

Thermodynamics of Ionic Surfactant Adsorption with Account for the Counterion Binding: Effect of Salts of Various Valency

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Received August 31, 1998. In Final Form: November 30, 1998

The effect of counterion binding on the surface tension and surface potential of ionic surfactant solutions is accounted for theoretically. It turns out that no every couple of surfactant and counterion adsorption isotherms are thermodynamically compatible. To solve the problem, we develop a formalism which enables one to obtain the counterion adsorption isotherm corresponding to a given surfactant adsorption isotherm. Further, these adsorption isotherms are integrated to obtain the respective expression for the surface tension. The results are extended to the case when the solution contains ionic–nonionic surfactant mixtures and electrolytes of various valency. The integral, which takes into account the electrostatic interactions, is solved analytically for aqueous solutions containing 1:1, 2:1, 1:2, and 2:2 electrolytes. It is demonstrated that the derived equations can be applied to process experimental data for the surface tension as a function of the surfactant and salt concentrations. As a result one determines the adsorptions of surfactant and counterions and the surface electric potential. The derived equations can also be applied to calculate the surface elasticity of ionic surfactant adsorption monolayers and the diffusion relaxation time in the kinetics of adsorption.

1. Introduction

1.1. Motivation of the Study. We have been motivated to undertake this study challenged by some problems in the field of adsorption kinetics and surface rheology. To extend our theoretical study¹ on adsorption kinetics of ionic surfactants, we needed an equilibrium adsorption isotherm which accounts for the existence of an electric double layer and counterion binding. It turned out that none of the available theoretical isotherms could satisfy these requirements. Another problem is related to the experimental results for the surface (Gibbs) elasticity, defined as

$$E_G = -\Gamma_1 \frac{\partial \sigma}{\partial \Gamma_1} \quad (1.1)$$

where σ and Γ_1 denote surface tension and surfactant adsorption. The values of E_G determined for the same solutions by means of dynamic methods, viz. the oscillating drop method² and the maximum bubble pressure method,³ are several times (and even orders of magnitude) smaller than the values of E_G obtained by differentiating the respective equilibrium surface tension isotherm in accordance with eq 1.1. Moreover, such a great difference between the values of E_G determined by “dynamic” and

“static” methods appears only for solutions of ionic surfactants. In contrast, for nonionic surfactants it has been established^{3,4} that the “dynamic” and “static” methods give very close values of E_G . The adsorption layers of ionic surfactants differ from those of nonionics mostly due to effects related to the surface electric potential and the counterion binding. Therefore, one reason for the controversial values of E_G could be the nonadequate account of these effects in the available thermodynamic theories of ionic surfactant adsorption.

The counterion binding alters the interactions in surfactant adsorption monolayers and the average surface charge density. This effect has been widely investigated for micellar surfactant solutions because of the pronounced influence of salt on the critical micelle concentration (cmc) and on the size and shape of micelles.^{5–9} Below we focus our attention on the experimental studies of counterion binding to planar surfactant adsorption layers at liquid interfaces.

1.2. Experimental Studies on Ionic Surfactant Adsorption. Van Voorst Vader¹⁰ has established that the counterions affect the value of the saturation adsorption as determined from the slope of the surface tension isotherm in the surfactant concentration range just before the cmc. A comprehensive experimental study of ionic surfactant adsorption has been carried out by Tajima et

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al.^{11–13} who measured independently σ and Γ_1 for various salt concentrations. To measure directly Γ_1 , *radiotracer* experiments have been performed with tritiated sodium dodecyl sulfate (TSDS). By using thermodynamic considerations, the adsorption of counterions Γ_2 and that of nonamphiphilic coions Γ_3 have also been determined. Here and hereafter we use the subscripts 1 for surfactant ions, 2 for counterions, and 3 for coions. The results obtained in ref 13 confirm the assumption of other authors^{10,14} that $\Gamma_3 \approx 0$; that is, the adsorption of coions is negligible compared to that of surfactant ions and counterions. Moreover, the validity of the Gibbs adsorption isotherm¹⁵ was confirmed by comparing data for the independently measured σ and Γ_1 . The existence of saturation adsorption (constancy of adsorption) in a wide concentration range was confirmed by the direct measurement of Γ_1 .^{11–13}

Another method for direct determination of surfactant adsorption Γ_1 is *neutron reflection*, which has been shown to be particularly powerful for both measuring surface excess and studying the structure of a surfactant layer at the air–water interface.^{16–19} In ref 18 the adsorption of dodecyl sulfates of the alkali metals at their cmcs was measured; it was established that Γ_1 at the cmc is markedly larger for the less hydrated counterions (Rb and Cs) as compared to the more hydrated ones (Li, Na). This finding is consonant with the expectation that the Cs⁺ ion should bind to the amphiphilic layer much more strongly than Li⁺. The exact position of the bound counterions in the adsorption layer cannot be determined by neutron reflection experiments because the scattering lengths of metal counterions are too small for them to be determined accurately.¹⁸

Direct measurement of counterion adsorption (binding) can be achieved also by radiochemical techniques, as demonstrated by Cross and Jayson.²⁰ These authors studied the binding of Ca²⁺ to SDS adsorption monolayers by using CaCl labeled with ⁴⁵Ca. Competitive binding of Na⁺ and Ca²⁺ ions was established. The adsorption of Ca²⁺ initially increases with the rise of SDS concentration and then decreases for higher surfactant concentrations.²⁰ This effect could be attributed to the preferential binding of Ca²⁺ to submicellar and micellar aggregates. Similar results have been reported by Alargova et al.²¹ for anionic surfactant solutions containing Na⁺ and Al³⁺ ions.

Another group of experimental methods, which bring information about the counterion binding, is related to the determination of the surface electric potential ψ_s . Johnson et al.²² determined ψ_s from the force between surfactant coated silica surfaces measured by means of an atomic force microscope. These authors also carried out electrophoretic measurements of the ζ -potential. The

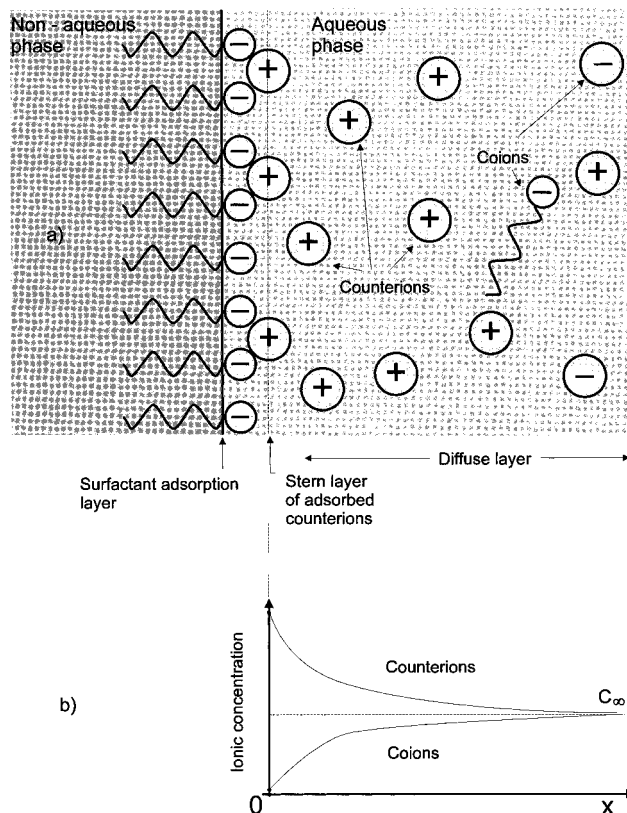


Figure 1. Sketch of the electric double layer in the vicinity of an adsorption monolayer of ionic surfactant. (a) The Stern layer consists of adsorbed (immobilized) counterions, whereas the diffuse layer contains free ions involved in Brownian motion. (b) Near the charged surface there is an accumulation of counterions and a depletion of co-ions, their bulk concentrations being equal to c_∞ .

results for solutions of hexadecyltrimethylammonium bromide (CTAB) + KBr show that 89–95% of the electric charge of the adsorbed surfactant ions is neutralized by bound Br[−] counterions. A similar value, $\theta \approx 86\%$, was obtained for the occupancy of the adsorption layer of sodium dodecyl dioxyethylene sulfate (SDP2S) by bound Na⁺ counterions.²¹ The maximum value of the occupancy of the Stern layer by bound Ca²⁺ counterions directly measured in ref 20 is also about 85%. Most complicated is the case of amphoteric surfactants (betaines),²³ when both cations (H⁺) and anions (Cl[−]) can bind to the surfactant adsorption layer depending on the value of the pH. The measurement of the surface Volta (ΔV) potential is another method bringing information about the interfacial ionization state; this method can be applied to both air–water and oil–water interfaces; see for example ref 24.

In summary, using various experimental techniques, one could measure the surface tension σ , the surfactant, counterion, and coion adsorptions Γ_1 , Γ_2 , and Γ_3 , and the surface potential ψ_s .

1.3. Theoretical Studies on Ionic Surfactant Adsorption. The widely accepted model of the electric double layer (EDL), originating from the works by Gouy,²⁵ Chapman,²⁶ and Stern,²⁷ is illustrated in Figure 1. Davies

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and Rideal²⁸ have hypothesized that in some cases the bound counterions, belonging to the Stern layer, could (at least partially) enter among the surfactant headgroups, whereas in other cases the counterions could be expelled from the space among the headgroups to form an adsorption layer parallel to that of the headgroups. To explain the effect of electrolyte on the surface tension of ionic surfactant solutions, Davies²⁹ considered the adsorbed surfactant to form a two-dimensional gas of mobile ions exerting additional surface pressure due to electrical repulsion. Thus, he arrived at the following expression^{28,29}

$$\sigma_0 - \sigma = \frac{kT\Gamma_\infty\Gamma_1}{\Gamma_\infty - \Gamma_1} + \sqrt{\frac{8\epsilon I(kT)^3}{\pi e^2}} \left(\cosh \frac{e\psi_s}{2kT} - 1 \right) \quad (1.2)$$

where Γ_∞ is the maximum possible value of Γ_1 corresponding to close packing of the headgroups of the adsorbed surfactant molecules, σ_0 is the surface tension of the pure solvent, k is the Boltzmann constant, T is temperature, e is the elementary electric charge, ϵ is the dielectric permittivity of the solvent (water), and I is the total bulk ionic strength of the solution (in cm^{-3}),

$$I = \frac{1}{2} \sum_i Z_i^2 c_{i\infty} \quad (1.3)$$

Z_i is the valency of the i th ionic species, and $c_{i\infty}$ is its bulk concentration. For a noncharged surface ($\psi_s = 0$), eq 1.2 reduces to the known isotherm of Volmer.³⁰ The physical meaning and the application of the Davies isotherm, eq 1.2, became a subject of discussion in the literature.³¹ Hachisu derived the Davis equation in three different ways in order to confirm its validity.³¹ However, the comparison of the Davies equation with experimental data shows only qualitative, but not quantitative, agreement.^{11,32} To fit their data for TSDS, Tajima et al.¹¹ proposed a semiempirical modified version of the Davies equation.

Lucassen-Reynders³² developed a different theoretical approach based on a model expression for the chemical potential of the adsorbed molecules due to Butler:³³

$$\mu_i = \mu_i^s - \sigma\omega_i + kT \ln \gamma_i^s x_i^s \quad (1.4)$$

Here μ_i^s is the standard chemical potential of the adsorbed molecule, ω_i is the excluded area per adsorbed molecule, and x_i^s and γ_i^s are respectively the molecular fraction and the activity coefficient in the adsorption layer. Equation 1.4 is a surface analogue of the expression for the chemical potential of molecules in the bulk of an incompressible liquid solution (with the pressure p instead of $-\sigma$ and the excluded volume v_i instead of ω_i). Complementing eq 1.4 with a convention about the sum of all adsorptions, Lucassen-Reynders has developed a theoretical model which compares well with the experiment.³² Recently Vaughn and Slattery³⁴ demonstrated that this theoretical model, along with an assumption that the surfactant is ionized in the solution but not at the surface, agrees well with a set of data for σ versus surfactant and salt concentrations. Fainerman and Miller³⁵ extended the

approach of Lucassen-Reynders to describe aggregation in the surfactant adsorption monolayer.

