Adsorption Kinetics of Ionic Surfactants after a Large Initial Perturbation. Effect of Surface Elasticity

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This theoretical study is devoted to the relaxation of surface tension of an ionic surfactant solution for submicellar concentrations. The effects of added nonamphiphilic electrolyte and counterion binding are taken into account. We consider a large initial deviation from equilibrium, which is defined as the formation of a new interface: there is no adsorbed surfactant and electric double layer at the initial moment. Next, the surfactant solution and its interface are allowed to relax without any subsequent perturbation. The electrodiffusion equations, which describe the adsorption kinetics, are nonlinear, and it is impossible to find a general analytical solution, especially in the case of large initial deviations. Nevertheless, the problem can be linearized in the asymptotic case of long times. The derived theoretical expressions show that the relaxation times in the cases of large and small initial perturbations are numerically close to each other. For that reason the relaxation time can be considered as a general kinetic property of the adsorption monolayer. The theory predicts also the slope of the experimental plot of dynamic surface tension vs inverse square root of time; this makes the theory useful for interpretation of experimental data. The theoretical expressions involve the surface (Gibbs) elasticity, whose definition for adsorption monolayers of soluble ionic surfactants is discussed in detail. The Gibbs elasticity of such monolayers is found to increase strongly with the rise of salt concentration. The derived asymptotic expressions are verified against an exact computer solution of the electrodiffusion problem, and excellent agreement is found.

1. Introduction

The characteristic time of surfactant adsorption at a fluid interface is an important parameter for surfactant-stabilized dynamic systems, like foams and emulsions. For example, it is expected that surfactant solutions with faster adsorption kinetics do exhibit a greater foaminess.[1,2] Sutherland,[3] derived an expression describing the relaxation of a *small* dilatation of an initially equilibrium adsorption monolayer from a soluble *nonionic* surfactant

$$\frac{\sigma(t) - \sigma^{(e)}}{\sigma(0) - \sigma^{(e)}} = \frac{\Gamma_1(t) - \Gamma_1^{(e)}}{\Gamma_1(0) - \Gamma_1^{(e)}} = \exp\left(\frac{t}{\tau_1}\right) \text{erfc}\left[\left(\frac{t}{\tau_1}\right)^{1/2}\right] \quad (1.1)$$

where t is time

$$\tau_1 \equiv \frac{1}{D_1}\left(\frac{\partial \Gamma_1}{\partial c_1}\right)^2 \quad (1.2)$$

is characteristic relaxation time, σ is surface tension, c_1, Γ_1, and D_1 are surfactant concentration, adsorption, and diffusivity; here and hereafter the superscript "(e)" denotes the equilibrium value of the respective parameter; $\text{erfc}(x)$ is the complementary error function.[4−6] Using the asymptotics of the latter function for $x \gg 1$, one obtains

$$\frac{\sigma(t) - \sigma^{(e)}}{\sigma(0) - \sigma^{(e)}} = \frac{\Gamma_1(t) - \Gamma_1^{(e)}}{\Gamma_1(0) - \Gamma_1^{(e)}} = \left(\frac{\tau_1}{\pi t}\right)^{1/2} + O(t^{-3/2}) \quad (1.3)$$

$$t \gg \tau_1$$

Equation 1.3 is often used as a test to verify whether the adsorption process is under diffusion control: data for the dynamic surface tension $\sigma(t)$ are plotted vs $1/t^{1/2}$ and it is checked if the plot complies with a straight line; the extrapolation of this line to $1/t^{1/2} \to 0$ is used to determine the equilibrium surface tension, $\sigma^{(e)}$.[1,7]

In the experiment one often deals with *large* initial deviations from equilibrium. In such a case there is no general analytical expression for the dynamic surface tension $\sigma(t)$ since the adsorption isotherms (except that of Henry) are nonlinear. In this case one can use either a computer solution[8,9] or apply the von Karman's approximate approach.[10,11] Moreover, analytical asymptotic expressions for long times ($t \to \infty$) can be obtained. Hansen[12] derived the long-time asymptotics of the subsurface concentration, $c_{1s}(t)$, of a *nonionic* surfactant:

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$$c_1^{(e)} - c_{1s}(t) = (\Gamma_1^{(e)} - \Gamma_1(0))\left(\frac{1}{\pi D_1 t}\right)^{1/2} \qquad (1.4)$$

$$t \to \infty$$

Equation 1.4 has been utilized and generalized by many authors.[13-17] The validity of eq 1.4 was reexamined and confirmed by Filippov.[18] By substitution of eq 1.4 in the Gibbs adsorption equation and integration, one obtains the long-time asymptotics of the surface tension of a *nonionic* surfactant solution after a *large* initial perturbation:

$$\sigma(t) - \sigma^{(e)} = (\Gamma_1^{(e)})^2 \frac{kT}{c_1^{(e)}}\left(\frac{1}{\pi D_1 t}\right)^{1/2} \qquad (1.5)$$

$$t \to \infty$$

T is the temperature, and k is the Boltzmann constant; when eq 1.5 was derived, the surfactant adsorption at the initial moment was set to zero, $\Gamma_1(0) = 0$.

