Comparison of the van der Waals and Frumkin Adsorption Isotherms for Sodium Dodecyl Sulfate at Various Salt Concentrations

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1. Introduction

The adsorption of ionic surfactants at the surface of an aqueous solution leads to a reduction in the surface tension, to an increase of the surface electric charge density, and to the development of an electric double layer.[1–10] The addition of nonamphiphilic electrolytes to the solutions of ionic surfactants is accompanied by adsorption (binding) of counterions at the oppositely charged headgroups of the adsorbed surfactant molecules. In other words, the counterions behave as a second surface-active component.[6–8] Thus the counterion adsorption causes a significant reduction in the magnitude of the net surface electric charge, which could be decreased by more than 50%.[8,11–13] The latter effect leads to increasing of the surface density of the adsorbed ionic surfactant but simultaneously suppresses the electric double layer. A recent review was published by Fainerman and Lucassen-Reynders.[14]

In refs 8 and 15, we demonstrated that the processing of experimental surface-tension isotherms by means of an adequate theoretical model can be rather informative. It can be used for a detailed computer modeling of equilibrium surfactant adsorption layers, of dynamic surface-tension isotherms, and of the properties of thin liquid films formed from the respective solutions. With this end in view, one has to first determine the adsorption

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(1) Davies, J. T.; Rideal, E. K. *Interfacial Phenomena*; Academic Press: London, 1963.
(2) Hachisu, S. *J. Colloid Interface Sci.* **1970**, *33*, 445.
(3) Borwankar, R. P.; Wasan, D. T. *Chem. Eng. Sci.* **1988**, *43*, 1323.
(4) Eriksson, J. C.; Ljunggren, S. *Colloids Surf.* **1989**, *38*, 179.
(5) Diamant, H.; Andelman, D. *J. Phys. Chem.* **1996**, *100*, 13732.
(6) Kalinin, V. V.; Radke, C. J. *Colloids Surf., A* **1996**, *114*, 337.
(7) Warszynski, P.; Barzyk, W.; Lunkenheimer, K.; Fruhner, H. *J. Phys. Chem. B* **1998**, *102*, 10948.
(8) Kralchevsky, P. A.; Danov, K. D.; Broze, G.; Mehreteab, A. *Langmuir* **1999**, *15*, 2351.
(9) Prosser, A. J.; Franses, E. I. *Colloids Surf., A* **2001**, *178*, 1.
(10) Karakashev, S. I.; Manev, E. D. *J. Colloid Interface Sci.* **2002**, *248*, 477.
(11) Cross, A. W.; Jayson, G. G. *J. Colloid Interface Sci.* **1994**, *162*, 45.
(12) Johnson, S. B.; Drummond, C. J.; Scales, P. J.; Nishimura, S. *Langmuir* **1995**, *11*, 2367.
(13) Alargova, R. G.; Danov, K. D.; Petkov, J. T.; Kralchevsky, P. A.; Broze, G.; Mehreteab, A. *Langmuir* **1997**, *13*, 5544.
(14) Fainerman, V. B.; Lucassen-Reynders, E. H. *Adv. Colloid Interface Sci.* **2002**, *96*, 295.
(15) Danov, K. D.; Kolev, V. L.; Kralchevsky, P. A.; Broze, G.; Mehreteab, A. *Langmuir* **2000**, *16*, 2942.

constants as adjustable parameters from the best fit of the experimental data. Knowing these parameters and having the respective computer program, one can obtain information about many properties of the system. Indeed, for each combination of surfactant and nonamphiphilic electrolytes one can calculate the surface (interfacial) tension, the adsorption of each specific component (including the bound counterions), the surface electric potential, the surface dilatational (Gibbs) elasticity, and so forth.

The *two* experimental surface-tension isotherms previously fitted by us[8] were taken from papers by Tajima et al.[16–18] In fact, surface-tension isotherms of sodium dodecyl sulfate (SDS) for 11 different fixed NaCl concentrations can be found in refs 16–18. Our aims in this study are (i) to fit simultaneously all 11 isotherms (SDS at fixed NaCl concentration and temperature of 25 °C) with the same four-parameter model, as in ref 8, and (ii) to compare the fits provided by the Frumkin and van der Waals models.