Borwankar and Wasan³⁶ pointed out two major drawbacks of the Lucassen-Reynders treatment: (i) The interface is treated as being an *electroneutral* surface phase between two electroneutral uniform bulk phases. Thus, the existence of the electric double layer is ignored. (ii) The approach of Lucassen-Reynders is not compatible with the kinetic theory of ionic surfactant adsorption. Under dynamic conditions the surface and the bulk of the solution are out of equilibrium. For that reason the equilibrium relationships between surface and *bulk* properties, stemming from the approach of Lucassen-Reynders, are not applicable to the problems of adsorption kinetics.³⁶ On the other hand, in the case of adsorption under diffusion control, there is a *local* equilibrium between the surface layer (adsorbed surfactant + bound counterions) and the "subsurface", that is, and the nonadsorbed ions in the plane $x=0$; the latter represents the subsurface boundary of the diffuse EDL (see Figure 1b and refs 1 and 37). That is the reason why the kinetic theory of adsorption demands an equilibrium thermodynamic relation between adsorptions and *subsurface* concentrations to be available.

To overcome these obstacles, Borwankar and Wasan³⁶ developed another approach, in which adsorptions are assigned to the dividing surface and the electric double layer is considered to be a part of the aqueous phase. They arrived at the following surfactant adsorption isotherm:³⁶

$$\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-2\beta\frac{\Gamma_1}{\Gamma_\infty}\right) = K\gamma_\pm c_{1s},$$

$$c_{1s} = c_{1\infty} \exp\left(-\frac{Z_1 e\psi_s}{kT}\right) \quad (1.5)$$

where β is a parameter accounting for the interaction between the adsorbed surfactant molecules, K is the adsorption constant, c_{1s} and $c_{1\infty}$ are respectively the subsurface and bulk concentration of the surfactant ions, Z_1 is their valency, and γ_\pm is the activity coefficient. Equation 1.5 has the form of the Frumkin³⁸ isotherm, the new moment being that it is expressed in terms of the subsurface concentration c_{1s} . Further, Borwankar and Wasan³⁶ derived a surface tension isotherm,

$$\sigma_0 - \sigma = -kT\Gamma_\infty \left[\ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) + \beta\left(\frac{\Gamma_1}{\Gamma_\infty}\right)^2 \right] + \sqrt{\frac{8\epsilon I(kT)^3}{\pi e^2}} \left(\cosh \frac{e\psi_s}{2kT} - 1 \right) \quad (1.6)$$

following the approach of Hachisu.³¹ Note the coincidence of the electric terms (those containing ψ_s) in eqs 1.2 and 1.6. It was demonstrated³⁶ that eqs 1.5 and 1.6 agree well with various sets of experimental curves σ versus $c_{1\infty}$ for oil-water and air-water interfaces. The latter fact evidences that the underlying thermodynamic model is more adequate. Nevertheless, it has one shortcoming:

The counterion binding is completely neglected in ref 36. This assumption is in conflict with numerous evidences^{13,20-22} that the occupancy of the Stern layer by bound counterions can be above 80% for a planar adsorption layer. As a consequence, the theory from ref 36 can predict considerably higher values of the surface potential

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than those measured in the experiment; see for example section 9 below. Moreover, the account of counterion binding is a prerequisite for development of a quantitative theory of the dynamic surface tension of the ionic surfactant solution; see ref 39.

1.4. Aim and Structure of the Paper. Our aim in the present paper is to explicitly take into account the effect of counterion binding in the equilibrium thermodynamics of surfactant adsorption. This would allow a further application of the results in the theory of adsorption kinetics. In particular, our goal is to create a theoretical description which would enable one to determine the surfactant adsorption $\Gamma_1(c_{1\infty}, c_{2\infty})$, the counterion adsorption $\Gamma_2(c_{1\infty}, c_{2\infty})$, and the surface potential $\psi_s(c_{1\infty}, c_{2\infty})$ by processing only a set of data for the surface tension σ versus the surfactant and salt concentrations $c_{1\infty}$ and $c_{2\infty}$. With that end in view, in section 2 we consider the condition for thermodynamic compatibility between the surfactant and counterion adsorption isotherms. In section 3 we rearrange the Gibbs adsorption equation to separate the contributions from the adsorption and diffuse layers. Next, in section 4 we derive the contribution of the diffuse electric layer to the surface tension. In section 5 we combine the results to obtain the surface tension isotherm; an independent hydrostatic derivation of the diffuse layer contribution is given as well. Section 6 is devoted to the connections between the surfactant and counterion adsorption isotherms. Further, we consider the special cases of solutions of one surfactant and two salts (section 7) and two surfactants and one salt (section 8). The derived theoretical expressions are compared with a set of experimental data in section 9 below, where the numerical procedure of data processing is also described.

1.5. Activities and Activity Coefficients. We have to note in the very beginning that at higher ionic strengths (higher than 0.1 M) one should take into account the interaction between the ions through the activity coefficients. As demonstrated by Lucassen-Reynders³² and Borwankar and Wasan,³⁶ a good agreement between theory and experiment can be achieved by using the following expression for the activities $a_{i\infty}$ of the ionic species in the *bulk* of solution:

$$a_{i\infty} = \gamma_{\pm} c_{i\infty} \quad (1.7)$$

where $c_{i\infty}$ is the bulk concentration of the respective ion and the activity coefficient γ_{\pm} is to be calculated from the known semiempirical formula⁴⁰

$$\log \gamma_{\pm} = - \frac{A|Z_+Z_-|\sqrt{I}}{1 + Bd_i\sqrt{I}} + bI \quad (1.8)$$

stemming from the Debye–Hückel theory. When the solution contains a mixture of several electrolytes, then eq 1.8 defines γ_{\pm} for each separate electrolyte, with Z_+ and Z_- being the valencies of the cations and anions for this electrolyte but with I being the *total* ionic strength of the solution defined by eq 1.3. Note that the logarithm in eq 1.8 is decimal, d_i is the diameter of the ion, and A , B , and b are parameters whose values can be found in the book by Robinson and Stokes;⁴⁰ A and B are tabulated for various temperatures in Appendix 7.1 therein. For example, if the temperature is 25 °C and the ionic strength I is given in moles per liter (M), the parameters values,

which compare very well with experimental data for NaCl solutions, are⁴⁰ $A = 0.5115 \text{ M}^{-1/2}$, $Bd_i = 1.316 \text{ M}^{-1/2}$, and $b = 0.055 \text{ M}^{-1}$.

It should also be noted that once the bulk activity $a_{i\infty}$ of a given ion is determined, one can calculate the activity $a_i(x)$ of this ion at each point of the electric double layer from the rigorous expression⁴¹

$$a_i(x) = a_{i\infty} \exp\left(-\frac{Z_i e \psi(x)}{kT}\right) \quad (1.9)$$

where x is the distance from the Stern layer (Figure 1b) and $\psi(x)$ is the electric potential at this point. Equation 1.9, representing a Boltzmann type equation, is a corollary from the condition for uniformity of the respective (electro)-chemical potential throughout the electric double layer formed in the vicinity of the interface; see refs 41 and 42.

Below, we will work in terms of activities, which can be considered as effective concentrations of the ionic species. For ionic strengths $I < 0.1 \text{ M}$ the activities are practically equal to the respective concentrations.

2. Counterion Adsorption and the Euler Condition

In the case of adsorption of an ionic surfactant at the interface between two fluid phases, the Gibbs adsorption equation can be expressed in the form^{31,43–46}

$$d\sigma = -kT \sum_{i=1}^N \tilde{\Gamma}_i d \ln a_{i\infty} \quad (T = \text{constant}) \quad (2.1)$$

where

$$\tilde{\Gamma}_i \equiv \Gamma_i + \Lambda_i \quad (i = 1, 2, \dots) \quad (2.2)$$

The summation in eq 2.1 is carried out over all solutes, including the surfactant ions, counterions, and coions. As before, σ is the surface tension of the solution, $a_{i\infty}$ is the activity of the i th species in the bulk of solution, and $\tilde{\Gamma}_i$ is the total adsorption of the respective species, which includes contributions from the adsorption in the Stern layer Γ_i and from the diffuse electric double layer:

$$\Lambda_i = \int_0^{\infty} [c_i(x) - c_{i\infty}] dx \approx \int_0^{\infty} [a_i(x) - a_{i\infty}] dx \quad (2.3)$$

see also Figure 1. For ionic species one has $\Lambda_i \neq 0$ because of the nonzero difference between the ionic concentration in the double layer $c_i(x)$ and that in the bulk of solution $c_{i\infty}$. For counterions $\Lambda_i > 0$, whereas for coions (including the surfactant ions) $\Lambda_i < 0$; see Figure 1b.

If surfactant is absent, then $\Gamma_1 = \Gamma_2 = 0$, and $\Lambda_i < 0$ for all nonamphiphilic ionic species. As known, the latter negative adsorptions of ions at the water interface lead to an increase of the surface tension of salt solutions in comparison with that of pure water; see for example refs 47 and 48.

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For example let us consider a solution of an ionic surfactant which is a symmetric ($Z_1:Z_1$) electrolyte in the presence of an additional common symmetric ($Z_1:Z_1$) electrolyte (salt). For example, this can be a solution of sodium dodecyl sulfate (SDS) in the presence of NaCl. We denote by $c_{1\infty}$, $c_{2\infty}$, and $c_{3\infty}$ the bulk concentrations of the surface active ions, counterions, and coions, respectively. For the special system of SDS with NaCl, $c_{1\infty}$, $c_{2\infty}$, and $c_{3\infty}$ are the bulk concentration of the DS^- , Na^+ , and Cl^- ions, respectively. The requirement for the bulk solution to be electroneutral implies $c_{2\infty} = c_{1\infty} + c_{3\infty}$. The multiplication of the last equation by γ_{\pm} , which is the same for all monovalent ions, see eq 1.8, yields

$$a_{2\infty} = a_{1\infty} + a_{3\infty} \quad (2.4)$$

In view of eq 2.4 the Gibbs adsorption equation 2.1 can be presented in the form

$$d\sigma = -kT(G_1 d \ln a_{1\infty} + G_2 d \ln a_{2\infty}) \quad (2.5)$$

where

$$G_1 \equiv \tilde{\Gamma}_1 - \frac{a_{1\infty}}{a_{3\infty}} \tilde{\Gamma}_3; \quad G_2 \equiv \tilde{\Gamma}_2 + \frac{a_{2\infty}}{a_{3\infty}} \tilde{\Gamma}_3 \quad (2.6)$$

Note that the differentials on the right-hand side of eq 2.5 are independent (one can vary independently the concentrations of surfactant and salt), and moreover, $d\sigma$ is an exact (total) differential. Then the cross derivatives must be equal, viz.

$$\frac{\partial G_1}{\partial \ln a_{2\infty}} = \frac{\partial G_2}{\partial \ln a_{1\infty}} \quad (2.7)$$

Equation 2.7 is usually called the *Euler condition*.⁴¹ If eq 2.7 were not satisfied, then the surface tension σ , calculated by integrating eq 2.5, would depend on the path of integration. In other words, the equilibrium surface tension σ would depend on whether the surfactant or the salt is first dissolved in the aqueous phase, which would be nonsense. Consequently, a surfactant adsorption isotherm, $\Gamma_1 = \Gamma_1(a_{1\infty}, a_{2\infty})$, and a counterion adsorption isotherm, $\Gamma_2 = \Gamma_2(a_{1\infty}, a_{2\infty})$, are *thermodynamically compatible* if they satisfy eq 2.7; see also eqs 2.2 and 2.6.

