detected by the Wilhelmy plate method. The working solution had a total surfactant concentration was  $C_{\text{tot}} = 0.05$  M with 15:85 molar ratio of Betaine to SDS. The “short-time” line (like that in Figure 1) gave  $\sigma_{\text{eq}} = 54.4$  mN/m. After 15 hours, the tensiometer was showing  $\sigma = 34.0$  mN/m, and moreover,  $\sigma$  was continuing to decrease. The intercept of the “long-time” straight line gave  $\sigma_{\text{eq}} = 26.3$  mN/m.

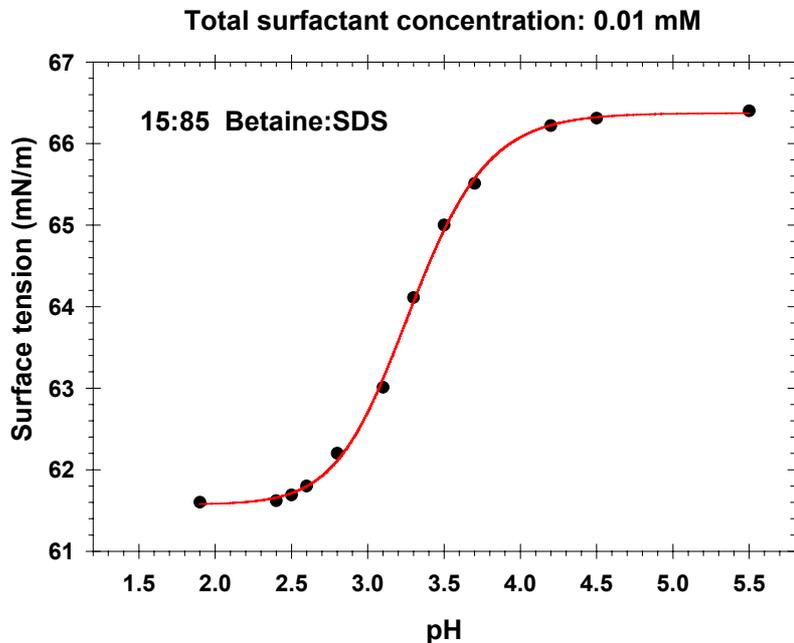
These, and other measurements with Betaine containing solutions show that the long-time linear dependence of the plot  $\sigma$  vs.  $t^{-1/2}$  gives physically irrelevant values for both  $\sigma_{\text{eq}}$  and the relaxation time of surface tension. This long-time dependence is most probably an artifact, due to a gradual increase of the three-phase contact angle at the Wilhelmy plate. This effect is well known for cationic surfactants, and it is explained with a gradual (evaporation driven) deposition of surfactant in the vicinity of the contact line, which results in a contact angle, which is greater than zero and increases with time.<sup>24-27</sup> Because at pH = 5.5 the Betaine is in its zwitterionic form (section 2.3), it turns out that a similar contact-angle effect can take place also with a zwitterionic surfactant (not only with a cationic one). To check that, we carried out test measurements of  $\sigma$  with the pendant drop method, which showed relaxation times, which are very close to those obtained from the short-time linear dependence (see Figure 1 and Table 1).

Our conclusion is that the surface tension of Betaine-containing solutions can be measured by means of the Wilhelmy plate method, supposedly the equilibrium surface tension is determined from the intercept of the short-time linear dependence (Figure 1). The experimental surface-tension isotherms thus obtained are smooth and the characteristic relaxation times agree with the estimates based on diffusion-controlled relaxation (see below). The long-time dependence of surface tension is most probably an artifact due to the increasing of contact angle at the plate, because of surfactant deposition. Fortunately, the two processes have rather different relaxation times and can be clearly distinguished. This enables one to carry out correctly the extrapolation (Figure 1) and to determine the true equilibrium surface tension. These circumstances should be taken into account, especially when using automatic versions of the Wilhelmy plate method. An additional discussion on the kinetics of surface tension relaxation in the presence of Betaine is given in section 5 below.

**2.3. Transition between the Zwitterionic and Cationic Forms of Betaine.** In solution, the Betaine can be present in two forms: zwitterionic and cationic. In most of our experiments, we work at natural pH = 5.5. We expect that at this pH, the zwitterionic form is predominant. However, if even a trace amount of cationic Betaine is present in mixed SDS-Betaine solutions, it will be attracted by the negatively charged surface, its concentration in the subsurface layer will be considerably increased, and consequently, its contents in the mixed surfactant adsorption layer will be considerable. For example, if the surface potential (in the presence of SDS) is  $\psi_s = -125$  mV, and the molar fraction of the cationic Betaine is  $x_{\text{cationic}} = 0.01$  (relative to the total Betaine content), for the subsurface and bulk concentrations we obtain:

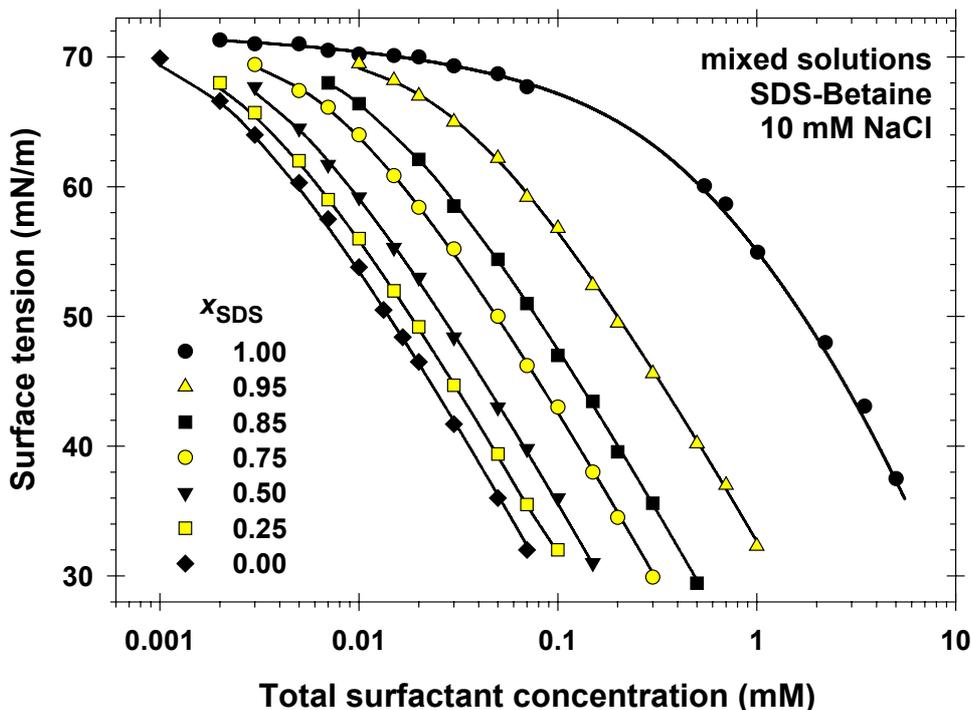
$$\left(\frac{C_{\text{cat}}}{C_{\text{zwit}}}\right)_{\text{subsurface}} = \left(\frac{C_{\text{cat}}}{C_{\text{zwit}}}\right)_{\text{bulk}} \exp\left(-\frac{e\psi_s}{kT}\right) = 0.01 \times 148 = 1.48 \quad (3)$$

( $C_{\text{cat}}$  and  $C_{\text{zwit}}$  denote concentrations of the cationic and zwitterionic forms). Equation 3 implies that the adsorption layer will contain more cationic than zwitterionic Betaine, despite the fact that the bulk content of the cationic form is negligible. Consequently, the surface tension is expected to be very sensitive to the cationic Betaine, and can be used as an indicator for its presence. To check this, we measured experimentally the effect of the solution's pH on the surface tension at a fixed molar ratio, 15:85 Betaine to SDS, and at a fixed total surfactant concentration,  $1 \times 10^{-5}$  M. The results are shown in Figure 2.