2. Theoretical Background

We will use the following numbering of the species: component 1 is the dodecyl sulfate ion, DS^-; component 2 is Na^+; and component 3 is Cl^-. The ionic valence is $Z_i = (-1)^i$, $i = 1,2,3$. The subsurface activity of the ith ionic species in the solution, a_{is}, is defined by the equation[19]

$$a_{is} = a_{i\infty} \exp\left(-\frac{Z_i e \psi_s}{kT}\right) \qquad (i = 1,2,3) \qquad (1)$$

which stems from the constancy of the electrochemical potential throughout the electric double layer; $a_{i\infty}$ is the bulk activity of this component, e is the electronic charge, ψ_s is the surface electric potential, k is the Boltzmann constant, and T is the temperature. The bulk activity is related to the respective concentration, $c_{i\infty}$, by means of the formula $a_{i\infty} = \gamma_\pm c_{i\infty}$, with $\gamma_\pm$ being the activity coefficient; for details see refs 3 and 8.

The *van der Waals* adsorption model, termed also the Hill–de Boer model,[20–22] is derived assuming *nonlocalized* adsorption of the two surfactant species.[22–24] The respective relation between subsurface concentration and surfactant adsorption is

$$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}\right) \qquad (2a)$$

Γ_1 is the surfactant concentration in the adsorption monolayer; K is an adsorption parameter, which depends on the subsurface activity of the counterions (see eq 4 below); Γ_∞^{-1} is the excluded area per adsorbed surfactant

(16) Tajima, K.; Muramatsu, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1991.
(17) Tajima, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3063.
(18) Tajima, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1767.
(19) Kirkwood, J. G.; Oppenheim, I. *Chemical Thermodynamics*; McGraw-Hill: New York, 1961.
(20) Jaycock, M. J.; Parfitt, G. D. *Chemistry of Interfaces*; Wiley: New York, 1981.
(21) de Boer, J. H. *The Dynamical Character of Adsorption*; Clarendon Press: Oxford, 1953.
(22) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Addison-Wesley: Reading, MA, 1962.
(23) Baret, J. F. *J. Colloid Interface Sci.* **1969**, *30*, 1.
(24) Kralchevsky, P. A.; Danov, K. D.; Denkov, N. D. In *Handbook of Surface and Colloid Chemistry*, 2nd ed.; Birdi, K. S., Ed.; CRC Press: Boca Raton, FL, 2002; Chapter 5.

molecule. The interaction between such adsorbed molecules is taken into account by the parameter β. For *oil–water* interfaces, the fits of data usually yield $\beta \approx 0$, whereas for *air–water* interfaces $\beta > 0$ is commonly obtained; the value of β in the latter case is being attributed to the van der Waals attraction between the hydrocarbon tails of the surfactant molecules across air.[1,3]

An alternative adsorption model is that of *Frumkin*,[25] which corresponds to *localized* adsorption, that is, to a two-dimensional lattice statistics in the Bragg–Williams approximation.[22–24] In the framework of the Frumkin model, the surfactant adsorption isotherm is

$$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT}\right) \qquad (2b)$$

The meaning of the parameters in eqs 2a and 2b is similar. Because the adsorption of surfactant at a fluid interface is nonlocalized, one may expect that in our case the van der Waals model should be more adequate than the Frumkin one. On the other hand, many authors report very good fits of surfactant adsorption data by means of the Frumkin model; see for example ref 26. To investigate the applicability of the two models, we fitted the experimental data using alternatively the van der Waals and Frumkin models, that is, eq 2a or eq 2b. The numerical results are compared and discussed in the next section.