In the case of *ionic* surfactants, the existence of a diffuse electric double layer essentially influences the thermodynamics and kinetics of adsorption. The process of adsorption is accompanied with a progressive increase of the surface charge density and electric potential. The charged surface repels the new surfactant molecules which results in a deceleration of the adsorption process.[19] The theoretical studies on dynamics of adsorption encounter difficulties with the nonlinear set of partial differential equations, which describes the electrodiffusion process. The quasi-equilibrium model developed by Dukhin et al.[20-23] employs the simplifying assumption that the characteristic diffusion time is much greater than the time of formation of the electric double layer. As a result the electrodiffusion process is modeled as a process of mixed barrier-diffusion control. A similar approach is followed by Borwankar and Wasan.[24] The solution of the problem for the case of small periodic surface perturbations, like those observed with the oscillating bubble technique,[25,26] was obtained by Bonfillon and Langevin;[27] the results were applied to interpret data obtained by means of the longitudinal-wave method for adsorption monolayers of ionic surfactant. MacLeod and Radke[28] obtained computer numerical solutions of the electrodiffusion problem, thus avoiding the simplifying assumptions of the quasi-equilibrium model. Such numerical solutions are mathematically rigorous, but they are very time-consuming when applied to process experimental data.
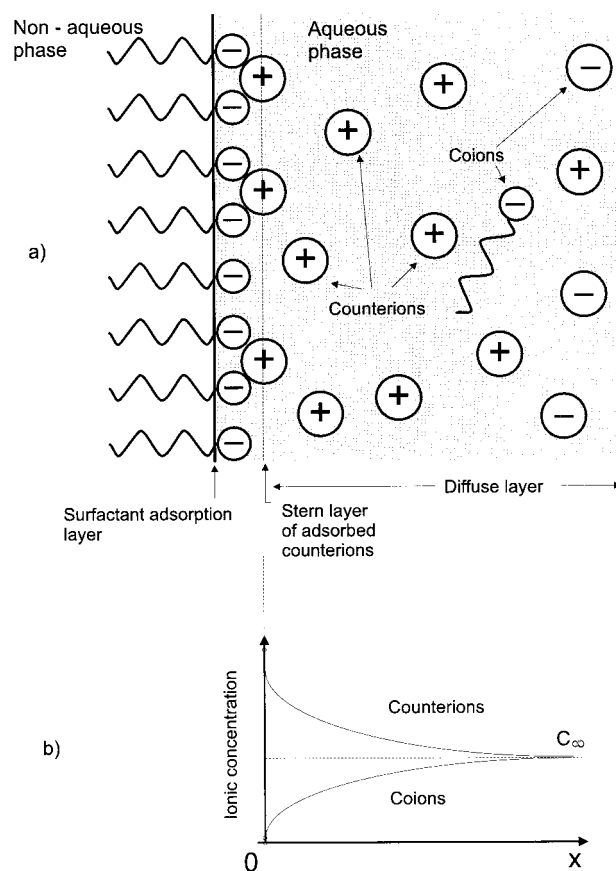
Figure 1. Schematic presentation of the electric double layer in a vicinity of an adsorption monolayer of ionic surfactant. (a) The diffuse layer contains free ions involved in Brownian motion, while the Stern layer consists of adsorbed (immobilized) counterions. (b) Near the charged surface there is an accumulation of counterions and a depletion of co-ions; their bulk concentrations are equal to c_∞.

Another important effect, which adds to the complexity of the problem, is the *adsorption (binding) of counterions* at the conversely charged surfactant headgroups in the adsorption layer; see Figure 1. The adsorbed (bound) counterions form the Stern layer,[29,30] which affects strongly the adsorption kinetics of ionic surfactants insofar as up to 70−90% of the surface electric charge could be neutralized by the bound counterions.[31-34] The addition of nonamphiphilic electrolyte (salt) in the solution increases the occupancy of the Stern layer.[34] It turns out that in the case of ionic surfactants (with or without salt), there are two adsorbing species: the surfactant ions and the counterions. The adsorption of counterions can be described by means of the Stern isotherm;[29] see refs 34−37. It is worthwhile noting that the counterion binding enhances the adsorption of surfactant;[34,38] formally, this

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appears as a linear increase of the surfactant adsorption parameter K with the rise of the subsurface concentration of counterions, c_{2s}, see eqs 6.4 and 7.1 below; details can be found in ref 34.

In a recent article[39] we addressed the problem about the kinetics of adsorption from an ionic surfactant solution in its full complexity, including the time evolution of the electric double layer, the effect of added salt, and the counterion binding. An analytical solution was found only in the asymptotic case of *small* initial deviations from equilibrium and long times of adsorption. Thus generalizations of eqs 1.2 and 1.3 for the case of ionic surfactants were obtained.

The aim of the present paper is to give a further extension of the theory to the case of *large* initial perturbations and to derive a generalization of the Hansen formula, eq 1.5, for the case of *ionic* surfactants. Note, that here and hereafter, a large initial deviation from equilibrium (perturbation) is defined as the formation of a new interface: there is no adsorbed surfactant and electric double layer at the initial moment. Next, the surfactant solution and its interface are allowed to relax without any subsequent perturbation.

The paper is structured as follows. In section 2 we give a brief outline of the thermodynamic and kinetic basis of the present study. Attention is paid to the results for *small* initial perturbations from ref 39, which are to be compared with the results for *large* initial perturbations obtained in the present study. In section 3 an asymptotic solution of the electrodiffusion problem is found for $t \to \infty$. In sections 4 and 5 asymptotic expressions for the relaxation times of adsorption and surface tension are derived, which involve the Gibbs (surface) elasticity E_G. In section 6 the problem about the correct definition of E_G for adsorption monolayers from soluble ionic surfactants is examined. Finally, section 7 contains illustrative numerical results for an experimental system, as well as a numerical text of the derived equations against the computer solution of MacLeod and Radke.[28] Some mathematical proofs and derivations of expressions are given in Appendices A and B (Supporting Information).