**Figure 2.** Plot of the measured surface tension as a function of the pH of the aqueous solutions, which contain Betaine and SDS at a fixed molar ratio, 15:85; total surfactant concentration, 0.01 mM; 10 mM added NaCl. The role of SDS is to make the surface potential, negative, to attract the cationic form of Betaine at the interface, and thus to render the surface tension sensitive to the presence of cationic Betaine.

The transition from cationic to zwitterionic form of the Betaine can be characterized with the inflection point, which is at  $\text{pH} \approx 3.2$  in Figure 2. The latter plot indicates that at  $\text{pH} = 5.5$  the Betaine is present entirely as a zwitterion. For  $\text{pH} \geq 5.5$ , the concentration of the cationic form is so small that it does not affect the surface tension. This conclusion makes easier the interpretation of our data in Figure 3 below.



**Figure 3.** Surface tension,  $\sigma$ , plotted vs. the total surfactant concentration in mixed SDS-Betaine aqueous solutions for seven different molar fraction of SDS,  $x_{\text{SDS}}$ , see eq 4. All solutions contain 10 mM added NaCl;  $\text{pH} = 5.5$ ;  $T = 25^\circ\text{C}$ . The symbols denote experimental points. The lines represent the best fit by means of the van der Waals isotherm, section 3.

**2.4. Surface Tension of the SDS–Betaine Mixed Solutions.** Figure 3 presents our experimental data for the surface tension of mixed solutions of SDS and Betaine at natural  $\text{pH} = 5.5$ . The different curves in the figure correspond to different compositions of the surfactant blend, characterized by the bulk mole fractions of SDS relative to the total surfactant concentration:

$$x_{\text{SDS}} = \frac{C_{\text{SDS}}}{C_{\text{SDS}} + C_{\text{B}}} \quad (4)$$

where  $C_{\text{SDS}}$  and  $C_{\text{B}}$  denote the bulk concentrations of SDS and Betaine. First, we obtained the experimental surface tension isotherms for  $x_{\text{SDS}} = 0, 0.25, 0.50, 0.75$  and 1. However, it turned out that all isotherms in the range  $0 \leq x_{\text{SDS}} \leq 0.5$  are situated close to each other and, while, on the

other hand, there is a wide empty space between the isotherms corresponding to  $x_{\text{SDS}} = 0.75$  and 1. For that reason, we measured two additional isotherms, at  $x_{\text{SDS}} = 0.85$  and 0.95 (Figure 3).

For pure SDS ( $x_{\text{SDS}} = 1$ ), the six experimental points on the right (Figure 3) have been measured by Tajima,<sup>28</sup> while the rest of the points (at the lower concentrations) are obtained in our present experiments. The respective theoretical curve ( $x_{\text{SDS}} = 1$ ) is drawn using the parameters of the van der Waals isotherm, determined in ref 13 by fitting the full set of surface-tension data by Tajima et al, for SDS at various salt concentrations. One sees that our new experimental points for  $x_{\text{SDS}} = 1$  excellently agree with the data by Tajima et al. and with the theoretical fit from ref 13.

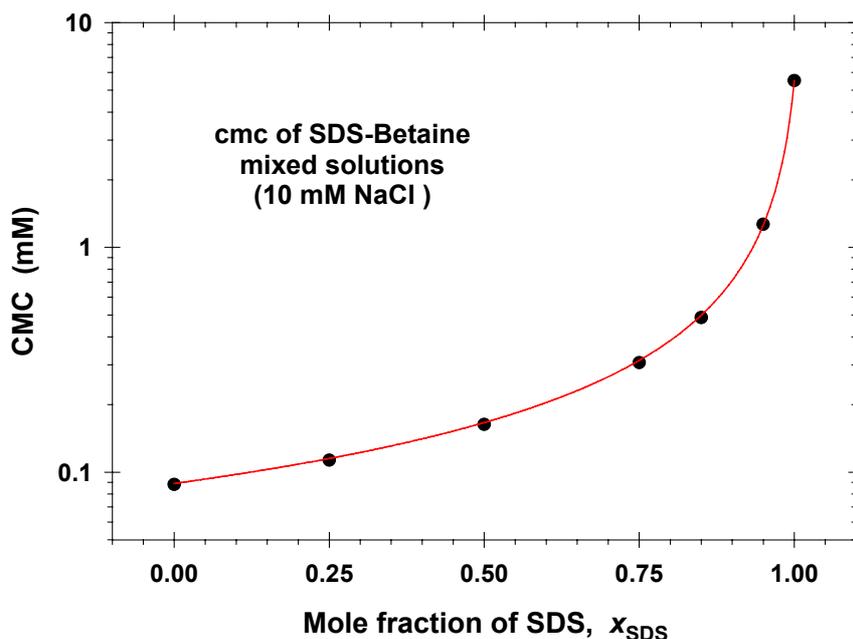
For the mixed solutions of SDS and Betaine (the curves for  $0 \leq x_{\text{SDS}} \leq 0.95$  in Figure 3), the data are fitted by the van der Waals isotherm for surfactant blends, as explained in section 3 below.

The data points in Figure 3 correspond to the region below the critical micellization concentration (cmc). We determined also the values of cmc, and of the surface tension at cmc,  $\sigma_{\text{cmc}}$ , for the investigated solutions of SDS and Betaine. The results are listed in Table 2.

**Table 2.** CMC of mixed SDS-Betaine solutions vs.  $x_{\text{SDS}}$  at 10 mM added NaCl; pH = 5.5.

No.	$x_{\text{SDS}}$	cmc (mM)	$\sigma_{\text{cmc}}$ (mN/m)
1	0.00	0.088	29.9
2	0.25	0.113	29.8
3	0.50	0.163	29.7
4	0.75	0.307	29.8
5	0.85	0.487	29.7
6	0.95	1.265	29.8
7	1.00	5.52	35.5

The dependence of cmc on  $x_{\text{SDS}}$  (Table 2) is monotonic, which is visualized in Figure 4. (The line in Figure 4 is a nonlinear regression with a four-parameter rational function.) No synergistic effects are observed with respect to the cmc. In contrast, at  $x_{\text{SDS}} \approx 0.25$  (1:3 SDS to Betaine), the rodlike mixed micelles of SDS and Betaine reach their maximal length, at constant cross-sectional diameter ( $\approx 5$  nm).<sup>21</sup> This is an evidence for the presence of synergism with respect to the micelle size. It is interesting to note that the appearance of synergistic minimum at ratio 1:3 (or 3:1) has been noticed by other authors<sup>29</sup> for other systems. Most probably, the ratio 3:1 is related to the hexagonal packing of the adsorbed surfactant molecules.<sup>29</sup> It should be noted also that for the Betaine containing solutions  $\sigma_{\text{cmc}}$  is practically constant (Table 2).



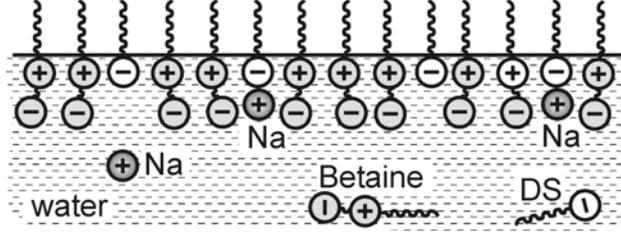
**Figure 4.** Plot of cmc of aqueous solutions vs. the mole fraction of SDS in the SDS-Betaine mixture at fixed 10 mM added NaCl; pH = 5.5 (data from Table 2).