For example, it is not obvious whether the *Langmuir* surfactant adsorption isotherm³⁶

$$\frac{\Gamma_1}{\Gamma_\infty} = \frac{Ka_{1s}}{1 + Ka_{1s}} \quad (2.8)$$

and the known *Stern* counterion adsorption isotherm^{27,28,49-51}

$$\theta \equiv \frac{\Gamma_2}{\Gamma_1} = \frac{K_{st}a_{2s}}{1 + K_{st}a_{2s}} \quad (2.9)$$

are thermodynamically compatible. Here Γ_∞ denotes the maximum possible value of Γ_1 , K is an adsorption parameter, θ denotes the occupancy of the "Stern layer"

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by adsorbed counterions (see Figure 1a), K_{st} is a constant, and a_{1s} and a_{2s} are the subsurface activities of surfactant ions and counterions, which are related to the respective bulk activities as follows:

$$a_{is} = a_{i\infty} \exp\left(-\frac{Z_i e \psi_s}{kT}\right) \quad (2.10)$$

Equation 2.10 is a special case of eq 1.9 for $x = 0$; see Figure 1. Here and hereafter the subscript s denotes quantities related with the surface of the solution.

As already mentioned, Borwankar and Wasan³⁶ have demonstrated that one can successfully fit interfacial tension data for ionic surfactants if the surfactant adsorption Γ_1 is related to the subsurface surfactant activity a_{1s} by means of the Langmuir isotherm (eq 2.8). Our purpose below is to establish the form of the counterion adsorption isotherm, which is thermodynamically compatible with eq 2.8. With that end in view we will first derive the compatibility condition (stemming from the Euler equation 2.7) in a form convenient for application.

3. Transformations of the Gibbs Equation

In general, we consider a solution of various species ($i = 1, 2, \dots, N$), both amphiphilic and nonamphiphilic. As before, we will use the index 1 to denote the surfactant, whose adsorption determines the sign of the surface electric charge and potential. It is convenient to introduce the dimensionless surface potential

$$\Phi_s \equiv \frac{Z_1 e \psi_s}{kT} \quad (3.1)$$

Φ_s thus defined is positive irrespective of whether the surfactant is anionic or cationic. In terms of Φ_s , eq 2.10 takes the form

$$a_{is} = a_{i\infty} \exp(-z_i \Phi_s) \quad z_i \equiv \frac{Z_i}{Z_1} \quad (3.2)$$

A substitution of $a_{i\infty}$ from eq 3.2 into eq 2.1 yields

$$-\frac{d\sigma}{kT} = \sum_{i=1}^N \tilde{\Gamma}_i d \ln a_{is} + \left(\sum_{i=1}^N z_i \tilde{\Gamma}_i\right) d\Phi_s \quad (3.3)$$

Since the solution as a whole is electroneutral, one can write^{31,45,46}

$$\sum_{i=1}^N z_i \tilde{\Gamma}_i = 0 \quad (3.4)$$

From eqs 2.2 and 3.4 one obtains the following expression for the surface electric charge density ρ_s :

$$\tilde{\rho}_s \equiv \frac{\rho_s}{Z_1 e} = \sum_{i=1}^N z_i \tilde{\Gamma}_i = -\sum_{i=1}^N z_i \Lambda_i \quad (3.5)$$

Further, in view of eqs 2.2, 3.2, and 3.4, one can transform eq 3.3 to read

$$-\frac{d\sigma}{kT} = \sum_{i=1}^N \tilde{\Gamma}_i d \ln a_{is} + \sum_{i=1}^N \Lambda_i d \ln a_{i\infty} - \left(\sum_{i=1}^N z_i \Lambda_i\right) d\Phi_s \quad (3.6)$$

With the help of eqs 1.9, 2.3, and 3.5, one can bring eq 3.6

in the form

$$-\frac{d\sigma}{kT} = \sum_{i=1}^N \Gamma_i d \ln a_{i_s} + \sum_{i=1}^N \tilde{\Lambda}_i da_{i_\infty} + \tilde{\rho}_s d\Phi_s \quad (3.7)$$

where

$$\tilde{\Lambda}_i \equiv \frac{\tilde{\Lambda}_i}{a_{i_\infty}} = \int_0^\infty [\exp(-z_i\Phi) - 1] dx \quad (3.8)$$

$$\Phi(x) \equiv \frac{Z_1 e \psi(x)}{kT} \quad (3.9)$$

Below we will employ the Poisson–Boltzmann equation to transform the last two terms in eq 3.7.

4. Contribution of Diffuse Double Layer to the Surface Tension

The Poisson equation relating the distribution of the electric potential $\psi(x)$ and electric charge density $\rho(x)$ across the diffuse double layer can be presented in the form⁵²

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi}{\epsilon} \rho \quad (4.1)$$

Combining eqs 1.9, 3.9, and 4.1, one obtains

$$\frac{d^2\Phi}{dx^2} = -\frac{1}{2\kappa_c^2} \tilde{\rho} = -\frac{1}{2\kappa_c^2} \sum_{i=1}^N Z_i a_{i_\infty} \exp(-z_i\Phi) \quad (4.2)$$

with

$$\tilde{\rho} \equiv \frac{\rho}{Z_1 e}, \quad \kappa_c^2 \equiv \frac{8\pi Z_1^2 e^2}{\epsilon kT} \quad (4.3)$$

As usual, the x -axis is directed along the normal to the interface, the latter corresponding to $x = 0$. To obtain eq 4.2, we have expressed the bulk charge density in terms of effective concentrations, that is, activities, $\rho(x) = \sum_i Z_i e a_i(x)$, rather than in terms of the net concentrations, $\rho(x) = \sum_i Z_i e c_i(x)$. For not-too-high ionic strengths there is no significant quantitative difference between these two expressions for $\rho(x)$, but the former one considerably simplifies the mathematical derivations; moreover, the former expression has been combined with eq 1.9, which is rigorous in terms of activities (rather than in terms of concentrations). Integrating eq 4.2, one can derive

$$\left(\frac{d\Phi}{dx}\right)^2 = \kappa_c^2 \sum_{i=1}^N a_{i_\infty} [\exp(-z_i\Phi) - 1] \quad (4.4)$$

where the boundary conditions $\Phi|_{x \rightarrow \infty} = 0$ and $(d\Phi/dx)|_{x \rightarrow \infty} = 0$ have been used. Integrating eq 4.4, along with eq 3.8, one can deduce

$$F \equiv \frac{1}{\kappa_c^2} \int_0^\infty \left(\frac{d\Phi}{dx}\right)^2 dx = \sum_{i=1}^N a_{i_\infty} \tilde{\Lambda}_i \quad (4.5)$$

From eq 4.5 one obtains

$$\delta F \equiv \sum_{i=1}^N \tilde{\Lambda}_i \delta a_{i_\infty} + \sum_{i=1}^N a_{i_\infty} \delta \tilde{\Lambda}_i \quad (4.6)$$

where δ denotes a variation of the respective thermodynamic parameter corresponding to a small variation in the composition of the solution. Further, with the help of eqs 3.8 and 4.2, one obtains

$$\begin{aligned} \sum_{i=1}^N a_{i_\infty} \delta \tilde{\Lambda}_i &= -\int_0^\infty \sum_{i=1}^N a_{i_\infty} z_i \exp(-z_i\Phi) \delta\Phi dx \\ &= -\int_0^\infty \tilde{\rho} \delta\Phi dx = \frac{2}{\kappa_c^2} \int_0^\infty \frac{d^2\Phi}{dx^2} \delta\Phi dx \\ &= -\frac{2}{\kappa_c^2} \left(\frac{d\Phi}{dx}\right)_{x=0} \delta\Phi_s - \frac{1}{\kappa_c^2} \int_0^\infty \delta\left(\frac{d\Phi}{dx}\right)^2 dx \quad (4.7) \end{aligned}$$

As is known,^{51,52} the gradient of the electric potential at the surface is related to the surface charge density $\tilde{\rho}_s$ by means of the equation

$$\left(\frac{d\Phi}{dx}\right)_{x=0} = -\frac{1}{2\kappa_c^2} \tilde{\rho}_s \quad (4.8)$$

($x = 0$ corresponds to the boundary diffuse-Stern layer). Then combining eqs 4.5, 4.7, and 4.8, one obtains

$$\sum_{i=1}^N a_{i_\infty} \delta \tilde{\Lambda}_i = \tilde{\rho}_s \delta\Phi_s - \delta F \quad (4.9)$$

A substitution of eq 4.9 into eq 4.6 yields

$$2 \delta F \equiv \sum_{i=1}^N \tilde{\Lambda}_i \delta a_{i_\infty} + \rho_s \delta\Phi_s \quad (4.10)$$

Finally, the substitution of eq 4.10 into the Gibbs adsorption equation 3.7 leads to

$$d\left(\frac{\sigma_0 - \sigma}{kT} - 2F\right) = \sum_{i=1}^N \Gamma_i d \ln a_{i_s} \quad (4.11)$$

where, as before, σ_0 is the surface tension of the pure solvent. The definition of F , eq 4.5, can be presented in an alternative form:

$$F \equiv -\frac{1}{\kappa_c^2} \int_0^{\Phi_s} \left(\frac{d\Phi}{dx}\right) d\Phi \quad (4.12)$$

Combining eq 4.4 with eq 4.12, one obtains a convenient expression for calculating F :

$$F = \frac{1}{\kappa_c^2} \int_0^{\Phi_s} \left\{ \sum_{i=1}^N a_{i_\infty} [\exp(-z_i\Phi) - 1] \right\}^{1/2} d\Phi \quad (4.13)$$

The integral in eq 4.13 can be solved *numerically* for every mixture of electrolytes in the solution. As shown below, the integral can be solved *analytically* for a 1:1 ionic surfactant in the presence of salts which are 1:1, 2:1, 1:2, or 2:2 electrolytes.

(52) Overbeek, J. Th. G. In *Colloid Science*, Vol. 1; Kruyt, H. R., Ed.; Elsevier: Amsterdam, 1953; *J. Colloid Sci.* **1953**, *8*, 420.

Another useful expression can be derived combining eqs 3.5, 4.4, and 4.8:

$$\sum_{i=1}^N z_i \Gamma_i = \frac{2}{\kappa_c} \left\{ \sum_{i=1}^N a_{i\infty} [\exp(-z_i \Phi_s) - 1] \right\}^{1/2} \quad (4.14)$$

In the special case, when both surfactant and salt are 1:1 electrolytes and there is only one type of counterion ($a_{i\infty} = 0$ for $i \geq 4$), then eq 2.4 holds and eq 4.14 reduces to the known Gouy equation:^{25,28}

$$\Gamma_1 - \Gamma_2 = \frac{4}{\kappa_c} \sqrt{a_{2\infty}} \sinh\left(\frac{\Phi_s}{2}\right) \quad (4.15)$$

In view of eq 3.5, one notes that eq 4.14 (or eq 4.15) expresses a connection between the surface charge density and the surface potential.