2. Equilibrium State and Basic Kinetic Equations

2.1. Thermodynamic Background. We consider a boundary between two fluid phases, which bears some electric charge due to the adsorption of charged amphiphilic molecules (ionic surfactant). The charged surface repels the *co-ions*, i.e., the ions having charge of the same sign, but it attracts the *counterions*, which bear charge of the opposite sign; see Figure 1. An electric double layer (EDL), i.e., a nonuniform distribution of the ionic species in the vicinity of the charged interface, appears.[40] The conventional model of the EDL stems from the works of Gouy,[41] Chapman,[42] and Stern.[29] The EDL is considered to consist of two parts: (i) *adsorption layer* and (ii) *diffuse layer*. The adsorption layer includes surfactant molecules, which are immobilized (adsorbed) at the phase boundary, as well as bound counterions, which form the Stern layer; see Figure 1. The diffuse layer consists of free ions in the aqueous phase, which are involved in Brownian motion and influenced by the electric field of the charged interface. The boundary, separating the adsorption from the diffuse layer (the plane $x = 0$ in Figure 1), is usually called the

Gouy plane; it can be used as a Gibbs dividing surface between the two neighboring phases.[24] The electric potential varies across the EDL: $\psi = \psi(x)$. The boundary values of $\psi(x)$ are

$$\psi(x=0) = \psi_s; \qquad \psi(x\to\infty) = 0 \qquad (2.1)$$

At equilibrium, the subsurface concentrations of the ionic species are related to the respective bulk concentrations by means of the Boltzmann distribution:[40−43]

$$c_{is}^{(e)} \equiv c_i^{(e)}(x=0) = c_{i\infty} \exp\left(-\frac{z_i e \psi_s^{(e)}}{kT}\right) \qquad (2.2)$$

$i = 1, 2, 3, ..., N$. Here e is the electronic charge; z_i is the valency of the ith ion. The Gibbs adsorption equation can be presented in the form:[24,34,44−46]

$$d\sigma = -kT\sum_{i=1}^{N} \tilde{\Gamma}_i \, d \ln c_{i\infty} \qquad (2.3)$$

$$T = \text{constant}$$

Equations 2.2 and 2.3 are rigorous in terms of activities of the ionic species, rather than in terms of concentrations; throughout this paper we will set the activities equal to the concentrations, which is a good approximation for ionic strengths below 0.1 M.[24,34,47] In eq 2.3, $\tilde{\Gamma}_i$ denotes the adsorption of the ith component; $\tilde{\Gamma}_i$ represents the surface excess of component "i" with respect to the *uniform* bulk solution. For an ionic species $\tilde{\Gamma}_i$ is a total adsorption, which includes contributions Γ_i and Λ_i, respectively, from the adsorption layer (adsorbed surfactant + counterions in the Stern layer) and the diffuse layer (Figure 1), which are defined as follows[34,44−46]

$$\Lambda_i \equiv \int_0^\infty [c_i(x) - c_{i\infty}] \, dx \qquad (2.4)$$

$$\Gamma_i \equiv \tilde{\Gamma}_i - \Lambda_i$$

Using the theory of EDL and eq 2.4, one can prove that the Gibbs adsorption equation, eq 2.3, can be represented in the following equivalent form[34]

$$d\sigma_a = -kT\sum_{i=1}^{N} \Gamma_i \, d \ln c_{is} \qquad (2.5)$$

$$T = \text{constant}$$

where $\sigma_a = \sigma - \sigma_d$ is the contribution of the adsorption layer into the surface tension, and σ_d is the contribution of the diffuse layer:[34,44]

$$\sigma_d = -\frac{\epsilon}{4\pi} \int_0^\infty \left(\frac{\partial\psi}{\partial x}\right)^2 dx \qquad (2.6)$$

ϵ is the dielectric permittivity of the aqueous phase. The integrand in eq 2.6 represents the anisotropy of the Maxwell electric stress tensor, which contributes to the interfacial tension in accordance with the known Bakker

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formula.[48,44,34] The comparison between eqs 2.3 and 2.5 shows that the Gibbs adsorption equation can be expressed either in terms of σ, $\tilde{\Gamma}_i$, and $c_{i\infty}$, or in terms of σ_a, Γ_i, and c_{is}. In ref 34 it is proven that for quasi-static processes these two forms of the Gibbs adsorption equation are equivalent. In the *dynamic* treatment below we will assume equilibrium between surface and subsurface, that is, we consider surfactant adsorption under electrodiffusion control. In such a case we can use eq 2.5 and it is convenient to work in terms of the variables σ_a, Γ_i, and c_{is}. The total surface tension is

$$\sigma = \sigma_a + \sigma_d \tag{2.7}$$

Note that σ_d represents a nonlocal, integral contribution of the whole diffuse electric double layer, whereas σ_a is related to the two-dimensional state of the adsorbed surfactant ions and bound counterions; see eqs 5.1 and 5.5 below.

2.2. The Equilibrium State. In the present study we consider a solution of ionic surfactant, which is a symmetric *z:z* electrolyte, in the presence of additional nonamphiphilic *z:z* electrolyte (salt). We assume that the counterions due to the surfactant and salt are identical. 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 (1), counterions (2), and co-ions (3), 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

$$c_{2\infty} = c_{1\infty} + c_{3\infty} \tag{2.8}$$

The binding of *co-ions* due to the nonamphiphilic salt is expected to be equal to zero

$$\Gamma_3 = 0 \tag{2.9}$$

because they are repelled by the similarly charged interface.[34] However, $\Lambda_3 \neq 0$: the integral in eq 2.4 gives a negative Λ_3, see Figure 1; hence $\tilde{\Gamma}_3 = \Lambda_3 \neq 0$. The difference between the adsorptions of surfactant ions and counterions determines the surface charge density, $\rho_s = ez(\Gamma_1 - \Gamma_2)$, which at equilibrium is related to the surface potential by means of the Gouy formula:[41,30,34]

$$\Gamma_1^{(e)} - \Gamma_2^{(e)} = \frac{4c_{2\infty}}{\kappa} \sinh\left(\frac{\phi_s^{(e)}}{2}\right) \tag{2.10}$$

where $\phi_s^{(e)}$ is the dimensionless surface potential and κ is the Debye screening parameter:

$$\phi_s^{(e)} \equiv \frac{ze\psi_s^{(e)}}{kT} \tag{2.11}$$

$$\kappa^2 \equiv \frac{8\pi z^2 e^2 c_{2\infty}}{\epsilon kT}$$

$$z \equiv z_1 = -z_2 = z_3$$

The equilibrium Boltzmann distribution of the ionic species within the EDL can be written in the form