The dependence of  $\sigma$  on  $x_{\text{SDS}}$  (Figure 3) is monotonic. In other words, at the same total surfactant concentration, the values of  $\sigma$  for the *mixed* solutions are always greater than for the solution with 100 % Betaine. Hence, synergism is missing with respect to  $\sigma$ , although it is present with respect to the micelle size. In this respect, our experimental results differ from those in ref 19, where a strong synergism with respect to  $\sigma$  is reported. One possible reason for this difference could be related to the chemical nature of the used betaine: C<sub>12</sub>Betaine in ref 19, vs. cocoamidopropyl betaine in our experiments.

### 3. Theoretical Aspects

**3.1. Theoretical Background.** Our purpose here is to fit the experimental surface-tension isotherms in Figure 3 by means of the two-component van der Waals model and to calculate the interfacial properties, such as adsorptions of the separate components, composition of the mixed adsorption layer, surface potential and elasticity, etc. In general, the van der Waals adsorption model, termed also Hill–de Boer model,<sup>30-32</sup> is derived statistically assuming *nonlocalized* adsorption of *interacting* molecules.<sup>11,32,33</sup> The latter assumptions make this model appropriate for describing surfactant adsorption at a liquid-gas interface. The surface equation of state, corresponding to this model, is a two-dimensional analogue of the known van der Waals equation in the theory of the non-ideal gases.<sup>32,34</sup> The generalization of the single-component van der Waals

adsorption model for the case of *two* components is nontrivial. First, this generalization was given for monolayers of water-insoluble non-charged molecules (phospholipids).<sup>35</sup> Next, in ref 14, the van der Waals model was extended to the case of a mixed solution of ionic and nonionic surfactants, with account for the effect of counterion binding.



**Figure 5.** Sketch of the adsorption layer, which is composed of Betaine zwitterions, dodecyl sulfate (DS) anions, and  $\text{Na}^+$  counterions that are bound to the negatively charged headgroups of DS.

Here, we will employ the model from ref 14 to describe theoretically the adsorption of *two* surfactants, one ionic (SDS) and one nonionic (zwitterionic Betaine), in the presence of added non-amphiphilic electrolyte (NaCl), see Figure 5. As in ref 14, we will use the following numbering of the species: component 1 – surfactant ion (dodecyl sulfate,  $\text{DS}^-$ ); component 2 – non-amphiphilic counterion ( $\text{Na}^+$ ); component 3 – non-amphiphilic coion ( $\text{Cl}^-$ ); component 4 – nonionic surfactant (zwitterionic Betaine). The surface pressure,  $\pi_s$ , of the mixed adsorption layer is expressed in the form:<sup>1,2,4,6,14</sup>

$$\pi_s \equiv \sigma_0 - \sigma = \pi_a + \pi_d \quad (5)$$

where  $\sigma_0$  and  $\sigma$  are the surface tensions of the pure solvent (water) and of the solution;  $\pi_a$  and  $\pi_d$  are the contributions from the adsorption layer and the diffuse electric double layer to the surface pressure.  $\pi_a$  is determined by the two-dimensional equation of state of van der Waals for two-component adsorption layer:<sup>14,35</sup>

$$(\pi_a + \beta\Gamma^2)(1 - \alpha\Gamma) = \Gamma kT \quad (6)$$

where  $\Gamma = \Gamma_1 + \Gamma_4$ ;  $\Gamma_1$  and  $\Gamma_4$  are the adsorptions of SDS and Betaine, respectively;  $k$  is Boltzmann constant;  $T$  is temperature; the compound excluded area,  $\alpha$ , and interaction parameter,  $\beta$ , are expressed as follows:

$$\alpha \equiv \alpha_{11}X_1^2 + 2\alpha_{14}X_1X_4 + \alpha_{44}X_4^2 \quad (7)$$

$$\beta \equiv \beta_{11}X_1^2 + 2\beta_{14}X_1X_4 + \beta_{44}X_4^2 \quad (8)$$

where

$$X_i = \frac{\Gamma_i}{\Gamma_1 + \Gamma_4} \quad (i = 1, 4) \quad (9)$$

is the mole fraction of the respective surfactant in the adsorption layer;  $\alpha_{ij}$  and  $\beta_{ij}$  are constant parameters; see Table 3. In addition, the contribution of the diffuse electric double layer to the surface pressure is:<sup>1,6,36</sup>

$$\pi_d = \frac{8kTI}{\kappa} \left[ \cosh\left(\frac{\Phi_s}{2}\right) - 1 \right] \quad (10)$$

where  $I$  is the ionic strength of the solution,  $\Phi_s$  is the dimensionless surface potential and  $\kappa$  is the Debye screening parameter:

$$\Phi_s = -\frac{e\psi_s}{kT}, \quad \kappa^2 = \frac{8\pi e^2 I}{\varepsilon kT} \quad (11)$$

$e$  is the electronic charge,  $\varepsilon$  is the dielectric constant of the solvent (water);  $\psi_s$  is the surface electric potential, which is determined mostly by the presence of adsorbed  $DS^-$  ions. Note that  $\psi_s$  is negative, and  $\Phi_s$  is positive by definition.

To compute the solution's surface tension,  $\sigma$ , for each given concentration of SDS, Betaine and NaCl, one has to solve numerically a system of seven equations, which is specified in section 3.5 of ref 14. Therein, in section 5.2, the principles of the numerical procedure are given. The aforementioned seven equations include eq 5 (along with eqs 6–10); the Gouy equation connecting the surface charge and potential; two Boltzmann equations for the distribution of the  $DS^-$  and  $Na^+$  ions in the electric double layer, and three adsorption isotherms, for  $DS^-$ , Betaine and  $Na^+$ . In particular, the Stern isotherm is used for the  $Na^+$  ions; see ref 14 for details. Each adsorption isotherm contains an adsorption parameter,  $K_i$ , which is related to the standard adsorption energy of the respective molecule,  $\Delta\mu_i^{(0)}$ , as follows:

$$K_i = \alpha_{ii} \delta_i \exp(E_i), \quad E_i \equiv \Delta\mu_i^{(0)}/(kT) \quad (12)$$

$i = 1, 2, 4$ ;  $\delta_i$  is the length of the respective molecule. In accordance with the Stern model, the  $DS^-$  ions at the interface serve as adsorption sites for the  $Na^+$  counterions. For this reason, in eq 12 we substitute  $\alpha_{22} = \alpha_{11}$ . The excluded area per Betaine molecule is different from that for  $DS^-$ :

$\alpha_{44} \neq \alpha_{11}$ . We determined  $\alpha_{44}$ , from the fit of the experimental data in Figure 3, as explained in the next section.

**3.2. Fit of the Data.** The two-component van der Waals model involves a set of 9 parameters (see Table 3), whose values have to be specified. These are the excluded areas  $\alpha_{ij}$ , the interaction parameters  $\beta_{ij}$ , and the adsorption energies  $E_i$ . The molecular length,  $\delta_i$ , is estimated from the known molecular size (Table 3). The adsorption constants  $K_i$  are calculated from the values of  $\alpha_{ij}$ ,  $\delta_i$  and  $E_i$  using eq 12. Furthermore,  $\alpha_{14}$  can be computed from the values of  $\alpha_{11}$  and  $\alpha_{44}$ .<sup>14,35</sup>

$$\alpha_{14} = \left( \frac{\alpha_{11}^{1/2} + \alpha_{44}^{1/2}}{2} \right)^2 \quad (13)$$

From computational viewpoint, it is more convenient to use the dimensionless form of the interaction parameters  $\beta_{ij}$ :

$$\hat{\beta}_{ij} = \frac{2\beta_{ij}}{kT\alpha_{ij}} \quad (i,j = 1, 4) \quad (14)$$

The values of all parameters (Table 3), referring only to SDS and NaCl are taken from ref 14. These parameters are  $\alpha_{11}$ ,  $\hat{\beta}_{11}$ ,  $E_1$ ,  $E_2$ ,  $\delta_1$ ,  $\delta_2$ ,  $K_1$  and  $K_2$ . Then, only four unknown parameters remain to be determined from the fit of the data in Figure 3:  $\alpha_{44}$ ,  $\hat{\beta}_{14}$ ,  $\hat{\beta}_{44}$ , and  $E_4$ ;  $K_4$  is to be calculated from eq 12 using the values of  $\alpha_{44}$ ,  $E_4$  and  $\delta_4$  (see Table 3).