Irrespective of the type of the surfactant adsorption isotherm, the binding of counterions can be described by the Stern isotherm.[1,27] Correspondingly, the surface concentration of bound Na^+ ions (component 2) per unit area of the Stern layer is

$$\Gamma_2 = \Gamma_1 \frac{K_2 a_{2s}}{K_1 + K_2 a_{2s}} \qquad (3)$$

where K_1 and K_2 are adsorption parameters. The co-ions, such as Cl^-, are not expected to bind in the Stern layer, that is, $\Gamma_3 = 0$. The condition for thermodynamic compatibility (see eqs 2.7 and 5.3 in ref 8) of the surfactant and counterion adsorption isotherms, eqs 2 and 3, leads to the relationship[8,28]

$$K = K_1 + K_2 a_{2s} \qquad (4)$$

where K_1 and K_2 are constant parameters, which are related to the respective adsorption energies:[8,29]

$$K_1 = \frac{\delta_1}{\Gamma_\infty} \exp\left(\frac{\Delta\mu_1^{(0)}}{kT}\right) \qquad \frac{K_2}{K_1} = \frac{\delta_2}{\Gamma_\infty} \exp\left(\frac{\Delta\mu_2^{(0)}}{kT}\right) \qquad (5)$$

δ_i is the thickness of the adsorption layer, which can be set equal to the characteristic dimension of the respective molecule or ion; $\Delta\mu_i^{(0)}$ is the standard free energy of adsorption of a molecule (or ion) from an ideal dilute solution in an ideal adsorption layer.

(25) Frumkin, A. *Z. Phys. Chem.* **1925**, *116*, 466.

(26) Fainerman, V. B.; Möbius, D.; Miller, R. *Surfactants: Chemistry, Interfacial Properties, Applications*; Elsevier: Amsterdam, 2001.

(27) Stern, O. *Z. Elektrochem.* **1924**, *30*, 508.

(28) Kralchevsky, P. A.; Nagayama, K. *Particles at Fluid Interfaces and Membranes*; Elsevier: Amsterdam, 2001; Chapter 1.

(29) Shchukin, E. D.; Pertsov, A. V.; Amelina, E. A. *Colloid Chemistry*; Moscow University Press: Moscow, 1982 (Russian); Elsevier: 2001 (English).
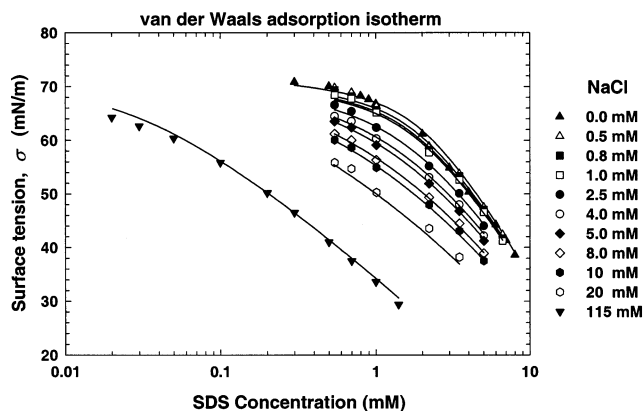
The solution's surface tension, σ, can be expressed in the form[2,8]

$$\sigma = \sigma_a + \sigma_d \qquad (6)$$

where σ_a is the contribution of the adsorption layer, which consists of the surfactant monolayer and the counterions bound in the Stern layer; σ_d is the contribution of the diffuse electric double layer. For the van der Waals and Frumkin adsorption models, we have, respectively,[8,22,25]

$$\sigma_a = \sigma_0 - kT\Gamma_1/(1 - \Gamma_1/\Gamma_\infty) + \beta\Gamma_1^2 \quad \text{(van der Waals)} \qquad (7a)$$

$$\sigma_a = \sigma_0 + kT\Gamma_\infty \ln(1 - \Gamma_1/\Gamma_\infty) + \beta\Gamma_1^2 \quad \text{(Frumkin)} \qquad (7b)$$

where σ_0 is the surface tension of the pure solvent (water). It is self-consistent to use either the van der Waals model, eqs 2a and 7a, or the Frumkin model, eqs 2b and 7b. The equations in each couple are connected by means of the Gibbs adsorption equation:[8] $d\sigma_a = -kT\sum_i \Gamma_i \, d \ln a_{is}$. In addition, one can calculate σ_d by means of the expression[1,2,8]

$$\sigma_d = -\frac{8}{\kappa_c}kT\sqrt{a_{2\infty}}\left[\cosh\left(\frac{Z_1 e\psi_s}{2kT}\right) - 1\right] \qquad (8)$$

where $\kappa_c^2 = (8\pi e^2)/(\epsilon kT)$ with ϵ being the dielectric permittivity of water. The full system of equations and the numerical procedure are described in ref 8.