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$$c_i^{(e)}(x) = c_{i\infty} \exp[(-1)^i \phi^{(e)}(x)] \tag{2.12}$$

$$\phi^{(e)} \equiv \frac{ze\psi_e}{kT}$$

($i = 1, 2, 3$). Note that $\phi^{(e)}$ and $\phi_s^{(e)}$ thus defined are always positive, irrespective of whether the surfactant is cationic or anionic. The respective solution of the Poisson–Boltzmann equation for the equilibrium state gives the following distribution of electric potential, $\phi^{(e)}(x)$:[40]

$$\tanh\left(\frac{\phi^{(e)}(x)}{4}\right) = \tanh\left(\frac{\phi_s^{(e)}}{4}\right)\exp(-\kappa x) \tag{2.13}$$

2.3. Kinetics of Adsorption: Basic Equations. The adsorption of surfactant at the interface creates surface charge, which is increasing with the advance of the adsorption process. The charged interface repels the newly arriving surfactant molecules but attracts the conversely charged counterions; some counterions bind to the surfactant headgroups, decrease the surface charge density, and favor the adsorption of new surfactant molecules. The transport of the ith ionic species, with valency z_i ($=\pm1$, ±2, ...) and diffusion coefficient D_i, under the influence of electrical potential ψ, is described by the set of electrodiffusion equations:[1,17,28]

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial x}\left(\frac{\partial c_i}{\partial_x} + \frac{z_i e}{kT} c_i \frac{\partial \psi}{\partial x}\right) \tag{2.14}$$

$$x > 0, \qquad t > 0, \qquad i = 1, 2, 3$$

As before, the indices $i = 1$, 2, and 3 denote the surfactant ion, the counterion, and the co-ion, respectively; c_i is the bulk concentration of the ith ion, which depends on time t and the distance x to the interface. The second term in parentheses in eq 2.14, the so-called "electromigration" term, accounts for the effect of electric field on diffusion. The electric potential ψ is related to the bulk charge density through the known Poisson equation

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi e}{\epsilon}[z_1 c_1 + z_2 c_2 + z_3 c_3] \tag{2.15}$$

We recall that there are two adsorbing species: surfactant ions and counterions (the co-ions due to the salt do not adsorb: $\Gamma_3 = 0$). The interfacial mass balance relates the increase of the adsorption with the supply of ions by the electrodiffusion flux:[1,17,28]

$$\frac{d\Gamma_i}{dt} = D_i\left(\frac{\partial c_i}{\partial x} + \frac{z_i e}{kT}c_i \frac{\partial \psi}{\partial x}\right) \tag{2.16}$$

$$x = 0, \qquad t > 0$$

$i = 1$, 2. Note that the supply of surfactant ions to the interface is promoted by the gradient of concentration, ∇c_1, but it is opposed by the gradient of electric field, $\nabla \psi$. The two effects compensate each other in such a way that the effect of ∇c_1 is slightly predominant (otherwise, there would not be surfactant adsorption). For the conversely charged counterions these tendencies have the opposite direction with a predominant effect of $\nabla \psi$. In addition, the electroneutrality condition implies

$$\int_0^\infty (z_1 c_1 + z_2 c_2 + z_3 c_3)\,dx + z_1 \Gamma_1 + z_2 \Gamma_2 = 0 \tag{2.17}$$

The *boundary* conditions in the bulk of solution ($x \rightarrow \infty$)

are

$$c_i(\infty,t) = c_{i\infty}, \qquad i = 1, 2, 3, \qquad \psi(\infty,t) = 0 \quad (2.18)$$

The difference between our previous paper, ref 39, and the present paper lies in the *initial* conditions: these two papers are devoted, respectively, to the cases of small and large initial deviation from equilibrium. In section 2.4 we summarize the results from ref 39 for the case of *small* deviations. As mentioned previously, our aim in the present paper is to derive counterparts of the respective equations for the case of *large* deviations and to compare the results for these two different cases.

2.4. Small Initial Deviation from Equilibrium. The respective initial condition (for $t = 0$) reads[39]

$$c_i(x,0) = \begin{cases} c_{is}^{(0)} \text{ at } x = 0, \\ c_i^{(e)}(x) \text{ at } x > 0; \end{cases} \qquad i = 1, 2, 3 \quad (2.19a)$$

$$(c_{is}^{(e)} - c_{is}^{(0)}) \ll c_{is}^{(e)} \qquad (2.19b)$$

where $c_i^{(e)} = c_i^{(e)}(x)$ depends on x due to the formation of EDL in a vicinity of the interface, cf. eqs 2.12 and 2.13; $c_{is}^{(0)}$ is the initial concentration of the ionic species in the subsurface layer of the solution; $c_{is}^{(0)}$ is different from the respective equilibrium value, $c_{is}^{(e)} \equiv c_i^{(e)}(0)$, because of the initial interfacial perturbation. For *small* deviations from equilibrium, $\Delta c_{is} \ll c_{is}^{(e)}$, the adsorption can be expressed as a truncated series expansion:

$$\Delta\Gamma_i(t) \equiv \Gamma_i(t) - \Gamma_i^{(e)} \approx \left(\frac{\partial\Gamma_i}{\partial c_{1s}}\right)^{(e)} \Delta c_{1s}(t) + \left(\frac{\partial\Gamma_i}{\partial c_{2s}}\right)^{(e)} \Delta c_{2s}(t)$$
$$(2.20)$$
$$i = 1, 2$$