**Table 3. Adsorption parameters of the van der Waals model for SDS-Betaine mixed solutions**

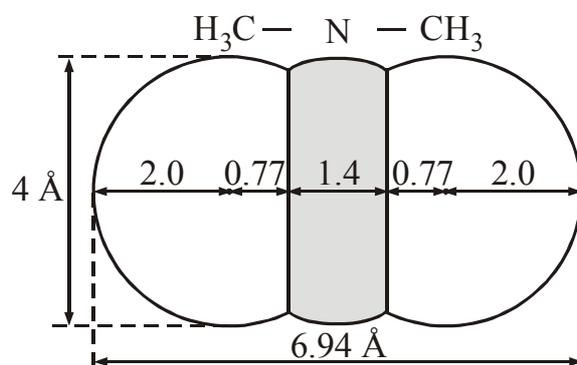
parameters			dimension
$\alpha_{11} = 29.76$	$\alpha_{14} = 28.77$	$\alpha_{44} = 27.78^*$	$\text{\AA}^2$
$\hat{\beta}_{11} = 2.73$	$\hat{\beta}_{14} = 3.13^*$	$\hat{\beta}_{44} = 3.24^*$	—
$E_1 = 12.53$	$E_2 = 1.64$	$E_4 = 12.69^*$	$kT$ units
$\delta_1 = 20$	$\delta_2 = 7$	$\delta_4 = 30$	$\text{\AA}$
$K_1 = 99.11$	$K_2 = 6.47 \times 10^{-4}$	$K_4 = 162.86$	$\text{m}^3/\text{mol}$

\*Determined as adjustable parameter from the best fit in Figure 3.

There are two approaches to process the data in Figure 3. (i) First to fit the lowest curve (that for 100% Betaine,  $x_{\text{SDS}} = 0$ ) and to determine  $\alpha_{44}$ ,  $\hat{\beta}_{44}$ , and  $E_4$ . After that, to fit simultaneously the five curves corresponding to mixed SDS-Betaine solutions, and to determine  $\hat{\beta}_{14}$ . (ii) Alternatively, it is possible to fit simultaneously all 71 experimental points in Figure 3 and to determine the four unknown parameters,  $\alpha_{44}$ ,  $\hat{\beta}_{14}$ ,  $\hat{\beta}_{44}$ , and  $E_4$ . We tried both approaches and obtained practically coinciding results, which are given in Table 3. The quality of the fit is excellent: the standard deviation is only 0.293 mN/m.

**3.3. Discussion.** As reported in ref 14, the parameters  $\alpha_{ii}$  of the van der Waals model practically coincide with the geometrical cross-sectional area of the adsorbed molecule. Thus  $\alpha_{11} = 29.79 \text{ \AA}^2$  is the cross-sectional area of the sulfate headgroup of the SDS molecule.

To interpret the obtained value of  $\alpha_{44}$  (Table 3), let us estimate the cross-sectional area of the  $\text{CH}_3\text{-N-CH}_3$  group of the Betaine molecule, see eq 1 and Figure 6. In Figure 7.1 of ref 37 we find that the covalent bond radii of the  $-\text{C}$  and  $-\text{N}$  atoms are, respectively, 0.77 and 0.70  $\text{\AA}$ ; in addition, the effective radius of the  $-\text{CH}_3$  group is 2.0  $\text{\AA}$ . As illustrated in Figure 6, the cross-sectional area of the  $\text{CH}_3\text{-N-CH}_3$  group is  $4 \times 6.94 = 27.76 \text{ \AA}^2$ . The latter value is very close to  $\alpha_{44} = 27.78 \text{ \AA}^2$  determined from the best fit (Table 3). This amazing coincidence confirms once again the adequacy of the van der Waals model for processing of data for surfactant adsorption at fluid interfaces. (Similar coincidence has been obtained also for alkanols, SDS and alkylbenzene sulfonates.<sup>14,15</sup>)



**Figure 6.** Schematic cross-section of the  $\text{CH}_3\text{-N-CH}_3$  group of the Betaine molecule. The shown values of the covalent bond radii of the  $-\text{C}$  and  $-\text{N}$  atoms, and the effective radius of the  $-\text{CH}_3$  group, are taken from Figure 7.1 in ref 37.

The values of the interaction parameters  $\hat{\beta}_{ij}$  (Table 3) increase from SDS to Betaine. Such a behavior is in agreement with the finding that the parameters  $\hat{\beta}_{ij}$  account for the van der Waals attraction between the hydrocarbon tails of the respective couples of adsorbed molecules (the tail of Betaine is longer than that of SDS).