3. Parameters of the Best Fit

The experimental points in Figure 1 represent the 11 surface-tension isotherms of SDS solutions measured by Tajima et al.[16–18] at 11 different fixed concentrations of NaCl, varying from 0 to 115 mM. All experimental points belong to the region below the critical micellization concentration (cmc). The data for all surfactant and salt concentrations are processed simultaneously to determine the parameters K_1, Γ_∞, and β using the procedure of calculations in ref 8. It turns out that the fit is not very sensitive to the constant K_2, that is, to the binding energy, $\Delta\mu_2^{(0)}$, of the Na^+ counterions at the headgroups of adsorbed DS^- ions. For $1.5 < \Delta\mu_2^{(0)}/kT < 2$, the standard deviation of the fit was almost the same (there was a flat minimum of dispersion). Therefore, in the present study we fixed the adsorption energy of Na^+ equal to that determined in ref 8, viz.,

$$\Delta\mu_2^{(0)} = 1.64kT \qquad (9)$$

In addition, in eq 5 we have used the same δ values as in ref 8, viz., $\delta_1 = 2$ nm and $\delta_2 = 0.7$ nm.

The continuous lines in Figure 1 represent the best theoretical fit obtained by means of the van der Waals model. A similar fit was obtained using the Frumkin model. The obtained parameter values are given in Table 1. The quality of the fits is practically the same for the two models (van der Waals' and Frumkin's); this is evidenced by the close values of the standard deviation of the fits (the last column of Table 1). The theoretical curves $\sigma(c_{1\infty})$ for the two models look almost identical; for that reason, we do not give a separate figure with the Frumkin fit.

The differences between the values of Γ_∞^{-1} in Table 1 can be attributed to the difference between the meanings of Γ_∞^{-1} in the two models. In the van der Waals model (nonlocalized adsorption), Γ_∞^{-1} is defined as the area excluded by the molecule itself. In contrast, in the framework of the Frumkin model (localized adsorption) Γ_∞^{-1} is the area per adsorption site (per molecule in a saturated adsorption layer).[22]

Figure 1. Plot of the surface tension, σ, of the air–water interface versus the surfactant (SDS) concentration, $c_{1\infty}$, for 11 fixed NaCl concentrations denoted in the figure; $T = 25\,°C$. The symbols are experimental data by Tajima et al. (refs 16–18), and the curves represent the best fit by means of the van der Waals model; see the text.

Table 1. Parameters of the Best Fit of the Data in Figure 1

model	$\Delta\mu_1^{(0)}/kT$	Γ_∞^{-1} (Å²)	$2\beta\Gamma_\infty/kT$	std dev (mN/m)
van der Waals	12.53	29.8	2.73	0.815
Frumkin	12.51	39.5	0.81	0.817

The difference between the values of β obtained by means of the two models is not surprising, because there is a difference in the definition of the respective interaction parameters. This results in different *critical* values of the dimensionless parameter $2\beta\Gamma_\infty/kT$, which is 4 for the Frumkin isotherm and 6.75 for the van der Waals isotherm.[22] Hence, the values of $2\beta\Gamma_\infty/kT$ in Table 1 are well below the respective critical values (corresponding to the critical isotherm). In other words, there is a single surface phase, a two-dimensional gas, and there is no phase transition (liquid/gas) in the investigated surfactant adsorption monolayers.

The fact that the theoretical model provides a very good fit of 11 isotherms (Figure 1) is evidence in favor of the adequacy of the used theoretical approach, which accounts for the effect of counterion binding. As noted above, in ref 8 we fitted only two of these isotherms, those with 0 and 115 mM NaCl, using the Frumkin model; the parameter values obtained there, viz., $\Delta\mu_1^{(0)}/kT = 12.8$, $\Gamma_\infty^{-1} = 37.6$ Å², and $2\beta\Gamma_\infty/kT = 0.80$, are very close to the respective values in Table 1. This indicates stability of the theoretical fit. It is confirmed that one can determine the parameters of the model by fitting only two experimental surface-tension isotherms (as in ref 8), obtained at a low and a high concentration of added NaCl. Of course, the simultaneous processing of several isotherms increases the reliability of the fit.