As usual, the subscript "s" denotes subsurface concentration and the superscript "e" refers to the equilibrium state. As mentioned earlier, analytical results for the long-time asymptotics of adsorption and surface tension have been obtained in ref 39 without making simplifications of the physical model. Below we list the results and the used notation, which will be helpful for comparison with the case of large deviation (the subject of the present study). The long-time asymptotics of the adsorption relaxation, derived on the basis of eqs 2.14−2.20, is

$$\frac{\Delta\Gamma_i(t)}{\Delta\Gamma_i(0)} \equiv \frac{\Gamma_i(t) - \Gamma_i^{(e)}}{\Gamma_i(0) - \Gamma_i^{(e)}} = \left(\frac{\tau_i}{\pi t}\right)^{1/2} \qquad (2.21)$$
$$t \to \infty, \qquad i = 1, 2$$

where the adsorption relaxation time τ_i is defined as follows:[39]

$$\tau_i = \frac{1}{\kappa^2}\left(g_{i1}G_1(1) + \frac{2q}{p}g_{i2} + gG_2(1)\right)^2 \qquad (2.22)$$

small deviations

$i = 1, 2$, where

$$g \equiv g_{11}g_{22} - g_{12}g_{21}, \qquad g_{ji} \equiv \kappa\left(\frac{\partial\Gamma_j}{\partial c_{is}}\right)^{(e)} \quad (2.23)$$

$$i,j = 1, 2$$

$$p \equiv 1 + \zeta^2 + (g_{11} - g_{21})\eta\zeta^3 + (g_{22} - g_{12})/\zeta \qquad (2.24)$$

$$h \equiv \left(\frac{1-\eta}{D_1} + \frac{\eta}{D_3}\right)^{1/2} \qquad (2.25)$$

$$q \equiv \frac{1}{2^{1/2}}\left(\frac{\eta}{D_1} + \frac{1}{D_2} + \frac{1-\eta}{D_3}\right)^{1/2}$$

$$\zeta = \exp(-\phi_s^{(e)}/2) \qquad \eta \equiv \frac{c_{1\infty}}{c_{2\infty}} \qquad (2.26)$$

$$G_1(\lambda) = [2\eta\lambda q + (1-\eta)(1+\zeta^2)h]\frac{\zeta^2}{p} \qquad (2.27)$$

$$G_2(\lambda) \equiv [2\eta\lambda q + (1-\eta)h]\frac{\zeta}{p}$$

η expresses the fraction of the surfactant ions into the total ionic strength of the solution, cf. eq 2.8; λ is a dimensionless parameter, whose value is 1 in eq 2.22. The above algebraic equations allow one to calculate the relaxation times of surfactant and counterion adsorption, τ_1 and τ_2, using eq 2.22. To obtain explicit expressions for the coefficients g_{ij}, the Stern isotherm for counterion adsorption

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_{st}c_{2s}}{1 + K_{st}c_{2s}} \qquad (2.28)$$

can be used, where K_{st} is a constant; see ref 34 for details. Thus the following expressions have been obtained:[39]

$$g_{21} = \frac{\Gamma_2}{\Gamma_1}g_{11}, \qquad g_{12} = \frac{\Gamma_2c_{1s}}{\Gamma_1c_{2s}}g_{11} \qquad (2.29)$$

$$g_{22} = \frac{\Gamma_2^2c_{1s}}{\Gamma_1^2c_{2s}}g_{11} + \frac{\kappa\Gamma_2^2}{K_{st}\Gamma_1c_{2s}^2} \qquad (2.30)$$

$$g_{11} = \frac{\kappa\Gamma_1}{c_{1s}J_{\Gamma1}}, \qquad J_{\Gamma1} \equiv \frac{E_G}{kT\Gamma_1} \qquad (2.31)$$

Here $E_G \equiv -\Gamma_1(\partial\sigma/\partial\Gamma_1)_T$ is the Gibbs (surface) elasticity. Expressions for E_G, corresponding to various adsorption isotherms, are listed in Table 1; Γ_∞, m, and β are constant parameters; for details see ref 34 and Table 1 in ref 17. The result for the long-time asymptotics of the surface tension relaxation (small deviations from equilibrium) is

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} \equiv \frac{\sigma(t) - \sigma^{(e)}}{\sigma(0) - \sigma^{(e)}} = \left(\frac{\tau_\sigma}{\pi t}\right)^{1/2} \qquad (2.32)$$

$$t \to \infty$$

where the characteristic relaxation time is determined by the expression (see Appendix B)

$$\tau_\sigma^{1/2} = (1 + w)\tau_1^{1/2} - w\tau_2^{1/2} - \frac{2qw}{\kappa}\tanh\frac{\phi_s^{(e)}}{4} \qquad (2.33)$$

small deviations

$$w \equiv \frac{2}{J_{\Gamma1}}\tanh\frac{\phi_s^{(e)}}{2} \qquad (2.34)$$

where, as usual, $\phi_s^{(e)}$ is the equilibrium value of the

Table 1. Gibbs (Surface) Elasticity E_G for Various Surface Tension Isotherms

type of isotherm	expression for E_G
Henry	$E_G = kT\Gamma_1$
Freundlich	$E_G = kT\dfrac{\Gamma_1}{m}$
Langmuir	$E_G = kT\Gamma_1\dfrac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1}$
Volmer	$E_G = kT\Gamma_1\dfrac{\Gamma_\infty{}^2}{(\Gamma_\infty - \Gamma_1)^2}$
Frumkin	$E_G = kT\Gamma_1\left(\dfrac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} - \dfrac{2\beta\Gamma_1}{kT}\right)$
van der Waals	$E_G = kT\Gamma_1\left[\dfrac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2} - \dfrac{2\beta\Gamma_1}{kT}\right]$