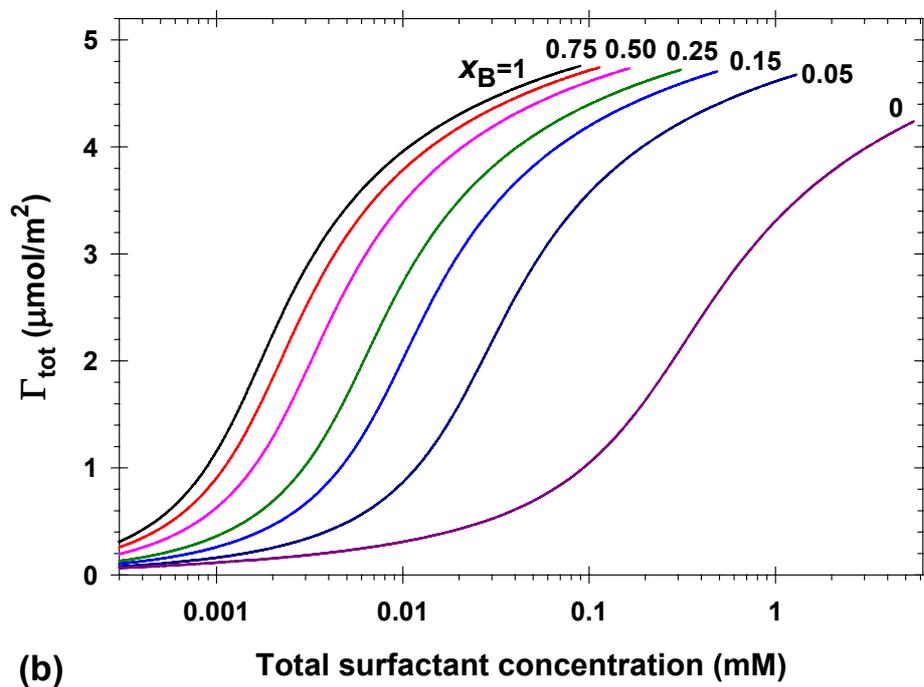
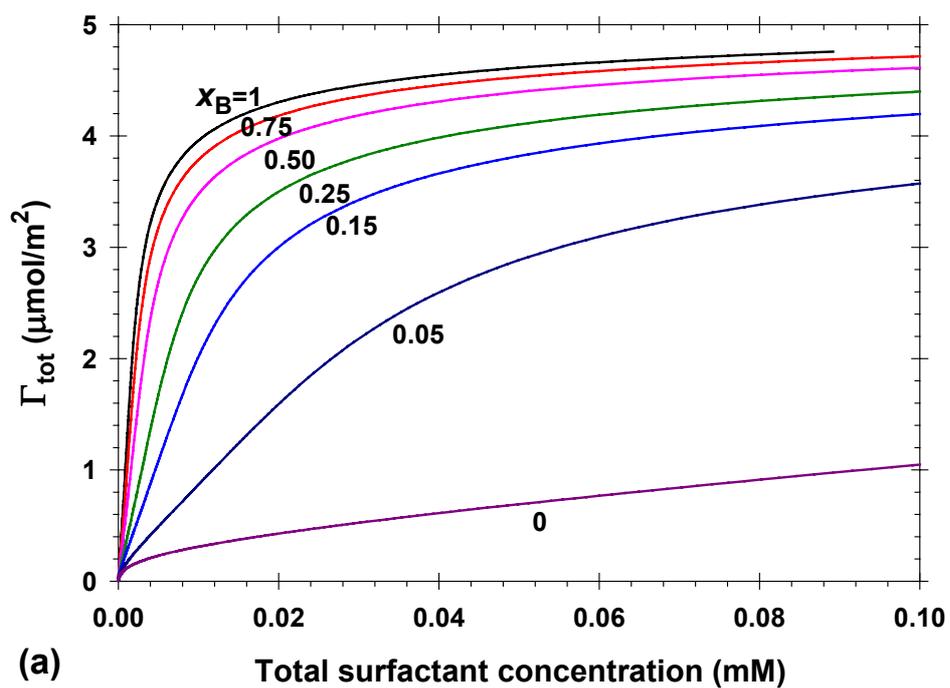
The adsorption energy of Betaine,  $E_4$ , is only slightly greater than that of SDS,  $E_2$  (Table 3). This, and the greater length of the Betaine molecule, lead to a greater adsorption constant:  $K_4 = 162.86 \text{ m}^3/\text{mol}$  for Betaine vs.  $K_1 = 99.11 \text{ m}^3/\text{mol}$  for SDS. This result reflects the greater surface activity of Betaine.

#### 4. Numerical Results and Discussion

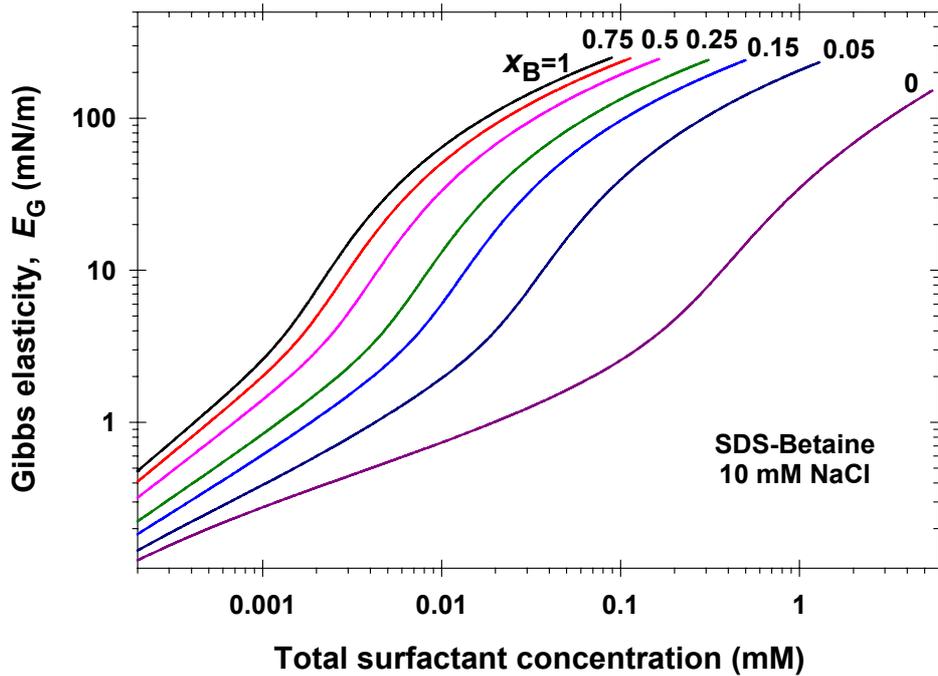
A fit of surface tension data, like that in Figure 3, provides information about many properties of the interfacial layer. As mentioned in the beginning, having once determined the parameters of the model (see Table 3), one is able to compute: (i) the surface tension  $\sigma$ , (ii) the adsorptions of SDS and Betaine,  $\Gamma_{\text{SDS}} = \Gamma_1$  and  $\Gamma_{\text{B}} = \Gamma_4$ ; (iii) the adsorption (binding) of  $\text{Na}^+$  counterions in the Stern layer,  $\Gamma_{\text{Na}}$ , and (iv) the surface electric potential  $\psi_s$ , etc., each of them for every chosen surfactant and salt concentrations; see Figures 7–10. Details about the computational procedure can be found in ref 14.

Figure 7 shows the total surfactant adsorption,  $\Gamma_{\text{tot}} = \Gamma_{\text{SDS}} + \Gamma_{\text{B}}$ , plotted vs. the total surfactant concentration in the bulk of solution. The same numerical data are presented in linear scale (Figure 7a) to visualize better the Henry region (the linear dependence of  $\Gamma_{\text{tot}}$  on  $C_{\text{tot}}$  at low surfactant concentrations), and in log scale (Figure 7b) to illustrate the behavior of  $\Gamma_{\text{tot}}$  in the vicinity of cmc. The comparison of the different curves implies that  $\Gamma_{\text{tot}}$  monotonically increases with the rise of the Betaine bulk mole fraction,  $x_{\text{B}} = 1 - x_{\text{SDS}}$ . The Betaine exhibits a greater adsorption than SDS for two main reasons: (i) greater adsorption constant,  $K_4 > K_1$  (Table 3); (ii) higher subsurface concentration: the subsurface concentration of Betaine is the same as in the bulk of solution, while the negatively charged interface repels the  $\text{DS}^-$  ions, and consequently, their subsurface concentration,  $c_s$ , is lower than the bulk one,  $c_\infty$ :  $c_s = c_\infty \exp(-\Phi_s)$ .

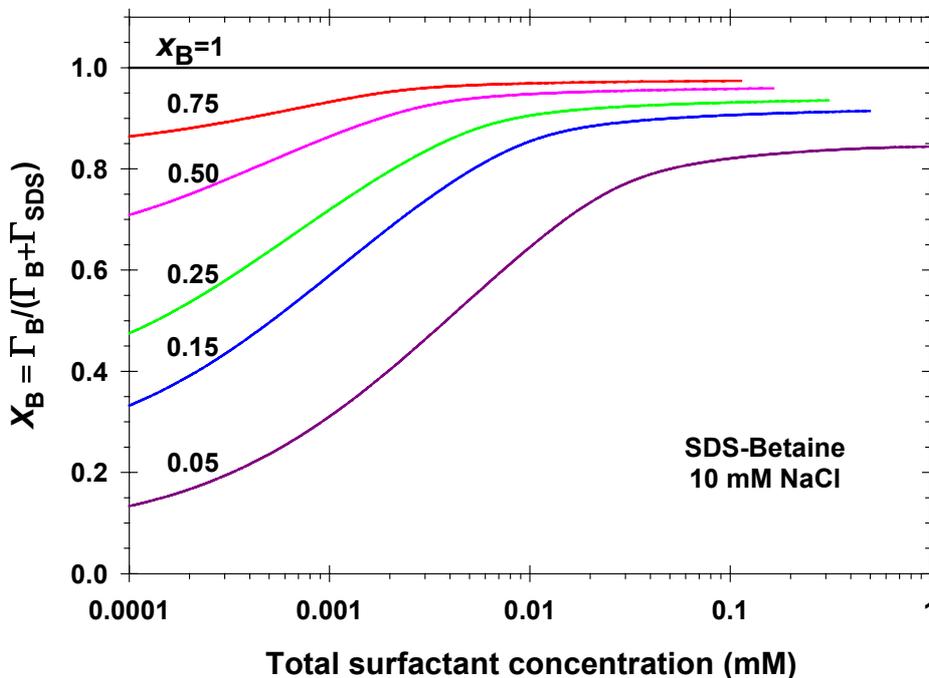
Figure 8 shows a plot of the calculated surface dilatational (Gibbs) elasticity,  $E_G$ , vs. the total surfactant concentration. For a mixed surfactant monolayer,  $E_G$  is determined by the expression:<sup>14</sup>