4. Numerical Results and Discussion

As already mentioned, having once determined the parameters of the fit (Γ_∞, β, K_1, and K_2), one is able to compute many properties of the system: the surface tension σ; the surfactant adsorption, Γ_1; the adsorption (binding) of counterions in the Stern layer, Γ_2; the surface electric potential ψ_s; the surface dilatational (Gibbs) elasticity, E_G; and so forth, each of them for every chosen couple of surfactant and salt concentrations below the cmc; see Figures 2 and 3.

Figure 2a shows the dependence of the surfactant adsorption, Γ_1, on the SDS concentration, calculated with
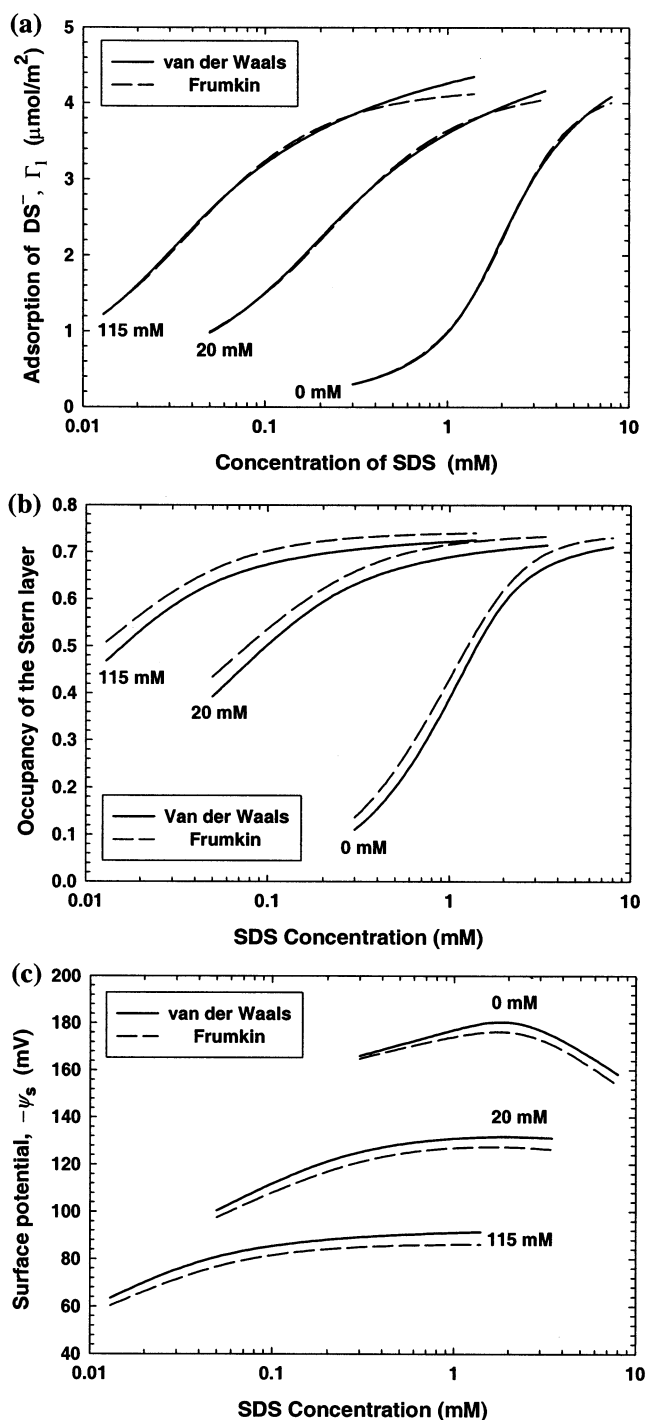