5. Surface Tension Isotherm of Ionic Surfactant in the Presence of Salts

5.1. Integration of the Gibbs Adsorption Equation.

Let the indices 1, 2, and 3 have the same meaning as in section 2 above. In addition, let $i = 4, 6, 8, \dots, N-1$ denote counterions of *other* dissolved nonamphiphilic salts and $i = 5, 7, 9, \dots, N$ denote the respective co-ions. As discussed above, one can expect that co-ions do not bind to the similarly charged surfactant headgroups in the adsorption layer; that is

$$\Gamma_3 = \Gamma_5 = \Gamma_7 = \dots = \Gamma_N = 0 \quad (5.1)$$

Then eq 4.11 reduces to

$$d\left(\frac{\sigma_0 - \sigma}{kT} - 2F\right) = \Gamma_1 d \ln a_{1s} + \sum_{i=2,4,6,\dots} \Gamma_i d \ln a_{is} \quad (5.2)$$

The number of the differentials on the right-hand side of eq 5.2 is equal to the number of chemical compounds (electrolytes) dissolved in the solution; that is, it is equal to the number of independent thermodynamic parameters which one can vary at constant temperature and outer pressure. Then the Euler condition for the cross derivatives can be applied to eq 5.2 to yield

$$\frac{\partial \Gamma_i}{\partial \ln a_{1s}} = \frac{\partial \Gamma_1}{\partial \ln a_{is}} \quad i = 2, 4, 6, \dots \quad (5.3)$$

Integrating eq 5.3, one obtains

$$\Gamma_i = \frac{\partial J}{\partial \ln a_{is}} \quad i = 2, 4, 6, \dots \quad (5.4)$$

where we have introduced the notation

$$J \equiv \int_0^{a_{1s}} \Gamma_1(\hat{a}_{1s}, a_{2s}, a_{4s}, \dots) \frac{d\hat{a}_{1s}}{\hat{a}_{1s}} \quad (5.5)$$

To determine the integration constant in eq 5.4, we have used the condition that for $a_{1s} = 0$ (no surfactant in the solution) we have $\Gamma_1 = 0$ (no surfactant adsorption) and $\Gamma_i = 0$ for $i = 2, 4, 6, \dots$ (no binding of counterions at the headgroups of adsorbed surfactant). The integral J in eq

Table 1. Most Frequently Used Surfactant Adsorption Isotherms and Respective Surface Tension Isotherms

Surfactant Adsorption Isotherm	
Henry	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty}$
Langmuir	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}$
Freundlich	$\frac{\Gamma_1}{\Gamma_F} = (Ka_{1s})^m$
Volmer	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}\right)$
Frumkin	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT}\right)$
van der Waals	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}\right)$
Surface Tension Isotherm, Eq (5.7): $\sigma = \sigma_0 - kT(J + 2F)$	
Henry	$J = \Gamma_1$
Langmuir	$J = -\Gamma_\infty \ln(1 - \Gamma_1/\Gamma_\infty)$
Freundlich	$J = \Gamma_1/m$
Volmer	$J = \Gamma_\infty \Gamma_1 / (\Gamma_\infty - \Gamma_1)$
Frumkin	$J = -\Gamma_\infty \ln(1 - \Gamma_1/\Gamma_\infty) - \beta\Gamma_1^2/(kT)$
van der Waals	$J = \Gamma_\infty \Gamma_1 / (\Gamma_\infty - \Gamma_1) - \beta\Gamma_1^2/(kT)$

5.5 can be taken analytically for all popular surface tension isotherms; see Table 1. Differentiating eq 5.5, one obtains

$$\Gamma_1 = \frac{\partial J}{\partial \ln a_{1s}} \quad (5.6)$$

A substitution of eqs 5.4 and 5.6 into eq 5.2 yields (after integration) the surface tension isotherm in the form

$$\frac{\sigma_0 - \sigma}{kT} = J + 2F \quad (5.7)$$

where F and J are determined by means of eqs 4.5 and 5.5, respectively. Expressions for J , corresponding to various adsorption isotherms, are listed in Table 1; expressions for F can be obtained by integrating eq 4.13 (see eqs 7.10, 7.16, 7.22, and 7.27 below).

In the special case when both surfactant and salt are 1:1 electrolytes, eq 2.4 holds and $a_{i\infty} = 0$ for $i \geq 4$. Then eq 4.13 can be easily integrated to yield

$$2F = \frac{8\sqrt{a_{2\infty}}}{\kappa_c} \left[\cosh\left(\frac{\Phi_s}{2}\right) - 1 \right] \\ = \frac{4\sqrt{a_{2s}}}{\kappa_c} \left[1 - \exp\left(-\frac{\Phi_s}{2}\right) \right]^2 \quad (1:1 \text{ electrolyte}) \quad (5.8)$$

The “electric” term $2F$ in eq 5.8 is in fact identical with the respective term obtained by Davies; see for example ref 28. Therefore, if the expression for J , corresponding to the Volmer isotherm (see Table 1), is combined with eqs 5.7 and 5.8 (with $\gamma_{\pm} = 1$), one recovers the isotherm of Davies, eq 1.2. Alternatively, if the expression for J , corresponding to the Frumkin isotherm (see Table 1), is combined with eqs 5.7 and 5.8, one obtains the isotherm of Borwankar and Wasan, eq 1.6.

5.2. Hydrostatic Derivation of the Electric Term.

The term $2F$ on the right-hand side of eq 5.7 represents the contribution of the diffuse part of the electric double layer to the surface tension. Indeed, if there is no electric double layer, then $(d\Phi/dx) \equiv 0$ and eq 4.5 gives $F = 0$.

Following Davies^{28,29} and Hachisu,³¹ one can express the surface pressure $\pi_s \equiv \sigma_0 - \sigma$ in the form

$$\pi_s = \pi_a + \pi_d = \sigma_0 - \sigma_a - \sigma_d \quad (5.9)$$

where the subscripts a and d denote contributions from the adsorption and diffuse layer, respectively. Comparing eqs 5.7 and 5.9, one can write

$$\pi_a = \sigma_0 - \sigma_a = kTJ; \quad \pi_d = -\sigma_d = 2kTF \quad (5.10)$$

From eqs 4.5 and 5.10 it follows that

$$\sigma_d = -\frac{2kT}{\kappa_c} \int_0^\infty \left(\frac{d\Phi}{dx}\right)^2 dx \quad (5.11)$$

One can independently deduce the diffuse layer contribution σ_d from a general expression for the pressure tensor P_{ik} given by Landau and Lifshitz.⁵³

$$P_{ik} = \left(p + \frac{\epsilon E^2}{8\pi}\right) \delta_{ik} - \frac{\epsilon}{4\pi} E_i E_k \quad (i, k = 1, 2, 3) \quad (5.12)$$

Here δ_{ik} is the Kronecker symbol (the unit tensor), $\mathbf{E} = -\nabla\psi$ is the electric field in the continuous medium, and p is an isotropic hydrostatic pressure.

In the case of a diffuse electric double layer (Figure 1) p depends on the distance from the interface because of the varying composition:

$$p = p(x) \equiv p_0 + kT \sum_I c_I(x) \quad (5.13)$$

Here p_0 is the pressure of pure solvent in chemical equilibrium with the solution. The components of the pressure tensor, acting along the normal and tangent to the interface (Figure 1), are

$$P_N = p(x) - \frac{\epsilon}{8\pi} \left(\frac{d\psi}{dx}\right)^2 \quad (5.14)$$

$$P_T = p(x) + \frac{\epsilon}{8\pi} \left(\frac{d\psi}{dx}\right)^2 \quad (5.15)$$

Using the Poisson–Boltzmann equation and eq 5.13, one can verify that P_N is constant across the electric double layer, as it should be at hydrostatic equilibrium.⁴⁸ The surface tension can be expressed by means of the Bakker hydrostatic formula:⁵⁴

$$\sigma = \int_{-\infty}^{+\infty} (P_N - P_T) dx \quad (5.16)$$

In view of eqs 5.9 and 5.16, one can write

$$\sigma = \sigma_a + \sigma_d; \quad \sigma_a \equiv \int_{-\infty}^0 (P_N - P_T) dx; \quad \sigma_d \equiv \int_0^{+\infty} (P_N - P_T) dx \quad (5.17)$$

As before, the plane $x = 0$ is located at the boundary between the Stern and diffuse layers (see Figure 1). Combining eqs 5.14, 5.15, and 5.17, one derives the

following expression for the diffuse double-layer contribution:

$$\sigma_d = -\frac{\epsilon}{4\pi} \int_0^\infty \left(\frac{d\psi}{dx}\right)^2 dx \quad (5.18)$$

Using eqs 3.9 and 4.3, one can check that eq 5.18 is equivalent to eq 5.11. This result confirms the validity of the expression (eq 4.5) for the electrostatic contribution, $2F$, in the surface tension isotherm, eq 5.7.

Note that σ_d , as given by eq 5.18, is always negative. Moreover, the *form* of eq 5.18 is not sensitive to the number and valency of electrolytes dissolved in the solution, as well as to the presence or absence of counterion binding. On the other hand, the latter factors influence the magnitude of both $(d\psi/dx)$ and σ_d ; this influence is quantified in section 7 below.

Note also that in view of eqs 5.9 and 5.10 the Gibbs adsorption equation 4.11 can be represented in the form

$$d\sigma_a = -kT \sum_{i=1}^N \Gamma_i d \ln a_{is} \quad (T = \text{constant}) \quad (5.19)$$

The comparison between eqs 2.1 and 5.19 shows that the Gibbs adsorption equation can be expressed either in terms of σ , $\bar{\Gamma}_i$, and a_{is} or in terms of σ_a , Γ_i , and a_{is} . Our theoretical considerations in sections 3, 4, and 5 prove that these two forms of the Gibbs adsorption equation are equivalent.

6. Connections between the Surfactant and Counterion Adsorption Isotherms

6.1. Parameters in the Surfactant Adsorption Isotherms. The parameter K in the adsorption isotherms in Table 1 (except that in the empirical Freundlich isotherm) can be related to the standard chemical potentials of a surfactant ion in the bulk, $\mu_1^{(0)}$, and at the interface, $\mu_{1s}^{(0)}$; see for example ref 55:

$$K = \frac{\delta_1}{\Gamma_\infty} \exp\left(\frac{\mu_1^{(0)} - \mu_{1s}^{(0)}}{kT}\right) \quad (6.1)$$

where δ_1 is a parameter of the order of the thickness of the adsorption layer and Γ_∞ is the maximum possible surfactant adsorption corresponding to a close packing of the surfactant headgroups. The other parameter, β , which enters the Frumkin and van der Waals adsorption isotherms (Table 1) is related to the energy of interaction between two adsorbed molecules $u(r)$; in the case of the Frumkin equation, β is the interaction parameter in the Bragg–Williams lattice model;⁵⁶ in the case of van der Waals equation, the following expression holds:^{56,57}

$$\beta = -\pi kT \int_{r_c}^\infty \left[1 - \exp\left(-\frac{u(r)}{kT}\right)\right] r dr \approx -\pi \int_{r_c}^\infty u(r) r dr \quad (6.2)$$

where r denotes distance and r_c is the intermolecular center-to-center distance at contact, that is, $u(r) \rightarrow \infty$ for $r < r_c$. In fact, Γ_∞ and β account for the hard-core and long-range interactions, respectively. The conventional electrostatic interactions are not expected to contribute to β insofar as they are taken into account in the framework

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(54) Bakker, G. *Kapillarität und Oberflächenspannung*; Handbuch der Experimentalphysik, Band 6; Akademische Verlagsgesellschaft: Leipzig, 1928.

(55) Shchukin, E. D.; Pertsov, A. V.; Amelina, E. A. *Colloid Chemistry*; Moscow University Press: Moscow, 1982 (in Russian).

(56) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Addison-Wesley: Reading, MA, 1962.

(57) Gurkov, T. D.; Kralchevsky, P. A.; Nagayama, K. *Colloid Polym. Sci.* **1996**, *274*, 227.

of the double-layer theory. When β is negligible, the Frumkin and van der Waals surface tension isotherms reduce to the Langmuir and Volmer isotherms, respectively (see Table 1). (As known,⁵⁶ the Frumkin and Langmuir isotherms correspond to the statistical model of *localized* adsorption, whereas the van der Waals and Volmer isotherms correspond to *nonlocalized* adsorption.) The comparison between theory and experiment shows that surface tension data for ionic surfactants at an *oil*-water interface can be fitted with $\beta \approx 0$; on the other hand, the data for the same surfactant at an *air*-water interface agree with theoretical fits with $\beta > 0$; see for example refs 28 and 36. The fact that $\beta > 0$ for an *air*-water interface is attributed to the excess van der Waals attraction between the surfactant hydrocarbon tails in the air;^{28,36} note that there should be no such excess attraction if the nonaqueous phase is a liquid hydrocarbon (oil).

Since β is related to van der Waals interactions between the surfactant tails, then β is not expected to depend on the subsurface concentration of ions. On the other hand, in general the adsorption constant K could depend on the subsurface concentration of the counterions, $K = K(a_{2s}, a_{4s}, \dots)$. Then the dependence of Γ_1 on a_{is} , $i = 2, 4, 6, \dots$, comes from $K(a_{2s}, a_{4s}, \dots)$ for the surfactant adsorption isotherms in Table 1. Moreover, note that for each of these isotherms Γ_1 depends on the product Ka_{is} ; that is, $\Gamma_1 = \Gamma_1(Ka_{is})$. Then eq 5.5 can be transformed to read

$$J \equiv \int_0^{Ka_{is}} \Gamma_1(X) \frac{dX}{X} \quad (6.3)$$

Differentiating eq 6.3, one can bring eq 5.4 into the form

$$\Gamma_i = \Gamma_1 \frac{\partial \ln K}{\partial \ln a_{is}} \quad (i = 2, 4, 6, \dots) \quad (6.4)$$

which holds for each of the surfactant adsorption isotherms in Table 1. Note that eq 6.4 is valid for a general form of the dependence $K = K(a_{2s}, a_{4s}, \dots)$.