**Figure 7.** Plot of the calculated total adsorption,  $\Gamma_{\text{tot}} = \Gamma_{\text{SDS}} + \Gamma_{\text{B}}$ , vs. the total bulk surfactant concentration, presented (a) in linear, and (b) in logarithmic scale. The different curves correspond to different bulk mole fractions of Betaine,  $x_{\text{B}}$ , denoted in the figure; 10 mM NaCl; pH = 5.5.



**Figure 8.** Plot of the calculated surface dilatational (Gibbs) elasticity,  $E_G$ , vs. the total surfactant concentration in mixed SDS-Betaine solutions. The different curves correspond to different bulk mole fractions of Betaine,  $x_B$ , denoted in the figure; pH = 5.5.



**Figure 9.** Plot of the calculated surface mole fraction of Betaine,  $X_B$ , vs. the total bulk surfactant concentration in mixed SDS-Betaine solutions. The different curves correspond to different bulk mole fractions of Betaine,  $x_B$ , denoted in the figure; pH = 5.5.

$$E_G = \Gamma_1 \left( \frac{\partial \pi_a}{\partial \Gamma_1} \right)_{\Gamma_4} + \Gamma_4 \left( \frac{\partial \pi_a}{\partial \Gamma_4} \right)_{\Gamma_1} \quad (15)$$

see eqs 6–9. First of all, in Figure 8 one sees that the increase of the mole fraction of Betaine strongly increases the surface elasticity,  $E_G$ . For example, at total surfactant concentration 0.1 mM, the increase of  $x_B$  from 0 to 0.05 increases  $E_G$  about 10 times. This effect leads to the formation of (kinetically) more stable foam films,<sup>38</sup> and correlates with the use of Betaine as foam booster.<sup>16,17</sup> As the curves in Figures 7b and 8 look similar, it seems that the Betaine increases  $E_G$  through the increase of  $\Gamma_{\text{tot}}$ .

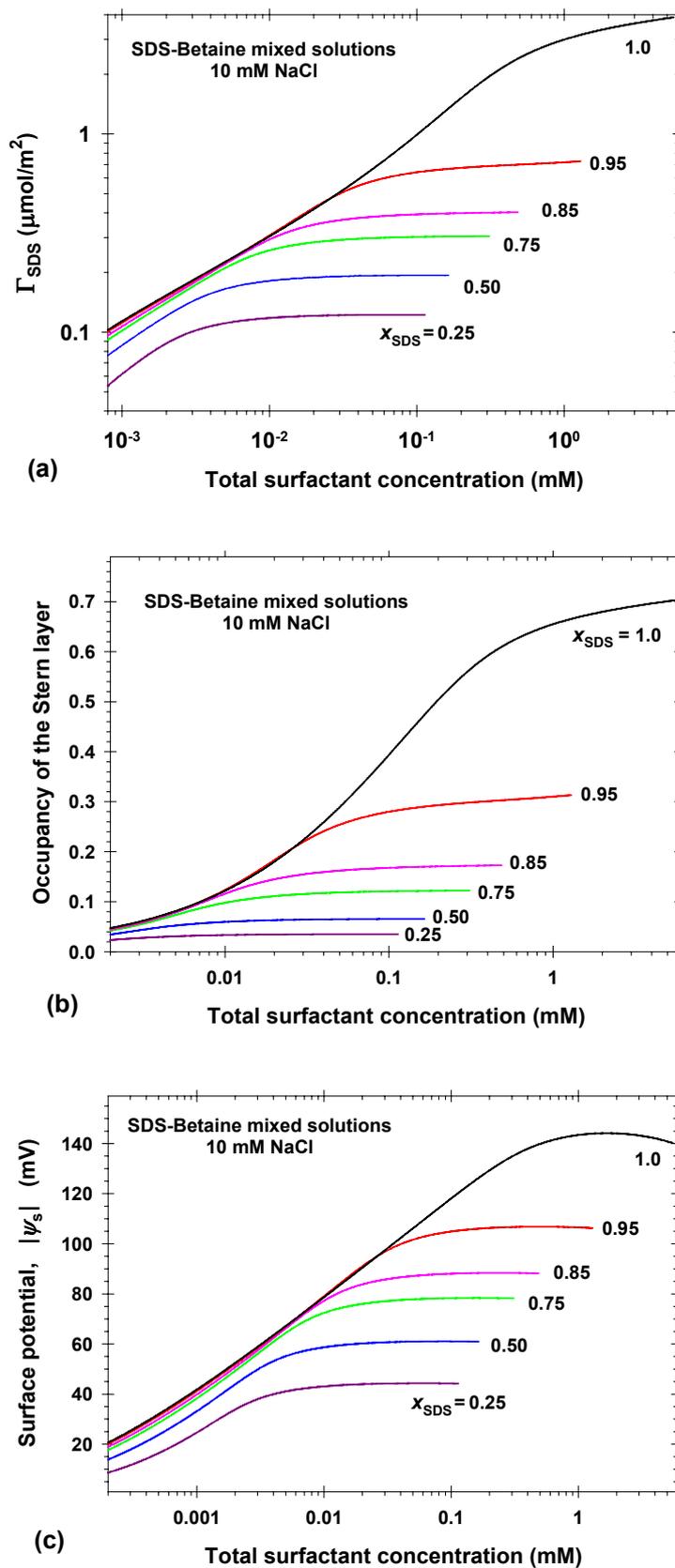
Figure 9 represents a plot of the surface mole fraction of Betaine,  $X_B$ , vs. the total bulk surfactant concentration. By definition, we have:

$$X_B = \frac{\Gamma_B}{\Gamma_{\text{SDS}} + \Gamma_B} \quad (16)$$

Each curve in Figure 9 corresponds to a fixed bulk mole fraction of Betaine,  $x_B$ . One sees that the surface mole fraction of Betaine is systematically greater than the bulk one,  $X_B > x_B$ . This should be expected in view of the greater surface activity of Betaine in comparison with SDS. The difference is especially pronounced for the curve with  $x_B = 0.05$ , for which  $X_B$  rises up to 0.84. It should be noted also that, first,  $X_B$  increases with the total surfactant concentration, and then  $X_B$  levels off (Figure 9). Hence, it turns out that the dense surfactant adsorption layers have a fixed composition, which depends on the bulk mole fractions of SDS and Betaine.