Figure 2. Concentration dependencies of (a) surfactant adsorption, Γ_1, (b) occupancy of the Stern layer by adsorbed counterions, Γ_2/Γ_1, and (c) surface electric potential, ψ_s, calculated using parameter values corresponding to the van der Waals and Frumkin models (Table 1); the separate curves refer to fixed concentrations of NaCl: 0, 20, and 115 mM.

parameter values from Table 1. Despite the different physical picture behind the Frumkin and van der Waals isotherms (localized vs nonlocalized adsorption), which results in different theoretical expressions (eqs 2a,b and 7a,b), the two models predict practically the same values of the surfactant adsorption, Γ_1, in the whole physically reasonable range of variation of the SDS and NaCl concentrations. Small differences between the two models with respect to Γ_1 are observed only at the highest surfactant and salt concentrations. Note that the relative
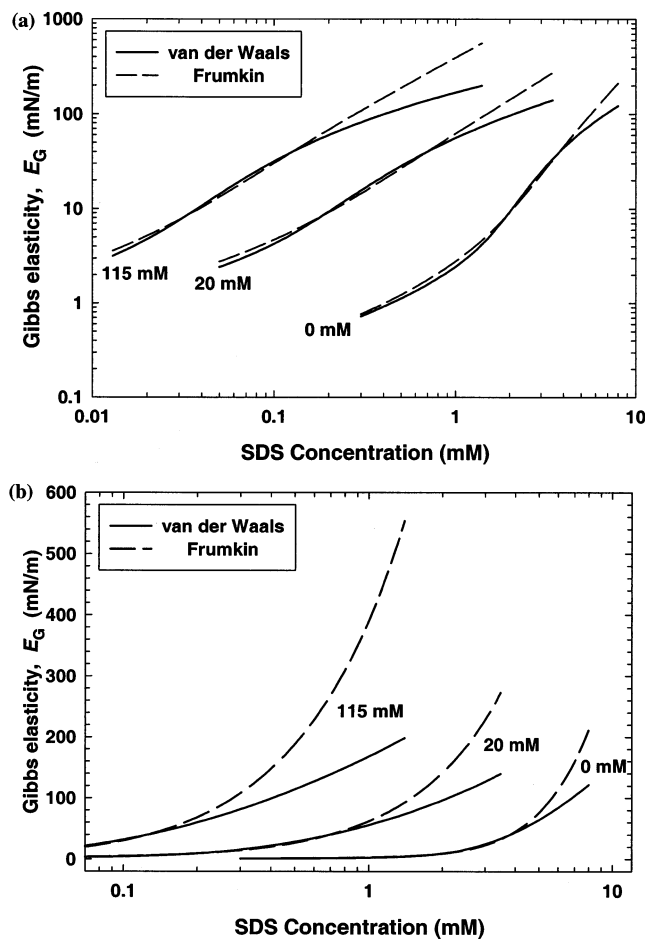
Figure 3. Dependence of the Gibbs elasticity, E_G, on the SDS concentration, calculated with the parameter values in Table 1 for the Frumkin and van der Waals models, the dashed and continuous lines, respectively; the curves correspond to fixed concentrations of NaCl: 0, 20, and 115 mM. (a) E_G in log scale; (b) E_G in linear scale.

adsorptions, Γ_1/Γ_∞, are different for the two types of isotherms because of the different values of Γ_∞; see Table 1.

Tajima et al.[16−18] directly measured Γ_1 by means of a radiotracer method. For example, for 115 mM NaCl, at the cmc ($c_{1\infty} = 1.62$ mM SDS), they obtained $\Gamma_{1,cmc} = 4.33$ μmol/m^2, which excellently compares with the values computed by means of the van der Waals and Frumkin isotherms, viz., $\Gamma_{1,cmc} = 4.38$ and 4.13 μmol/m^2, respectively.