6.2. Stern Isotherm of Counterion Adsorption. Let us consider a linear dependence $K = K(a_{2s}, a_{4s}, \dots)$; that is

$$K = K_1 + \sum_{i=2,4,6,\dots} K_i a_{is} \quad (6.5)$$

where K_i ($i = 2, 4, 6, \dots$) are constants. The substitution of eq 6.5 into eq 6.4 yields

$$\frac{\Gamma_i}{\Gamma_1} = \frac{K_i a_{is}}{K_1 + K_2 a_{2s} + K_4 a_{4s} + \dots} \quad (i = 2, 4, 6, \dots) \quad (6.6)$$

Equation 6.6 is in fact a general form of the *Stern isotherm* for a solution containing several types of counterions ($i = 2, 4, 6, \dots$) which exhibit a competitive binding to the headgroups of adsorbed surfactant molecules. Since eq 6.6 is a corollary from the Euler condition, eq 5.3, it turns out that eq 6.5 is the necessary and sufficient condition for thermodynamic compatibility of the Stern isotherm of counterion adsorption (binding) with either of the *surfactant* adsorption isotherms in Table 1.

In the special case, when there is only one type of counterions ($a_{is} = 0$ for $i \geq 4$), eqs 6.5 and 6.6 reduce to

$$K = K_1 + K_2 a_{2s} \quad (6.7)$$

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_2 a_{2s}}{K_1 + K_2 a_{2s}} \quad (6.8)$$

Equation 6.8 is equivalent to eq 2.9, with $K_{st} = K_2/K_1$. One can conclude that a given isotherm from Table 1, say the Langmuir isotherm, eq 2.8, is thermodynamically compatible with the Stern isotherm, eq 6.8, only if the adsorption parameters K , K_1 , and K_2 in these isotherms are related by means of eq 6.7.

The constants K_1 and K_2 have a straightforward physical meaning. Indeed, in view of eqs 6.1 and 6.7, one can write

$$K_1 = \frac{\delta_1}{\Gamma_\infty} \exp\left(\frac{\Delta\mu_1^{(0)}}{kT}\right) \quad (6.9)$$

where $\Delta\mu_1^{(0)}$ has the meaning of the standard free energy of adsorption of surfactant from an ideal dilute solution to an ideal adsorption monolayer in the absence of dissolved nonamphiphilic salt; the thickness of the adsorption layer δ_1 is about 2 nm for SDS or DTAB. Note that the Langmuir and the Stern isotherms, eqs 2.8 and 2.9, have a similar form, which corresponds to a statistical model considering the interface as a lattice of equivalent, distinguishable, and independent adsorption sites, without interactions between bound molecules.⁵⁶ Consequently, an expression analogous to eq 6.9 holds for the counterion adsorption parameter $K_{st} = K_2/K_1$:

$$\frac{K_2}{K_1} = \frac{\delta_2}{\Gamma_\infty} \exp\left(\frac{\Delta\mu_1^{(0)}}{kT}\right) \quad (6.10)$$

where δ_2 is the thickness of the Stern layer (ca. the diameter of a hydrated counterion) and $\Delta\mu_1^{(0)}$ has the meaning of the standard free energy of adsorption (binding) of a counterion from an ideal dilute solution in an ideal Stern layer (no interactions between adsorbed counterions). In summary, the parameters K_1 and K_2 are related to the standard free energies of surfactant and counterion adsorption.

6.3. Complete Set of Equations. Our final goal is to obtain a full set of equations for calculating the surface tension as a function of the bulk surfactant and salt concentrations, $\sigma = \sigma(a_{1s}, a_{2s}, a_{4s}, \dots)$. In general, let us consider a solution containing n types of counterions, denoted by $i = 2, 4, \dots, 2n$. In such a case we have $2n + 4$ unknown variables: σ , Φ_s , a_{1s} , Γ_1 ; a_{2s} , a_{4s} , ..., a_{2ns} ; and Γ_2 , Γ_4 , ..., Γ_{2n} . These unknown variables are to be determined from a set of $2n + 4$ equations, which are the following. Equation 3.2 for $i = 1, 2, 4, \dots, 2n$ and eq 6.6 provide $2n + 1$ equations. The remaining three equations are eqs 4.14 and 5.7 and one surfactant adsorption isotherm from Table 1, say the Langmuir isotherm, eq 2.8. The procedure of calculations and its application to the interpretation of experimental data are described in section 9 below.

The above general set of equations is specified below for surfactant solutions containing salts of various valency.

7. Solution of One Ionic Surfactant and Two Salts

7.1. Basic Equations. Here we consider solution of an ionic surfactant containing two added salts, which will be termed below salt I and salt II. For example, this can be a solution of sodium dodecyl sulfate (SDS) + NaCl + MgSO₄. Another example can be cetyltrimethylammonium bromide (CTAB) + KBr + Na₂SO₄. It is assumed that the counterions dissociated from the ionic surfactant and salt I are *the same* (these are Na⁺ ions in the first example and Br⁻ in the second example). (The case of ionic surfactant + *only one* salt can be deduced as a special case setting

to zero the concentration of the other salt in the equations derived below.)

We will use the following subscripts to denote the various solutes: 1, surfactant (amphiphilic) ion; 2, counterion of the surfactant and salt I; 3, coion of salt I; 4, counterion of salt II; 5, co-ion of salt II. As before, we denote by Z_i , Γ_i , $a_{i\infty}$, and a_{is} ($i = 1, \dots, 5$) the valence, adsorption, bulk, and subsurface activities of the respective species; their bulk concentrations are denoted by $c_{i\infty}$. The following relationships hold in the system under consideration:

$$Z_1 = Z_3 = -Z_2 \Rightarrow a_{2\infty} = a_{1\infty} + a_{3\infty} \quad (7.1)$$

see eq 2.4. Note that $a_{1\infty}$, $a_{2\infty}$, and $a_{3\infty}$ are to be calculated from eqs 1.7 and 1.8 with $|Z_+Z_-| = Z_1^2$. In addition, concerning salt II, one can write $|Z_4|c_{4\infty} = |Z_5|c_{5\infty}$. The multiplication of the last equation by γ_{\pm} , which for salt II is determined by eq 1.8 with $|Z_+Z_-| = |Z_4Z_5|$, yields

$$|Z_4|a_{4\infty} = |Z_5|a_{5\infty} \quad (7.2)$$

As before, we assume that co-ions do not adsorb at the interface; that is, $\Gamma_3 = \Gamma_5 = 0$. The adsorption of counterions can be described by means of the Stern isotherm, eq 6.6, which in the present case reduces to

$$\frac{\Gamma_i}{\Gamma_1} = \frac{K_i a_{is}}{K_1 + K_2 a_{2s} + K_4 a_{4s}} \quad (i = 2, 4) \quad (7.3)$$

The surfactant adsorption Γ_1 can be expressed by means of one of the adsorption isotherms in Table 1, in which the adsorption parameter K is related to the constants K_1 , K_2 , and K_4 as follows:

$$K = K_1 + K_2 a_{2s} + K_4 a_{4s} \quad (7.4)$$

cf. eq 6.5. The surface tension isotherm is given by eq 5.7. To determine the term F in eq 5.7, let us consider the expression

$$S(\Phi) \equiv \sum_{i=1}^5 a_{i\infty} [\exp(-z_i \Phi) - 1] \quad (7.5)$$

which enters both eqs 4.13 and 4.14. With the help of eqs 3.2, 7.1, and 7.2, one can bring eq 7.5 into the form

$$S(\Phi) = a_{2\infty} (e^{\Phi} - 2 + e^{-\Phi}) + a_{4\infty} \left[e^{-z_4 \Phi} - 1 + \frac{|Z_4|}{|Z_5|} (e^{-z_5 \Phi} - 1) \right] \quad (7.6)$$

Below we specify the expression for F , eq 4.13, and the form of the Gouy equation, eq 4.14, for several special cases.

7.2. All Solutes (Surfactant, Salt I, and Salt II) Are 1:1 Electrolytes. In this relatively simple case

$$z_4 = -z_5 = -1 \quad (7.7)$$

Then eq 7.6 reduces to

$$S(\Phi) = 4(a_{2\infty} + a_{4\infty}) \sinh^2\left(\frac{\Phi}{2}\right) \quad (7.8)$$

Substituting eq 7.8 into eq 4.14, one obtains the Gouy equation in the form

$$\Gamma_1 - \Gamma_2 - \Gamma_4 = \frac{4}{\kappa_c} \sqrt{a_{2\infty} + a_{4\infty}} \sinh\left(\frac{\Phi_s}{2}\right) \quad (7.9)$$

Γ_2 and Γ_4 are to be substituted from eq 7.3; expressions for Γ_1 are available in Table 1, in which the parameter K is determined by eq 7.4. The substitution of eq 7.7 into eq 4.13 yields

$$F = \frac{4}{\kappa_c} \sqrt{a_{2\infty} + a_{4\infty}} \left[\cosh\left(\frac{\Phi_s}{2}\right) - 1 \right] \quad (7.10)$$

Equation 7.10 is to be substituted in eq 5.7 to obtain the surface tension isotherm. For $a_{4s} = 0$ (no salt II in the solution) eqs 7.9 and 7.10 reduce to eqs 4.15 and 5.8, as must be expected. Note also that if the ionic components 2 and 4 are identical, say Na^+ (like in the case of SDS + NaCl + NaBr), then eqs 7.9 and 7.10 lead again to eqs 4.15 and 5.8 with $\Gamma_{\text{Na}} = \Gamma_2 + \Gamma_4$ and $a_{\text{Na}\infty} = a_{2\infty} + a_{4\infty}$, as should be expected.

Setting $a_{2\infty} = a_{1\infty}$ in the above equations, one obtains the respective expression for the special case of one ionic surfactant and one electrolyte of different counterions ($K_2 \neq K_4$). The substitution $a_{4s} = 0$ and $a_{2\infty} = a_{1\infty}$ corresponds to the simplest case of ionic surfactant solution without salt.

7.3. The Surfactant and Salt I Are 1:1 Electrolytes; Salt II Is a 2:1 Electrolyte. An example can be SDS + NaBr + MgCl₂. Another example can be CTAB + NaBr + K₂SO₄. In such a case one has

$$z_4 = -2, \quad z_5 = 1 \quad (7.11)$$

Then eq 7.6 reduces to

$$\begin{aligned} S(\Phi) &= a_{2\infty} (e^{\Phi/2} - e^{-\Phi/2})^2 + a_{4\infty} (e^{2\Phi} - 3 + 2e^{-\Phi}) \\ &= I_1 e^{-\Phi} (e^{\Phi} - 1)^2 + a_{4\infty} e^{-\Phi} (e^{\Phi} - 1)^3 \\ &= I_1 e^{-\Phi} (e^{\Phi} - 1)^2 (1 - \lambda^2 + \lambda^2 e^{\Phi}) \end{aligned} \quad (7.12)$$

where

$$I_1 \equiv a_{2\infty} + 3a_{4\infty}; \quad \lambda^2 \equiv a_{4\infty}/I_1 \quad (7.13)$$

I_1 is the ionic strength of this solution. In view of eqs 7.5 and 7.12, the Gouy equation, eq 4.14, takes the form

$$\Gamma_1 - \Gamma_2 - 2\Gamma_4 = \frac{2}{\kappa_c y} \sqrt{I_1} (y^2 - 1) g_1 \quad (7.14)$$

where

$$y \equiv \exp(\Phi_s/2); \quad g_1 \equiv (1 - \lambda^2 + \lambda^2 y^2)^{1/2} \quad (7.15)$$

Γ_2 and Γ_4 are to be substituted from eq 7.3; expressions for Γ_1 are available in Table 1, in which the parameter K is determined by eq 7.4. For $\lambda \rightarrow 0$ (no salt II in the solution) eq 7.14 reduces to eq 4.15. Further, having in mind eq 7.5, we substitute eq 7.12 into eq 4.13; the result of integration yields

$$F = \frac{\sqrt{I_1}}{\kappa_c} \left[\left(y + \frac{2}{y} \right) g_1 - 3 + \frac{1 - 3\lambda^2}{\lambda} \ln \left| \frac{\lambda y + g_1}{\lambda + 1} \right| \right] \quad (7.16)$$

Equation 7.16 is to be substituted in eq 5.7 to obtain the surface tension isotherm. One can check that for $\lambda \rightarrow 0$ (no salt II in the solution) eq 7.16 reduces to eq 5.8.