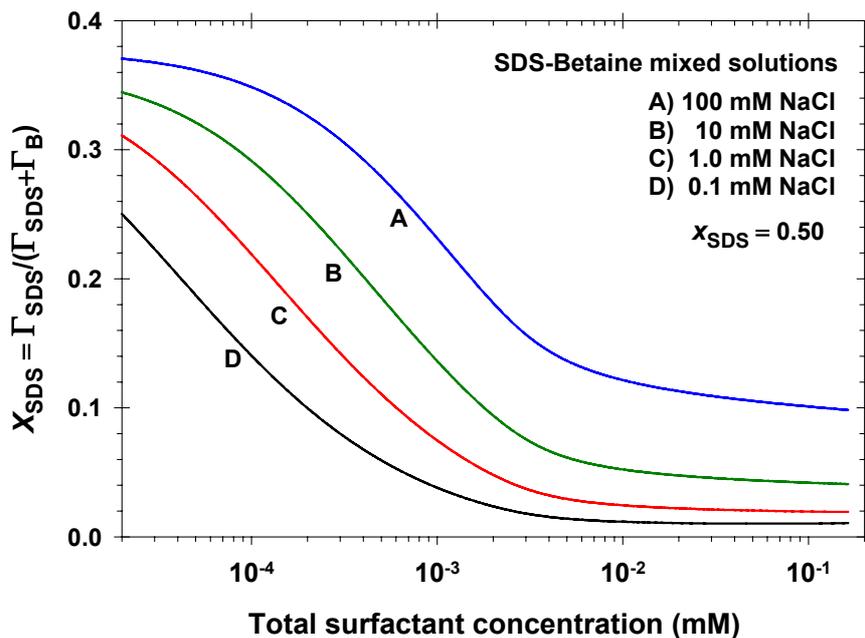
Figures 7–9 indicate that in the mixed Betaine-SDS solutions, Betaine dominates the surfactant adsorption and surface elasticity. On the other hand, SDS controls the interfacial electric properties. The latter is illustrated in Figure 10. As it could be expected,  $\Gamma_{\text{SDS}}$  increases with both the total surfactant concentration and the SDS mole fraction in the bulk,  $x_{\text{SDS}}$  (Figure 10a). Figure 10b shows the calculated occupancy,  $\Gamma_{\text{Na}}/\Gamma_{\text{SDS}}$ , of the Stern layer with adsorbed  $\text{Na}^+$  ions. The occupancy rises up to 0.7 for  $x_{\text{SDS}} = 1$ , but it is below 0.1 for  $x_{\text{SDS}} \leq 0.5$ . It is not surprising that, qualitatively, the shape of the curves in Figure 10b resembles that of the curves in Figure 10a: in fact, the headgroups of the adsorbed SDS molecules serve as adsorption centers for the  $\text{Na}^+$  ions.

Figure 10c shows the magnitude of the calculated surface potential,  $|\psi_s|$  vs. the total surfactant concentration. Following the behavior of  $\Gamma_{\text{SDS}}$  (Figure 10a),  $|\psi_s|$  first increases, and then levels off at the higher surfactant concentrations. With the rise of  $x_{\text{SDS}}$  from 0.25 to 1,  $|\psi_s|$  increases from 45 to 145 mV. The computed values of  $\psi_s$  provide a possibility to test the predictions of the used theoretical model against experimental data for the zeta-potential of bubbles or for the equilibrium thickness of foam films formed from the respective solutions. This can be the subject of a subsequent study.



**Figure 10.** Plots of (a) the SDS adsorption,  $\Gamma_{\text{SDS}}$ , (b) the occupancy of the Stern layer,  $\Gamma_{\text{Na}}/\Gamma_{\text{SDS}}$ , and (c) the magnitude of the surface potential,  $|\psi_s|$ , vs. the total bulk surfactant concentration in mixed SDS-Betaine solutions. The different curves correspond to different bulk mole fractions of SDS,  $x_{\text{SDS}}$ , denoted in the figures; pH = 5.5.

In Figures 7–10 the concentration of NaCl was fixed to 10 mM. As we have determined all parameters of the model (Table 3), we are able to predict the composition of the surfactant adsorption layer also for other concentrations of NaCl. As an illustration, in Figure 11 we show the effect of NaCl on the surface mole fraction of SDS,  $X_{\text{SDS}} = 1 - X_{\text{B}}$ . In general,  $X_{\text{SDS}}$  increases with the rise of the NaCl concentration. This can be explained with the reduction of the electrostatic repulsion between the  $\text{DS}^-$  ions and the interface with the rise of the solution's ionic strength. Then both the subsurface concentration of  $\text{DS}^-$  and  $X_{\text{SDS}}$  increase.



**Figure 11.** Plot of the calculated surface mole fraction of SDS,  $X_{\text{SDS}}$ , vs. the total bulk surfactant concentration in mixed SDS-Betaine solutions at fixed  $x_{\text{SDS}} = 0.50$ . The different curves correspond to different bulk concentrations of NaCl, denoted in the figure; pH = 5.5.

## 5. Relaxation Kinetics

For the specific example in Figure 1, the short-time linear dependence ends at some moment,  $t_{\text{end}} = 8.61$  min. As discussed in section 2.2, the short-time linear dependence should be used to determine (by extrapolation) the equilibrium surface tension when the Wilhelmy plate method is applied. (The long-time linear dependence of  $\sigma$  on  $t^{-1/2}$  is, most probably, an artifact due to the gradual hydrophobization of the Wilhelmy plate by adsorbed Betaine.) From practical viewpoint, it would be helpful to know  $t_{\text{end}}$ , and to carry out measurements of  $\sigma$  for  $t \leq t_{\text{end}}$  (to avoid the misleading long-time kinetics of  $\sigma$ ). It turns out that  $t_{\text{end}}$  exhibits a strong, nonmonotonic dependence on the total surfactant concentration,  $C_{\text{tot}}$ : this is illustrated in Table 4

with experimental data for  $t_{\text{end}}$  at two different fixed molar fractions of Betaine:  $x_B = 1$  and 0.5. One sees that the dependence of  $t_{\text{end}}$  on  $C_{\text{tot}}$  has a maximum.

**Table 4.** Comparison of the experimental  $t_{\text{end}}$  with the theoretical  $t_{\text{rel}}$  for various  $C_{\text{tot}}$ .

$x_B = 1.0$			$x_B = 0.5$		
$C_{\text{tot}}$ (mM)	$t_{\text{end}}$ (s)	$t_{\text{rel}}$ (s)	$C_{\text{tot}}$ (mM)	$t_{\text{end}}$ (s)	$t_{\text{rel}}$ (s)
0.001	350	12.81	0.003	420	33.57
0.002	1440	51.44	0.005	650	52.51
0.003	1700	63.09	0.007	630	51.83
0.005	1460	53.53	0.010	520	42.31
0.007	1110	41.20	0.015	370	30.51
0.010	780	28.42	0.020	270	22.51
0.013	490	21.59	0.030	180	14.68
0.017	460	17.00	0.050	100	8.058
0.020	370	13.31	0.070	66	5.384
0.030	230	8.503	0.100	45	3.626
0.050	140	4.704	0.150	30	2.372