dimensionless surface potential, cf. eq 2.11, and the relaxation times τ_1 and τ_2 are given by eq 2.22. Note that for nonionic surfactants the relaxation time is the same for adsorption and surface tension ($\phi_s^{(e)} = 0$, $\tau_\sigma = \tau_1$), whereas for ionic surfactants these relaxation times are different: usually $\tau_\sigma > \tau_1 > \tau_2$. The difference between these three relaxation times (sometimes by order of magnitude) originates from the presence of diffuse electric double layer; the increase of salt concentration in the solution suppresses the diffuse EDL and decreases the differences between τ_σ, τ_1 and τ_2, see section 7 for details.

The experiment shows that for long times $\sigma(t) - \sigma^{(e)} \propto 1/t^{1/2}$ irrespective of whether the initial deviation from equilibrium is large or small.[7,49−51] Our aim below is to derive theoretical expressions for the relaxation times τ_1, τ_2, and τ_σ in the case of *large* initial perturbations and to check how much they differ from the above expressions, eqs 2.22 and 2.33, obtained assuming *small* initial perturbations.

3. Large Initial Deviation from Equilibrium

3.1. Formulation of the Problem. Let us consider a sudden creation of a new interface; for example, this could happen when surfactant solution is poured in the cell for surface tension measurements. In the very beginning the interface is assumed to be free of adsorbed surfactant ions, and consequently, surface charge and electric double layer are absent; the concentrations of the ionic species in the initial moment $t = 0$ are uniform and equal to the bulk concentrations $c_{i\infty}$

$$c_i(x,0) \equiv c_{i\infty}, \qquad \Gamma_i(0) \equiv 0, \qquad \psi(x,0) \equiv 0 \quad (3.1)$$

($i = 1, 2, 3$). Note that the initial condition 3.1 is essentially different from the initial condition 2.19a, which corresponds to the existence of an equilibrium double layer, $c_i(x,0) = c_i^{(e)}(x)$ for $x > 0$, at the initial moment; see eq 2.12.

After the creation of a new interface of the initially homogeneous solution, the latter is allowed to relax without any further external disturbance. Adsorption of surfactant ions and binding of counterions spontaneously take place at the initially "bare" interface, which gives rise to diffusion transport of the respective solutes. Thus

(49) Joos, P.; van Hunsel, L. *Colloids Surf.* **1988**, *33*, 99.
(50) Geeraerts, G. Ph.D. Thesis, Department of Chemistry, University of Antwerpen, 1994.
(51) Geeraerts, G.; Joos, P. *Colloids Surf., A* **1993**, *75*, 243.

the surface electric charge appears and the electric double layer develops and relaxes. The evolution of the system can be described by combining the initial condition 3.1 with eqs 2.14−2.18. As in our previous studies,[39,52] it is convenient to introduce dimensionless parameters, defined as follows

$$\Phi \equiv \frac{ze}{kT}(\psi - \psi^{(e)}), \qquad y \equiv \kappa x, \qquad \tau \equiv D_1\kappa^2 t \quad (3.2)$$

$$C_i \equiv \frac{c_i - c_i^{(e)}}{c_{2\infty}}, \qquad d_i \equiv \frac{D_i}{D_1} \quad (3.3)$$

$$i = 1, 2, 3$$

where Φ and C_i are dimensionless perturbations of the electric potential and the concentrations of the ionic species; y and τ are dimensionless distance and time. With the help of eqs 2.12, 3.2, and 3.3 we represent the electrodiffusion equation 2.14 and the Poisson equation 2.15 in terms of the dimensionless variables

$$\frac{\partial C_i}{\partial \tau} = (-1)^i d_i \frac{\partial}{\partial y}\left[(-1)^i \frac{\partial C_i}{\partial y} - C_i \frac{d\phi^{(e)}}{dy} - \eta_i \right.$$
$$\left. \exp((-1)^i\phi^{(e)})\frac{\partial \Phi}{\partial y} - C_i \frac{\partial \Phi}{\partial y}\right] \quad (3.4)$$

$$\eta_1 = \eta, \qquad \eta_2 = 1, \qquad \eta_3 = 1 - \eta \quad (3.5)$$

$$\frac{\partial^2 \Phi}{\partial y^2} = \frac{1}{2}(C_2 - C_1 - C_3) \quad (3.6)$$

$i = 1, 2, 3$; η is defined by eq 2.26; in eq 3.6 we have taken into account that $z \equiv z_1 = -z_2 = z_3$. Next, using the initial condition, eq 3.1, we apply a Laplace transformation with respect to time; thus we bring eqs 3.4 and 3.6 into the form

$$s\tilde{C}i - C_{i0}(y) = \frac{\partial J_i}{\partial y} \quad (3.7)$$

$$i = 1, 2, 3$$

$$s\frac{\partial \tilde{\Phi}}{\partial y} = \frac{1}{2}(J_2 - J_1 - J_3) - \frac{d\phi^{(e)}}{dy} \quad (3.8)$$

where $\tilde{C}_i(x,s)$ and $\tilde{\Phi}(x,s)$ are the Laplace images of $C_i(x,\tau)$ and $\Phi(x,\tau)$, respectively, $C_{i0} \equiv C_i|_{t=0}$. To derive eq 3.8, we first substituted eq 3.7 into the Laplace transform of eq 3.6, and then integrated with respect to y. With the help of eqs 2.8, 2.12, and 3.3 one obtains a

$$C_{i0} = \eta_i[1 - \exp((-1)^i\phi^{(e)})] \quad (3.9)$$

$$i = 1, 2, 3$$

the Laplace images of the electrodiffusion fluxes, J_i, are defined by the expressions

$$J_i = (-1)^i d_i\left[(-1)^i\frac{\partial \tilde{C}_i}{\partial y} - \tilde{C}_i \frac{d\phi^{(e)}}{dy} - \right.$$
$$\left. \eta_i \exp((-1)^i\phi^{(e)})\frac{\partial \tilde{\Phi}}{\partial y} - N_i\right] \quad (3.10)$$

where N_i is the Laplace image of the nonlinear term in

(52) Vlahovska, P. M.; Danov, K. D.; Mehreteab, A.; Broze, G. *J. Colloid Interface Sci.* **1997**, *192*, 194.