Setting $a_{2\infty} = a_{1\infty}$ in the above equations (no salt I in the solution), one obtains the respective expressions for the special case of one 1:1 ionic surfactant and one 2:1 electrolyte.

7.4. The Surfactant and Salt I Are 1:1 Electrolytes; Salt II Is a 1:2 Electrolyte. An example can be SDS + NaBr + K₂SO₄. Another example can be CTAB + NaBr + MgCl₂. In such a case one has

$$z_4 = -1, \quad z_5 = 2 \quad (7.17)$$

Then eq 7.6 reduces to

$$\begin{aligned} S(\Phi) &= a_{2\infty}(e^{\Phi/2} - e^{-\Phi/2})^2 + \frac{1}{2}a_{4\infty}(2e^\Phi - 3 + e^{-2\Phi}) \\ &= I_2e^\Phi(1 - e^{-\Phi})^2 - \frac{1}{2}a_{4\infty}e^\Phi(1 - e^{-\Phi})^3 \\ &= I_2e^\Phi(1 - e^{-\Phi})^2(1 - \nu^2 + \nu^2e^{-\Phi}) \end{aligned} \quad (7.18)$$

where

$$I_2 \equiv a_{2\infty} + \frac{3}{2}a_{4\infty}; \quad \nu^2 \equiv a_{4\infty}/(2I_2) \quad (7.19)$$

I_2 is the ionic strength of this solution. In view of eqs 7.5 and 7.18, the Gouy equation, eq 4.14, takes the form

$$\Gamma_1 - \Gamma_2 - \Gamma_4 = \frac{2}{\kappa_c u} \sqrt{I_2}(1 - u^2)g_2 \quad (7.20)$$

where

$$u \equiv \exp(-\Phi_s/2); \quad g_2 \equiv (1 - \nu^2 + \nu^2 u^2)^{1/2} \quad (7.21)$$

Γ_2 and Γ_4 are to be substituted from eq 7.3; expressions for Γ_1 are available in Table 1, in which the parameter K is determined by eq 7.4. For $\nu \rightarrow 0$ (no salt II in the solution) eq 7.20 reduces to eq 4.15. Further, having in mind eq 7.5, we substitute eq 7.18 into eq 4.13; the result of integration yields

$$F = \frac{\sqrt{I_2}}{\kappa_c} \left[\left(u + \frac{2}{u} \right) g_2 - 3 + \frac{1 - 3\nu^2}{\nu} \ln \left| \frac{\nu u + g_2}{\nu + 1} \right| \right] \quad (7.22)$$

Equation 7.22 is to be substituted in eq 5.7 to obtain the surface tension isotherm. One can check that for $\nu \rightarrow 0$ (no salt II in the solution) eq 7.22 reduces to eq 5.8.

Setting $a_{2\infty} = a_{1\infty}$ in the above equations (no salt I in the solution), one obtains the respective expressions for the special case of one 1:1 ionic surfactant and one 1:2 electrolyte.

7.5. The Surfactant and Salt I Are 1:1 Electrolytes; Salt II Is a 2:2 Electrolyte. An example can be SDS + NaCl + Mg SO₄. Another example can be CTAB + NaBr + MgSO₄. In such a case one has

$$z_4 = -2, \quad z_5 = 2 \quad (7.23)$$

Then eq 7.6 reduces to

$$\begin{aligned} S(\Phi) &= a_{2\infty}(e^{\Phi/2} - e^{-\Phi/2})^2 + a_{4\infty}(e^\Phi - e^{-\Phi})^2 \\ &= 4a_{2\infty} \sinh^2\left(\frac{\Phi}{2}\right) \left[1 + \chi^2 \cosh^2\left(\frac{\Phi}{2}\right) \right] \end{aligned} \quad (7.24)$$

where

$$\chi^2 \equiv 4a_{4\infty}/a_{2\infty} \quad (7.25)$$

In view of eqs 7.5 and 7.24 the Gouy equation, eq 4.14, takes the form

$$\Gamma_1 - \Gamma_2 - 2\Gamma_4 = \frac{4}{\kappa_c} \sqrt{a_{2\infty}} \sinh\left(\frac{\Phi_s}{2}\right) \left[1 + \chi^2 \cosh^2\left(\frac{\Phi_s}{2}\right) \right]^{1/2} \quad (7.26)$$

Γ_2 and Γ_4 are to be substituted from eq 7.3; expressions for Γ_1 are available in Table 1, in which the parameter K is determined by eq 7.4. For $\chi \rightarrow 0$ (no salt II in the solution) eq 7.26 reduces to eq 4.15. Further, having in mind eq 7.5, we substitute eq 7.24 into eq 4.13; the result of integration yields

$$F = \frac{2}{\kappa_c} \sqrt{a_{2\infty}} \left[q \sqrt{1 + \chi^2 q^2} - \sqrt{1 + \chi^2} + \frac{1}{\chi} \ln \left| \frac{\chi q + \sqrt{1 + \chi^2 q^2}}{\chi + \sqrt{1 + \chi^2}} \right| \right] \quad (7.27)$$

$$q \equiv \cosh\left(\frac{\Phi_s}{2}\right) \quad (7.28)$$

Equation 7.27 is to be substituted in eq 5.7 to obtain the surface tension isotherm. One can check that for $\chi \rightarrow 0$ (no salt II in the solution) eq 7.27 reduces to eq 5.8.

Setting $a_{2\infty} = a_{1\infty}$ in the above equations (no salt I in the solution), one obtains the respective expressions for the special case of one 1:1 ionic surfactant and one 2:2 electrolyte.

8. Solution of Two Surfactants and One Electrolyte

Mixtures of an ionic surfactant and one nonionic surfactant are often used in practice. In the present section we consider a solution of ionic surfactant + salt + nonionic surfactant (that is the system considered in section 7 above, in which salt II is exchanged with a nonionic surfactant). For example, this can be a solution of sodium dodecyl sulfate (SDS) + NaCl + an arbitrary nonionic surfactant. Another example can be cetyltrimethylammonium bromide (CTAB) + KBr + an arbitrary nonionic surfactant. It is assumed that the counterions dissociated from the ionic surfactant and salt are *the same* (these are Na⁺ ions in the first example and Br⁻ in the second example).

As before, the ionic surfactant is a Z₁:Z₁ electrolyte and the salt is a Z₁:Z₁ electrolyte. We will use the following subscripts to denote the various solutes: 1, surfactant (amphiphilic) ion; 2, counterion; 3, coion; 4, nonionic surfactant. We denote by Γ_i , $a_{i\infty}$, and a_{iS} ($i = 1, \dots, 4$) the adsorption, bulk, and subsurface activities of the respective species; their bulk concentrations are denoted by $c_{i\infty}$. As before, the requirement for the bulk solution to be electroneutral implies $a_{2\infty} = a_{1\infty} + a_{3\infty}$, cf. eq 2.4. As the distribution of the molecules of the nonionic surfactant is uniform, that is, it is not affected by the electric field, one can write

$$c_{4S} = c_{4\infty} \approx a_{4\infty} = a_{4S} \quad (8.1)$$

In addition, as before, we assume that co-ions do not adsorb at the interface; that is, we presume that $\Gamma_3 \approx 0$. For this system eq 5.2 reduces to

$$d\left(\frac{\sigma_0 - \sigma}{kT} - 2F\right) = \sum_{i=1,2,4} \Gamma_i d \ln a_{iS} \quad (8.2)$$

Since one can vary independently the concentrations of ionic surfactant, salt, and nonionic surfactant, then a_{1s} , a_{2s} , and a_{4s} are independent variables. The condition that the left-hand side of eq 8.2 is a total differential leads to the Euler condition that the cross derivatives are equal:

$$\frac{\partial \Gamma_i}{\partial \ln a_{js}} = \frac{\partial \Gamma_j}{\partial \ln a_{is}} \quad i \neq j; i, j = 1, 2, 4 \quad (8.3)$$

Using eq 8.3 for $(i, j) = (1, 4)$, one can derive

$$\Gamma_i = \frac{\partial J_M}{\partial \ln a_{is}} \quad i = 1, 4 \quad (8.4)$$

where we have introduced the notation

$$J_M \equiv \int_{(0,0)}^{(a_{1s}, a_{4s})} \left(\frac{\Gamma_1}{a_{1s}} da_{1s} + \frac{\Gamma_4}{a_{4s}} da_{4s} \right) \quad (8.5)$$

Table 2 contains explicit expressions for J_M corresponding to the most popular adsorption isotherms used for binary surfactant mixtures, those of Langmuir, Volmer, Frumkin, and van der Waals.^{56–58} To obtain the expressions in Table 2, it is assumed that the excluded area per adsorbed molecule is the *same* for the two surfactants. Moreover, in the Frumkin and van der Waals isotherms (Table 2) the interaction parameters for the various couples of adsorbed surfactant molecules are assumed to be equal: $\beta_{11} = \beta_{14} = \beta_{44} = \beta$. Since the betas are known to account for the tail–tail attraction at the air–water interface (see section 6.1 above), the latter assumption seems reasonable when the hydrocarbon tails of the two surfactants have equal length. (A general expression for the van der Waals isotherm, which is not a subject of the above simplifications, can be found in ref 57.)

From eqs 8.3 and 8.4 one obtains

$$\frac{\partial \Gamma_2}{\partial \ln a_{is}} = \frac{\partial \Gamma_i}{\partial \ln a_{2s}} = \frac{\partial^2 J_M}{\partial \ln a_{2s} \partial \ln a_{is}}; \quad i = 1, 4 \quad (8.6)$$

$$\frac{\partial}{\partial \ln a_{is}} \left(\Gamma_2 - \frac{\partial J_M}{\partial \ln a_{2s}} \right) = 0; \quad i = 1, 4 \quad (8.7)$$

$$\Gamma_2 = \frac{\partial J_M}{\partial \ln a_{2s}} \quad (8.8)$$

In eq 8.8 we have set the integration constant to zero, which means that at zero surfactant adsorption there is no counterion binding at the interface. The substitution of eqs 8.4 and 8.8 into eq 8.2 yields (after integration) the surfactant adsorption isotherm

$$\frac{\sigma_0 - \sigma}{kT} = J_M + 2F \quad (8.9)$$

As usual, σ_0 is the surface tension of pure water; expressions for J_M are given in Table 2, and the term $2F$ is given by eq 5.8.

Since β is related to the van der Waals interactions between the surfactant tails, then β is not expected to depend on the subsurface concentration of the counterions a_{2s} . On the other hand, in general the adsorption constants K_1 and K_4 (see Table 2) could depend on the subsurface concentration of the counterions $K_i = K_i(a_{2s})$, $i = 1, 4$.

Table 2. Surfactant Adsorption and Surface Tension Isotherms for a Mixture of Two Surfactants: Components 1 and 4^a

Adsorption Isotherms for Surfactant Mixture	
Langmuir	$K_i a_{is} = \frac{\Gamma_i}{\Gamma_\infty - \Gamma}, \quad i = 1, 4$
Volmer	$K_i a_{is} = \frac{\Gamma_i}{\Gamma_\infty - \Gamma} \exp\left(\frac{\Gamma}{\Gamma_\infty - \Gamma}\right), \quad i = 1, 4$
Frumkin	$K_i a_{is} = \frac{\Gamma_i}{\Gamma_\infty - \Gamma} \exp\left(-\frac{2\beta\Gamma}{kT}\right), \quad i = 1, 4$
van der Waals	$K_i a_{is} = \frac{\Gamma_i}{\Gamma_\infty - \Gamma} \exp\left(\frac{\Gamma}{\Gamma_\infty - \Gamma} - \frac{2\beta\Gamma}{kT}\right), \quad i = 1, 4$
Surface Tension Isotherm, Eq (8.9): $\sigma = \sigma_0 - kT(J_M + 2F)$	
Langmuir	$J_M = -\Gamma_\infty \ln(1 - \Gamma/\Gamma_\infty)$
Volmer	$J_M = \Gamma_\infty \Gamma / (\Gamma_\infty - \Gamma)$
Frumkin	$J_M = -\Gamma_\infty \ln(1 - \Gamma/\Gamma_\infty) - \beta\Gamma^2/(kT)$
van der Waals	$J_M = \Gamma_\infty \Gamma / (\Gamma_\infty - \Gamma) - \beta\Gamma^2/(kT)$

^a The notation $\Gamma = \Gamma_1 + \Gamma_4$ is used.