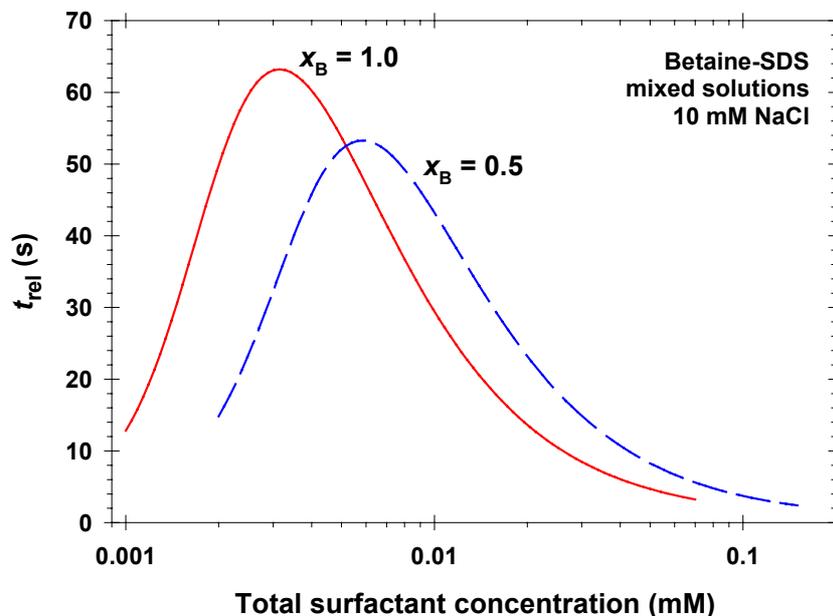
To understand why the dependence of  $t_{\text{end}}$  on  $C_{\text{tot}}$  is nonmonotonic, we recall that the characteristic relaxation time of  $\sigma$  in diffusion-controlled regime,  $t_{\text{rel}}$ , usually exhibits a maximum as a function of  $C_{\text{tot}}$ .<sup>11,12</sup> To check that for the case of Betaine we will use the long-time asymptotics of surface tension, in the Hansen limit (large initial deviations from equilibrium):<sup>11,12,39</sup>

$$\frac{\sigma(t) - \sigma_{\text{eq}}}{\sigma_{\text{eq}}} = \frac{1}{\pi} \left( \frac{t_{\text{rel}}}{t} \right)^{1/2}, \quad t_{\text{rel}} = \frac{\pi}{D} \left( \frac{kT}{\sigma_{\text{eq}}} \frac{\Gamma^2}{C_{\text{tot}}} \right)^2 \quad (17)$$

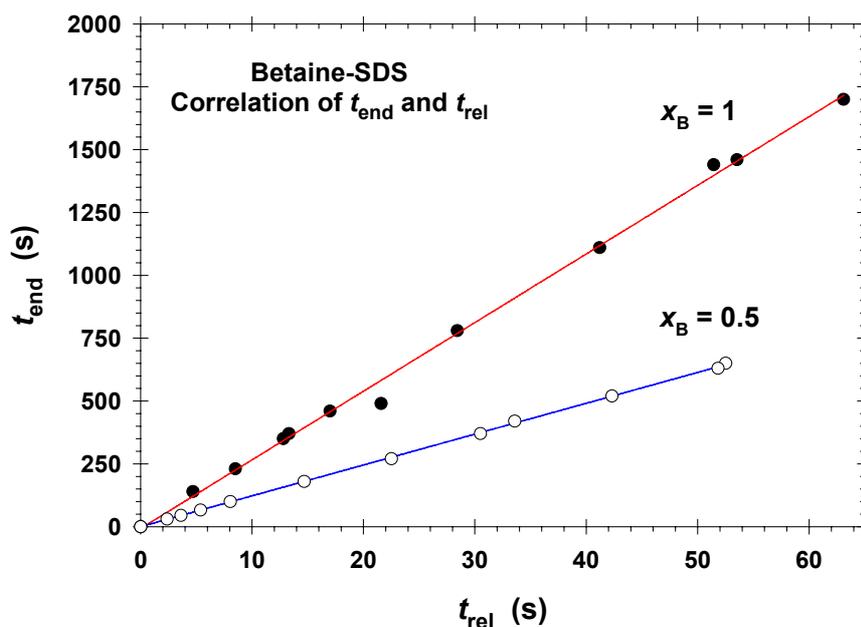
where  $\Gamma$  is the total surfactant concentration,  $D$  is the diffusion coefficient of the surfactant molecules;  $\sigma_{\text{eq}}$  is the equilibrium surface tension. As already mentioned, employing the theoretical model and the parameter values in Table 3, we are able to predict  $\Gamma$  and  $\sigma_{\text{eq}}$  for every  $C_{\text{tot}}$ . Thus, using eq 17, we calculated  $t_{\text{rel}}$  for the values of  $C_{\text{tot}}$  and  $x_B$  in Table 4; the diffusivity of SDS,  $5.5 \times 10^{-6} \text{ m}^2/\text{s}$ , was substituted for  $D$ . As illustrated in Figure 12, the dependence  $t_{\text{rel}}(C_{\text{tot}})$  has a well-pronounced maximum. Moreover, the calculated dependence  $t_{\text{rel}}(C_{\text{tot}})$  correlates very well with the experimental dependence  $t_{\text{end}}(C_{\text{tot}})$ , see the data in Table 4. This is visualized in Figure 13, where  $t_{\text{end}}$  is plotted vs.  $t_{\text{rel}}$ . Despite the fact that, separately,  $t_{\text{end}}$  and  $t_{\text{rel}}$  are nonmonotonic functions of  $C_{\text{tot}}$  (see Figure 12), Figure 13 shows that  $t_{\text{end}}(t_{\text{rel}})$  is a straight line. In other words, it

turns out that  $t_{\text{end}} \propto t_{\text{rel}}$ . The slopes of the two lines in Figure 13 are 27.13 and 12.28, respectively, for  $x_B = 1$  and 0.5.

In conclusion, it turns out that  $t_{\text{end}} \propto t_{\text{rel}}$  and that the nonmonotonic behavior of  $t_{\text{end}}$  correlate with the rate of adsorption under diffusion control, characterized by  $t_{\text{rel}}$ .



**Figure 12.** Plot of the calculated characteristic relaxation time of surface tension,  $t_{\text{rel}}$  (eq 17), vs. the total surfactant concentration.  $C_{\text{tot}}$ , for two fixed molar fractions of Betaine,  $x_B$ , denoted in the figure; pH = 5.5.



**Figure 13.** Correlation of the experimentally determined  $t_{\text{end}}$  and the calculated  $t_{\text{rel}}$  – plot of data from Table 4; 10 mM NaCl; pH = 5.5; details in the text.

## 6. Summary and Conclusions

Here we present experimental surface tension isotherms of mixed solutions of two surfactants, sodium dodecylsulfate (SDS) and cocoamidopropyl betaine (Betaine), measured by means of the Wilhelmy plate method. The kinetics of surface tension relaxation exhibits two characteristic timescales: one of them related to the diffusion-controlled surfactant adsorption, and another one, related to an apparent decrease of surface tension due to a gradual hydrophobization of the Wilhelmy plate (Figure 1 and section 5). The two timescales should be distinguished in order to determine correctly the equilibrium surface tension. The transition from the zwitterionic to the cationic form of Betaine is detected by surface tension measurements (Figure 2). The critical micellization concentration (cmc) increases monotonically with the rise of the mole fraction of SDS in the surfactant blend (Figure 4). The experimental surface tension isotherms are fitted by means of the two-component van der Waals model (section 3); the agreement between theory and experiment is excellent (Figure 3). The excluded area per Betaine molecule ( $\alpha_{44}$ ), determined from the best fit, coincides with the geometric cross-sectional area of the Betaine molecule (Figure 6 and the related text). Having determined the parameters of the model, we calculated different properties of the mixed surfactant adsorption layer at various concentrations of SDS, Betaine and salt. Such properties are the adsorptions of the two surfactants and the total adsorption; the surface dilatational (Gibbs) elasticity, the occupancy of the Stern layer by bound counterions, the surface electric potential, etc. (Figures 7–10). The results could be further applied to predict the thickness and stability of foam films, or the size of the rodlike micelles in the mixed solutions of SDS and Betaine.<sup>21</sup>

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