eq 3.4

$$N_i \equiv L\left[C_i \frac{\partial \Phi}{\partial y}\right], \qquad i = 1, 2, 3 \qquad (3.11)$$

Here and hereafter $L[f]$ symbolizes Laplace transform of the function $f(t)$.

3.2. Long-Time Asymptotics and Iterations. The set of eqs 3.7 and 3.8 (along with eq 3.10) has no general analytical solution. Our purpose is to find an *asymptotic* analytical solution for long times $t \to \infty$, i.e., for $s \to 0$. For that purpose we will use the following iteration procedure. First we assume that for $s \to 0$ the nonlinear term, N_i, in eq 3.10 can be neglected. Thus, in first approximation we obtain a linear set of four differential equations, these are eqs 3.8 and 3.10 (the latter for $i = 1,2,3$) for determining the four unknown functions J_1, J_2, J_3, and $\tilde{\Phi}$ (the functions $\tilde{C}_i$ are expressed by means of eq 3.7). Solving this linear set of equations, we determine the asymptotic behavior of the linear terms in the right-hand side of eq 3.10 for $s \to 0$ (see Appendix A, eqs A.33 and A.36)

$$\tilde{C}_i \propto \frac{\partial \tilde{C}_i}{\partial y} \propto \frac{\partial \tilde{\Phi}}{\partial y} \propto \frac{1}{s^{1/2}} \qquad (3.12)$$

$$\text{for } s \to 0$$

Using the latter results for the linear terms and eq 3.11, one determines the asymptotic behavior of the nonlinear terms, N_1, N_2, and N_3 (Appendix A, eq A.38)

$$\lim_{s \to 0} (N_i / \tilde{C}_i) = a \lim_{s \to 0} (s^{1/2} \ln s) = 0 \qquad (3.13)$$

$$i = 1, 2, 3$$

where a is a constant independent of s. The latter result shows that our iteration procedure (neglecting the nonlinear terms in first approximation) is self-consistent. Indeed, eqs 3.12 and 3.13 demonstrate that the nonlinear term N_i in eq 3.10 is really of higher order for $s \to 0$, as compared to the linear terms. Moreover, the fact that the leading terms in the asymptotics of the perturbation are $\propto 1/s^{1/2}$ for $s \to 0$ (see eq 3.12) implies that the perturbation decays as $1/t^{1/2}$ for $t \to \infty$, which is in agreement with the experimental observations.[1,50,51] These facts give us the confidence that the used iteration procedure is correct.

3.3. Solution of the Linear Nonhomogeneous Problem. We will restrict our calculations to the first approximation, which gives the leading term in the asymptotics for long times ($t \to \infty$). As already mentioned, neglecting the nonlinear terms, one obtains a linear set of equations, which is *nonhomogeneous* because of the terms $C_{i0}(y)$ and $d\phi^{(e)}/dy$ in eqs 3.7 and 3.8. This is the main difference with the case of small initial deviations from equilibrium considered in ref 39, where such non-homogeneous terms do not appear. As known,[53] the solution of a linear nonhomogeneous system of equations can be searched as a sum of the general solution of the homogeneous problem, $J_i^{(h)}$, and a specific solution of the nonhomogeneous problem, $J_i^{(nh)}$:

$$J_i(y) = J_i^{(h)}(y) + J_i^{(nh)}(y) \qquad (i = 1, 2, 3) \qquad (3.14)$$

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(53) Kamke, E. *Differentialgleichungen: Lösungsmethoden und Lösungen*; Akademische Verlagsgesellschaft: Leipzig, 1959.

$$\tilde{C}_i(y) = \tilde{C}_i^{(h)}(y) + \tilde{C}_i^{(nh)}(y) \qquad (i = 1, 2, 3) \qquad (3.15)$$

$$\tilde{\Phi}(y) = \tilde{\Phi}^{(h)}(y) + \tilde{\Phi}^{(nh)}(y) \qquad (3.16)$$

A specific solution of the nonhomogeneous problem is

$$J_i^{(nh)} = 2\eta_i[1 - \exp((-1)^i \phi^{(e)}/2)] + O(s) \qquad (3.17)$$

$$\tilde{\Phi}^{(nh)} = O(s) \qquad (3.18)$$

$\tilde{C}_i^{(nh)}$ can be determined by substitution of eqs 3.17 and 3.18 into the linearized eq 3.10. With the help of eqs 3.9 and 3.14−3.16, one can verify that eqs 3. 17 and 3.18 satisfy eqs 3.7 and 3.8; one is to have in mind that the term $s\tilde{C}_i^{(nh)}$ is of higher order for $s \to 0$ and that[40]

$$d\phi^{(e)}/dy = -2 \sinh(\phi^{(e)}/2) \qquad (3.19)$$

The linear *homogeneous* problem is identical with that solved in ref 39; the solution for $s \to 0$ is[39]