Then the dependence of Γ_1 and Γ_4 on a_{2s} comes from K_1 and K_4 for all surfactant adsorption isotherms in Table 2. Moreover, note that for each of these isotherms Γ_i ($i = 1, 4$) depends on the products $K_1 a_{1s}$ and $K_4 a_{4s}$; that is, $\Gamma_i = \Gamma_i(X_1, X_4)$, and $X_i \equiv K_i a_{is}$. Then eq 8.5 can be transformed to read

$$J_M \equiv \int_{(0,0)}^{(K_1 a_{1s}, K_4 a_{4s})} \left(\frac{\Gamma_1}{X_1} dX_1 + \frac{\Gamma_4}{X_4} dX_4 \right) \quad (8.10)$$

Differentiating eq 8.10, one can bring eq 8.8 into the form

$$\Gamma_2 = \Gamma_1 \frac{\partial \ln K_1}{\partial \ln a_{2s}} + \Gamma_4 \frac{\partial \ln K_4}{\partial \ln a_{2s}} \quad (8.11)$$

which holds for each of the surfactant adsorption isotherms in Table 2. Note that eq 8.11 is valid for a general form of the dependencies $K_i = K_i(a_{2s})$, $i = 1, 4$.

From a physical viewpoint one can expect that the counterions do bind *only* to the headgroups of the ionic surfactant in the adsorption layer and do not bind to the headgroups of the nonionic surfactant. In such a case one can assume

$$K_1 = K_0 + K_2 a_{2s}; \quad \partial K_4 / \partial a_{2s} \equiv 0 \quad (8.12)$$

where K_0 and K_2 are constants. The substitution of eq 8.12 into eq 8.11 yields

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_2 a_{2s}}{K_0 + K_2 a_{2s}} \quad (8.13)$$

Equation 8.13 is in fact the *Stern isotherm* of counterion adsorption for the considered solution containing salt and ionic and nonionic surfactants. Since eq 8.13 is a corollary from the Euler condition, eq 8.6, it turns out that eq 8.12 is the necessary and sufficient condition for thermodynamic compatibility of the Stern isotherm of counterion adsorption with either of the surfactant adsorption isotherms in Table 2.

For a solution of ionic and nonionic surfactant *without* added salt, one can use eq 8.13 with $a_{2s} \rightarrow a_{1\infty}$ to describe the adsorption of the counterions dissociated from the dissolved ionic surfactant.

On the other hand, the results of this section can be easily generalized to the case of a solution containing ionic and nonionic surfactants and *two* nonamphiphilic salts. One can prove that the surfactant adsorption isotherm is

(58) Lucassen-Reynders, E. H. *Anionic Surfactants—Physical Chemistry of Surfactant Action*; Marcel Dekker: New York, 1981.

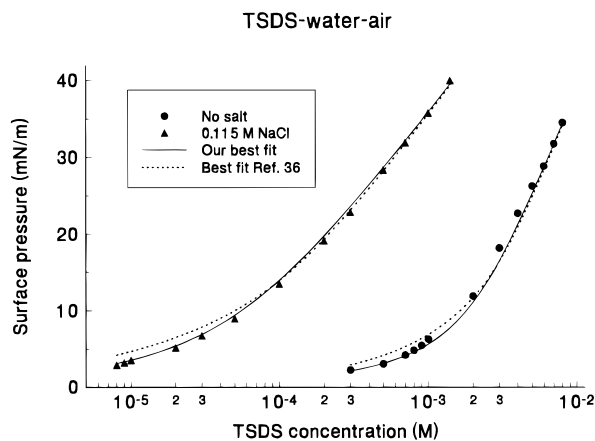


Figure 2. Plots of the surface pressure at the air–water interface $\sigma_0 - \sigma$ versus the surfactant (TSDS) concentration $c_{1\infty}$ for two fixed NaCl concentrations: 0 and 0.115 M. The symbols are experimental data from refs 11 and 12; the continuous and dotted lines represent the best fits by means of our theory and that from ref 36, respectively.

given again by eq 8.9, in which the electric term F is given by a counterpart of eq 7.10, 7.16, 7.22, or 7.27, depending on the type of valency of the second salt. (To avoid misunderstandings, we should note that the subscript 4 denotes salt II in section 7, but it denotes nonionic surfactant in section 8.)

9. Comparison of Theory and Experiment

9.1. Experimental System and Numerical Task.

Below we illustrate the application of the theory to the interpretation of a set of experimental data. We chose the data of Tajima et al.^{11,12} for the surface tension versus surfactant concentrations at two concentrations of NaCl: $c_{3\infty} = 0$ and $c_{3\infty} = 0.115$ M; see Figure 2. The ionic surfactant is TSDS, which is a 1:1 electrolyte.

Our goal is by processing this set of data for the interfacial tension $\sigma = \sigma(c_{1\infty}, c_{2\infty})$ as a function of the bulk concentrations of surfactant ions $c_{1\infty}$, and counterions $c_{2\infty}$ to determine the surfactant adsorption $\Gamma_1(c_{1\infty}, c_{2\infty})$, the counterion adsorption $\Gamma_2(c_{1\infty}, c_{2\infty})$, and the surface potential $\psi_s(c_{1\infty}, c_{2\infty})$. We compare the calculated values of these parameters with the respective values obtained by means of the theory by Borwankar and Wasan,³⁶ which does not take into account the effect of counterion binding.

To fit the data, we will make use of the Frumkin isotherm (see Table 1)

$$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT}\right) \quad (9.1)$$

which is appropriate for air–water interfaces, as discussed in section 6.1 above. The parameter K is given by eq 6.7, that is, $K = K_1 + K_2 a_{2s}$, and the counterion adsorption is determined by the Stern isotherm, eq 6.8. Combining eq 5.8 with the Frumkin surface tension isotherm in Table 1, one obtains

$$\frac{\sigma_0 - \sigma}{kT} = -\Gamma_\infty \ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) - \frac{\beta\Gamma_1^2}{kT} + \frac{8\sqrt{a_{2\infty}}}{\kappa_c} \left[\cosh\left(\frac{\Phi_s}{2}\right) - 1 \right] \quad (9.2)$$

One sees that the theoretical model contains four parameters, β , Γ_∞ , K_1 , and K_2 , which are to be determined

from the best fits of the experimental data. These four parameters can really be obtained from the best fit only if the set of data contains experimental points for $\sigma = \sigma(c_{1\infty}, c_{2\infty})$ for both high and low surfactant concentrations and for both high and low salt concentrations; the data by Tajima et al.^{11,12} satisfy the latter requirement, and that is the reason why it has been chosen. On the other hand, our experience with other sets of data shows that if this requirement is not satisfied, the merit function (see eq 9.3 below) exhibits a flat shallow minimum, and therefore it is practically impossible to determine the best fit.

9.2. Procedure of Calculations. We apply the derived set of equations to fit experimental data for the surface tension as a function of both surfactant and salt concentrations.

(1) As input data we have experimental points for the interfacial tension $\sigma = \sigma(c_{1\infty}, c_{2\infty})$. The activities $a_{1\infty}$ and $a_{2\infty}$, corresponding to a given couple $(c_{1\infty}, c_{2\infty})$ are calculated from eqs 1.7 and 1.8; κ_c is a known parameter, which is defined by eq 4.3.

(2) We assign tentative values of β , K_1 , K_2 , and Γ_∞ , which are to be determined as adjustable parameters from the best fit of the data.

(3) We give a tentative value of the dimensionless surface potential Φ_s ; a value in the interval $0 < \Phi_s < 10$ is appropriate.

(4) From eq 2.10 we calculate a_{1s} and a_{2s} .

(5) From eqs 6.6, 6.8, and 9.1 we calculate Γ_1 and Γ_2 .

(6) The calculated values of $\Gamma_1(\Phi_s)$ and $\Gamma_2(\Phi_s)$ are then substituted in eq 4.15, which becomes an implicit equation for determining Φ_s ; the latter is solved numerically.

(7) The theoretical value of the surface tension $\sigma(c_{1\infty}^{(m)}, c_{2\infty}^{(m)}; \beta, K_1, K_2, \Gamma_\infty)$, corresponding to a given couple of experimental concentrations $(c_{1\infty}^{(m)}, c_{2\infty}^{(m)})$, is then calculated from eq 9.2.

(8) The adjustable parameters β , K_1 , K_2 , and Γ_∞ are determined by means of the least squares method, that is, by numerical minimization of the merit function

$$\Psi(\beta, K_1, K_2, \Gamma_\infty) = \left\{ \frac{1}{N} \sum_{i=1}^N [\sigma^{(m)} - \sigma(c_{1\infty}^{(m)}, c_{2\infty}^{(m)}; \beta, K_1, K_2, \Gamma_\infty)]^2 \right\}^{1/2} \quad (9.3)$$

where $\sigma^{(m)}$ is the experimental value of σ , corresponding to the concentrations $c_{1\infty}^{(m)}$ and $c_{2\infty}^{(m)}$, and the summation in eq 3.16 is carried out over all experimental points $(c_{1\infty}^{(m)}, c_{2\infty}^{(m)}, \sigma^{(m)})$; N is their total number.

To see how important is the effect of counterion adsorption, we compare the same experimental data with the theoretical model by Borwankar and Wasan,³⁶ in which $\Gamma_2 \equiv 0$ (that is equivalent to $K_2 \equiv 0$) and $K \equiv K_1 = \text{constant}$. Correspondingly, when fitting the data with the theory from ref 36, at steps 2 and 8 we have a single constant K_1 ($K_2 \equiv 0$). Thus we can use the above procedure of calculation, in which step 5 is changed as follows:

(5) From eq 9.1 (with $K \equiv K_1 = \text{constant}$) we calculate Γ_1 and we set $\Gamma_2 \equiv 0$ ($K_2 \equiv 0$).

9.3. Numerical Results and Discussion. The experimental data for $\sigma(c_{1\infty})$ for two different fixed NaCl concentrations are obtained by Tajima et al.;^{11,12} see the symbols in Figure 2. To calculate the surface pressure $\pi_s = \sigma_0 - \sigma$, which is plotted in Figure 2, we determined σ_0 by linear extrapolation of the experimental dependence σ versus $c_{1\infty}$ for the lowest surfactant concentrations down to $c_{1\infty} = 0$. The continuous lines in Figure 2 are the best fits of the whole set of data by means of our theoretical model (section 9.2); the two curves correspond to 0.0 and

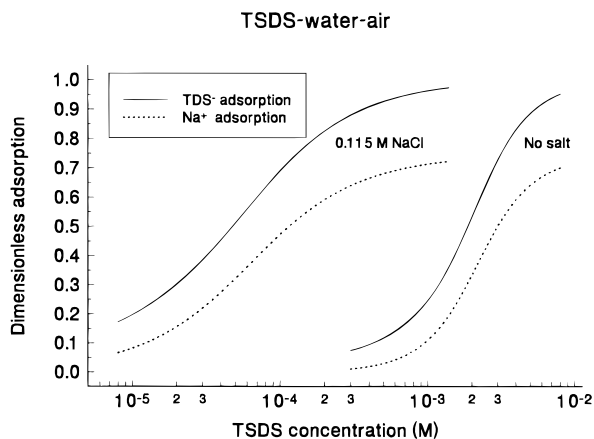


Figure 3. Plots of the calculated adsorptions of surfactant Γ_1/Γ_∞ (the full lines) and counterions Γ_2/Γ_∞ (the dotted lines) versus the surfactant (TSDS) concentration $c_{1\infty}$. The lines correspond to the best fits of the data in Figure 2 obtained by means of our model; see section 9.2.