In the absence of NaCl ($c_{3\infty} = 0$), at the cmc ($c_{1\infty} = 8.12$ mM SDS), Tajima et al.[16−18] obtained $\Gamma_{1,cmc} = 3.19$ μmol/m^2, whereas using the van der Waals and Frumkin isotherms we calculate $\Gamma_{1,cmc} = 4.10$ and 4.02 μmol/m^2, respectively (Figure 2a). This difference of about 20% between experiment and theoretical predictions could be attributed either to some inadequacy of our theoretical model or to the presence of traces of a nonionic amphiphile (like dodecanol) in the used SDS sample. (When there is no added electrolyte, the composition of the adsorption layer becomes very sensitive to the presence of dodecanol.) On the other hand, our calculated $\Gamma_{1,cmc}$ agrees very well with the experimental values $\Gamma_{1,cmc} = 4.2$ and 4.1 μmol/m^2 obtained, respectively, by Wilson et al.,[30] who have applied foam analysis, and by Lu et al.,[31] who have used neutron reflection.

(30) Wilson, A.; Epstein, M. B.; Ross, J. *J. Colloid Sci.* **1957**, *12*, 349.
(31) Lu, J. R.; Purcell, I. P.; Lee, E. M.; Simister, E. A.; Thomas, R. K.; Rennie, A. R.; Penfold, J. *J. Colloid Interface Sci.* **1995**, *174*, 441.

Figure 2b shows the calculated occupancy of the Stern layer with bound Na$^+$ ions. One sees that the occupancy is above 0.7 at the higher SDS and NaCl concentrations. The two models give close quantitative predictions; the Frumkin model gives slightly higher occupancy (Figure 2b) and slightly lower surface electric potential ψ_s (Figure 2c). The curve $|\psi_s(c_{1\infty})|$ for 0 NaCl has a maximum at $c_{1\infty} \approx 2$ mM. Such a behavior can be attributed to the competition of two effects:[8] (i) the increase of the surface electric charge with the rise of the surfactant adsorption and (ii) the decrease of the surface potential with the increase of the ionic strength due to the addition of ionic surfactant, which itself is an electrolyte. If there is no added NaCl, effect ii gets the upper hand at the higher $c_{1\infty}$, which explains the observed maximum. In contrast, the dependence $|\psi_s(c_{1\infty})|$ does not exhibit any maximum at 20 and 115 mM NaCl (Figure 2c) because in these cases the ionic strength is fixed by the added salt and effect ii does not appear.

Concerning the surface dilatational (Gibbs) elasticity, the two models give close values of E_G for the lower surfactant concentrations (Figure 3a); however, the Frumkin isotherm gives markedly greater E_G values at the higher surfactant concentrations (Figure 3b). We have used the following expressions to calculate the Gibbs elasticity:[15,28]

$$E_G = kT\Gamma_1\left[\frac{\Gamma_\infty{}^2}{(\Gamma_\infty - \Gamma_1)^2} - \frac{2\beta\Gamma_1}{kT}\right] \quad \text{(van der Waals)}$$
$$(10a)$$

$$E_G = kT\Gamma_1\left(\frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}\right) \quad \text{(Frumkin)} \quad (10b)$$

We could anticipate that at higher surfactant concentrations more reliable values of E_G are predicted by the van der Waals isotherm, insofar as it corresponds to nonlocalized adsorption, which is expected to be the case for a liquid interface. However, only the comparison with experimental data for E_G could reveal which of the two models is more adequate. This could be a subject of a subsequent study.

5. Summary and Conclusions

The theoretical model from ref 8 excellently fits all 11 surface-tension isotherms for SDS obtained by Tajima et al.[16−18] for 11 different concentrations of NaCl; see Figure 1. The parameters determined from the best fit have values which are close to those previously obtained by us using a fit of only two adsorption isotherms by means of the Frumkin model.

The Frumkin and van der Waals models provide equally good fits of the experimental surface-tension isotherms and predict practically the same values of the surfactant adsorption; see Figure 2a. The Frumkin model yields slightly higher occupancy of the Stern layer and slightly lower surface potential in comparison with the van der Waals model; see Figure 2b,c.

The most significant difference between the predictions of the two models is found for the surface dilatational elasticity, E_G, at the higher surfactant and electrolyte concentrations (Figure 3b): the Frumkin isotherm predicts considerably greater values of E_G.