0.115 M NaCl. The merit function Ψ , defined by eq 9.3, was minimized numerically by variation of the four parameters β , K_1 , K_2 , and Γ_∞ ; their values, corresponding to the best fit, are given in Table 3, where the minimum value Ψ_{\min} of the merit function in eq 9.3 is also given. The data for *all* surfactant and salt concentrations were processed simultaneously to determine β , K_1 , K_2 , and Γ_∞ . Substituting in eq 6.9 $K_1 = 156 \text{ m}^3/\text{mol}$ and $1/\Gamma_\infty = 37.6 \text{ \AA}^2$ (see Table 3), one estimates the standard free energy of adsorption to be $\Delta\mu_1^{(0)} = 12.8kT$ per SDS molecule, that is 31.3 kJ/mol, which seems to be a reasonable value. Likewise, substituting in eq 6.10 $K_2/K_1 = 8.21 \times 10^{-4} \text{ m}^3/\text{mol}$, $1/\Gamma_\infty = 37.6 \text{ \AA}^2$ (see Table 3), and $\delta_2 \approx 7 \text{ \AA}$, one estimates the standard free energy of counterion binding to be $\Delta\mu_2^{(0)} = 1.64kT$ per Na^+ ion, that is 4.04 kJ/mol, which also seems to be a reasonable value. The value of the parameter β is positive, which indicates attraction between the hydrocarbon tails of the adsorbed surfactant molecules.

Figure 3 shows calculated curves for the adsorptions of surfactant Γ_1 (the full lines) and counterions Γ_2 (the dotted lines) versus the TSDS concentration $c_{1\infty}$, obtained by means of our model. These curves show the variation of Γ_1 and Γ_2 along the two experimental curves in Figure 2. In Figure 3 one sees that both Γ_1 and Γ_2 are markedly greater when NaCl is present in the solution; only for the highest studied TSDS concentrations (just below the cmc) are the adsorptions in the presence and absence of salt close to each other. The highest value of Γ_1 for the curves in Figure 3 is 4.30×10^{-6} and $4.20 \times 10^{-6} \text{ mol/m}^2$ for the solutions with and without NaCl, respectively. The latter two values compare well with the saturation adsorptions measured by Tajima^{11,12} by means of the radiotracer method, viz. $\Gamma_1 = 4.33 \times 10^{-6}$ and $3.19 \times 10^{-6} \text{ mol/m}^2$ for the solutions with and without NaCl, respectively; the agreement is especially good for the solution with NaCl.

In Figure 3 one sees that the counterion (Na^+) adsorption Γ_2 is always smaller than the surfactant adsorption Γ_1 . This is visualized in Figure 4, where the occupancy of the Stern layer $\theta = \Gamma_2/\Gamma_1$ is plotted versus the surfactant concentration for the curves in Figure 3. Especially strong is the increase of the occupancy for the solution *without* NaCl as a function of the surfactant concentration: Γ_2/Γ_1 rises from 0.15 up to 0.74 and then exhibits a tendency to level off. As it could be expected, the occupancy Γ_2/Γ_1 is higher for the solution *with* NaCl; even at the TSDS concentration 10^{-5} M the occupancy is about 0.40; for the

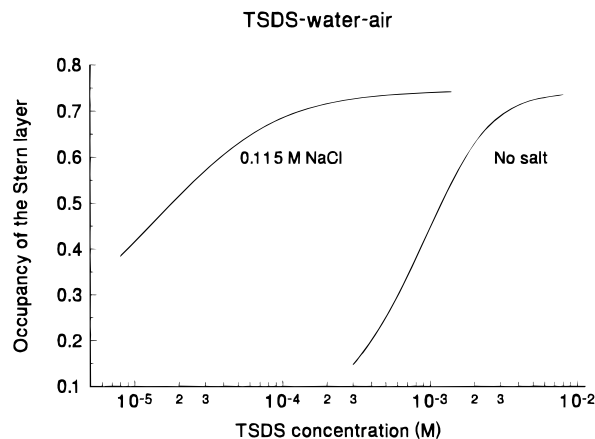


Figure 4. Plots of the calculated occupancy of the Stern layer by adsorbed counterions Γ_2/Γ_1 , versus the surfactant (TSDS) concentration $c_{1\infty}$ for two fixed NaCl concentrations: 0 and 0.115 M. The lines correspond to the best fits of the data in Figure 2 obtained by means of our model; see section 9.2.

higher surfactant concentrations it levels off at $\Gamma_2/\Gamma_1 = 0.74$ (Figure 4). The latter value of Γ_2/Γ_1 agrees with the data of other authors^{13,20–22} (see the Introduction), who have obtained values of Γ_2/Γ_1 up to 0.70–0.90. Once again this fact shows that the counterion adsorption must not be neglected. Note that in the model of Borwankar and Wasan³⁶ $\Gamma_2/\Gamma_1 \equiv 0$ by presumption.

The model of Borwankar and Wasan³⁶ also agrees well with the data in Figure 2 (see the dotted lines therein); the respective values of the parameters of the fit are given in Table 3. One sees that our best fit (the continuous lines) agrees better with the data than that from ref 36, although the differences are not so great. The difference between the two fits can be quantified by the minimal value of the merit function, which is $\Psi_{\min} = 0.69 \text{ mN/m}$ for our fit and $\Psi_{\min} = 1.06 \text{ mN/m}$ for the fit from ref 6 (see Table 3). The value of the interaction parameter β is 5 times greater for the model from ref 36; in other words this model requires a stronger attraction between the adsorbed surfactant molecules, which is to counterbalance the stronger electrostatic repulsion in the absence of bound counterions. The values of Γ_∞ given by the two models are close (see Table 3).

The differences between our model and that from ref 36 show up when one compares the values of the surface electric potential ψ_s , (see Figure 5). The curves in Figure 5 correspond to the same TSDS concentration ranges and to the same NaCl concentrations as those in Figure 2. For the solutions with salt our model predicts surface potentials varying in the range $|\psi_s| = 55\text{--}95 \text{ mV}$, whereas for the same solutions the model from ref 36 predicts $|\psi_s| = 80\text{--}165 \text{ mV}$ (see Figure 5) (note that ψ_s has a negative sign). Similar is the situation with the solutions without NaCl. This difference between the predictions of the two models is understandable, because the neglecting of the counterion binding in ref 36 leads to a higher calculated surface potential $|\psi_s|$. The latter fact can be used to verify which model is closer to reality by electrophoretic measurements of the ζ -potential of air bubbles in the respective solutions.

For the surfactant solutions without NaCl the plot of $|\psi_s|$ versus $c_{1\infty}$ exhibits a maximum (Figure 5), which can be attributed to the competition of two effects: (i) an increase of surface charge with the increase of surfactant adsorption Γ_1 and (ii) a decrease of the surface potential with the increase of the ionic strength of the solution. Effect i is predominant for the lower $c_{1\infty}$, whereas effect

Table 3. Parameters of Fits of the Data for TSDS in Figure 2 by Means of Our Theoretical Model (Section 9.2) and That from Ref 36

theoretical model	K_1 (m ³ /mol)	K_2 (m ⁶ /mol ²)	Γ_∞ ($\times 10^{-6}$ mol/m ²)	$2\beta\Gamma_\infty/kT$	Ψ_{\min} (mN/m)
our model (section 9.2)	156	0.128	4.42	0.800	0.69
model from ref 36	399	(0)	4.52	4.00	1.06

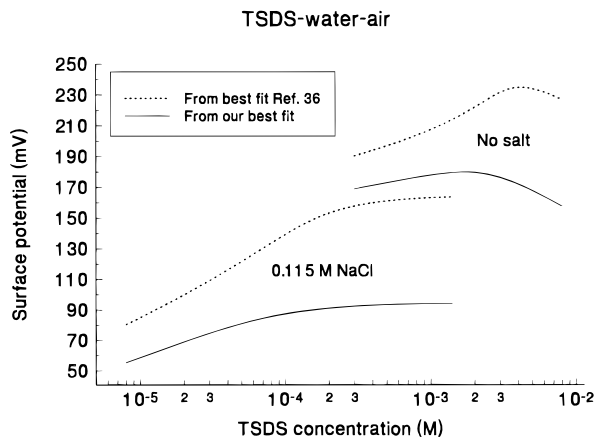


Figure 5. Plots of the calculated surface potential of the air–water interface $|\psi_s|$ versus the surfactant (TSDS) concentration $c_{1\infty}$. The continuous and dotted lines correspond to the best fits of the data in Figure 2 by means of our theory and that from ref 36, respectively.

ii gets the upper hand for the higher $c_{1\infty}$, for which Γ_1 is almost constant. In contrast, the plots of $|\psi_s|$ versus $c_{1\infty}$ at practically fixed ionic strength (0.115 M, Figure 5) are monotonic, because effect ii does not appear.

10. Concluding Remarks

This work is a theoretical study on thermodynamics of ionic surfactant adsorption from aqueous solutions in the presence of nonamphiphilic salts. The fact that the surfactant adsorption is accompanied by counterion binding and variation of the surface electric potential is taken into account. The Euler equation, eq 5.3, provides a condition for thermodynamic compatibility of a given couple of surfactant and counterion adsorption isotherms. To verify whether the couple of the known Langmuir and Stern isotherms, eqs 2.8 and 2.9, is thermodynamically compatible, we investigated the problem of how to obtain the counterion adsorption isotherm corresponding to a given surfactant adsorption isotherm. The Gibbs adsorption equation is analytically integrated to obtain an expression for the surface tension, eq 5.7, which contains contributions from the adsorption layer J (see Table 1) and from the diffuse electric double layer $2F$ (see eq 4.13). The expression for F is then specified for ionic surfactant solutions containing 1:1, 2:1, 1:2, and 2:2 electrolytes. In section 8 the results are extended to the case when the solution contains an ionic–nonionic surfactant mixture and salt.

One of the most important results in this study is the derived condition for thermodynamic compatibility between the surfactant adsorption isotherm (each of the isotherms in Tables 1 and 2) and the Stern isotherm of counterion binding, eq 6.6. In general, this compatibility condition takes the form of a linear dependence of the surfactant adsorption parameter on the subsurface activities of the counterions, see eq 6.5; eqs 6.7, 7.4, and 8.12 give the explicit form of this dependence for various specific cases. Note that counterion adsorption isotherms, which are different from the Stern isotherm, could be generated if a nonlinear expression for the adsorption parameter(s) K is substituted in eq 6.4 or 8.11. Another important conclusion is that the Gibbs adsorption equation can be presented in two alternative forms, cf. eqs. 2.1 and 5.19.

As an illustrative example of application of the theoretical model, the latter is used to interpret data by Tajima et al.^{11,12} for the surface tension of TSDS solutions versus surfactant and salt concentrations. The fact that this set of data covers a wide range of surfactant and salt concentrations allowed us to determine the four parameters of the model, β , K_1 , K_2 , and Γ_∞ (see Table 3), from the best fit. The parameter values thus obtained are reasonable. They allow one to predict the values of σ , Γ_1 , Γ_2 , and ψ_s for every surfactant and salt concentrations below the cmc. The calculated Γ_1 , corresponding to the experimental curves, is markedly higher for the higher NaCl concentration (Figure 3). The calculated occupancy of the Stern layer rises up to 74% for the higher surfactant and salt concentrations (Figure 4); in other words, the counterion adsorption (binding) can be considerable and should not be neglected. Its neglect leads to markedly greater calculated values of the surface electric potential (see Figure 5).

In summary, the derived equations can be applied to process experimental data for the surface tension as a function of the surfactant and salt concentrations. As a result one can determine the adsorptions of surfactant and counterions, as well as the surface electric potential and charge density, for various salt and surfactant concentrations. Further, the derived equations can be applied to calculate the Gibbs elasticity of ionic surfactant adsorption monolayers and the diffusion relaxation time in the kinetics of adsorption.³⁹

Acknowledgment. This work was supported by Colgate-Palmolive. The authors are indebted to Prof. I. B. Ivanov and Dr. N. Denkov for stimulating discussion and to Mr. D. Ganchev for drawing Figure 1.

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