$$J_1^{(h)} = \eta(-A_1 F_1 + A_2 F_2) + A_3 F_3 + O(s) \qquad (3.20)$$

$$J_2^{(h)} = (A_1 F_1 + A_2 F_2) \exp(\phi^{(e)}) + O(s) \qquad (3.21)$$

$$J_3^{(h)} = (1 - \eta)(-A_1 F_1 + A_2 F_2) - A_3 F_3 + O(s) \qquad (3.22)$$

where A_1, A_2, and A_3 are constants, which are to be determined from the boundary conditions, and F_1, F_2, and F_3 are known functions of y and s:[39]

$$F_i = \frac{1 + \exp(-\phi^{(e)}) + 2\beta_i \exp(-\phi^{(e)}/2)}{1 + \exp(-\phi_s^{(e)}) + 2\beta_i \exp(-\phi_s^{(e)}/2)} \exp(-\beta_i y) \qquad (3.23)$$

$$i = 1, 2$$

$$F_3 = \frac{1 + 2\beta_3 \exp(-\phi^{(e)}/2)}{1 + 2\beta_3 \exp(-\phi_s^{(e)}/2)} \exp(-\beta_3 y) \qquad (3.24)$$

where $\phi^{(e)}$ depends on y, see eqs 2.13 and 3.2; the other parameters are

$$\beta_1 \equiv 1, \qquad \beta_2 = q(sD_1)^{1/2}, \qquad \beta_3 = h(sD_1)^{1/2} \qquad (3.25)$$

q and h are defined by eq 2.25.

4. Adsorption Relaxation after a Large Initial Deviation

4.1. Adsorption Relaxation Times. First, let us define the deviations of the adsorptions and subsurface concentrations from their equilibrium values as

$$\Delta\Gamma_i(t) \equiv \Gamma_i(t) - \Gamma_i^{(e)} \quad \text{and} \quad \Delta c_{is}(t) \equiv c_{is}(t) - c_{is}^{(e)} \qquad (4.1)$$

where, as usual, the subscript "s" denotes the values of the concentrations in the subsurface, i.e., at $y = 0$. Irrespective of the fact that we consider large *initial* deviations, for $t \to \infty$ the perturbation relaxes; then both $\Delta\Gamma_i(t)$ and $\Delta c_{is}(t)$ become small quantities, and the truncated expansion, eq 2.20, can be applied. In view of eqs 2.23, 3.2, and 3.3 the Laplace transform of eq 2.20 can be presented in the form

$$\Delta\tilde{\Gamma}_i = \frac{c_{2\infty}}{\kappa}(g_{i1}\tilde{C}_{1s} + g_{i2}\tilde{C}_{2s}) \tag{4.2}$$

$$i = 1, 2$$

where $\Delta\tilde{\Gamma}_i \equiv \boldsymbol{L}[\Delta\Gamma_i]$. Next we apply a Laplace transformation to the boundary condition 2.16 taking into account eqs 3.1−3.3, 3.10, and 4.1:

$$s\Delta\tilde{\Gamma}_i + \Gamma_i^{(e)} = \frac{c_{2\infty}}{\kappa}J_i|_{y=0} \tag{4.3}$$

$$i = 1, 2$$

Further, we combine eqs 4.2 and 4.3 to eliminate $\Delta\tilde{\Gamma}_i$:

$$s(g_{i1}\tilde{C}_{1s} + g_{i2}\tilde{C}_{2s}) + \frac{\kappa}{c_{2\infty}}\Gamma_i^{(e)} = J_i|_{y=0} \tag{4.4}$$

$$i = 1, 2$$

We recall that J_1 and J_2 are the Laplace transforms of the electrodiffusion fluxes of surfactant ions and counterions, respectively. Since co-ions do not adsorb (see eq 2.9), one obtains an additional boundary condition:

$$J_3|_{y=0} = 0 \tag{4.5}$$

Equations 4.4 and 4.5 represent a set of three equations for determining the three unknown constants of integration, A_1, A_2, and A_3; see eqs 3.20−3.22. The mathematical transformations are outlined in Appendix A. The final result for the long-time asymptotics of the adsorption relaxation reads

$$\frac{\Gamma_i^{(e)} - \Gamma_i(t)}{\Gamma_1^{(e)}} = \left(\frac{t_i}{\pi t}\right)^{1/2} \tag{4.6}$$

$$t \to \infty, \quad i = 1, 2$$

where t_1 and t_2 are constant parameters, defined by the expression

$$t_i = \frac{1}{\kappa^2}\left(g_{i1}G_1(\lambda) + \frac{2\lambda q}{p}g_{i2} + gG_2(\lambda)\right)^2 \tag{4.7}$$

$$i = 1, 2 \text{ (large deviations)}$$

$$\lambda = \frac{1 + \zeta\Gamma_2^{(e)}/\Gamma_1^{(e)}}{1 + \zeta} \tag{4.8}$$

see eqs 2.23−2.27 for the notation. In fact, t_1 and t_2 are the characteristic relaxation times of surfactant adsorption and counterion binding in the considered case of *large* initial deviations from equilibrium. It is worthwhile noting that t_1 and t_2 depend on equilibrium properties of the surfactant solution and its surface, and on the diffusivities of the solutes. We recall that the coefficients g_{ij} ($i,j = 1, 2$) can be calculated by means of eqs 2.29−2.31 and Table 1.

4.2. Discussion. The expressions for the surfactant and counterion adsorption relaxation times in the case of *large* initial deviations, t_1 and t_2, and in the case of *small* initial deviations, τ_1 and τ_2, are to be compared. If $\lambda = 1$, eq 4.7 for t_1 and t_2 reduces to eq 2.22 for τ_1 and τ_2, i.e.

$$\tau_i = t_i|_{\lambda=1} \quad (i = 1, 2) \tag{4.9}$$

If the surfactant concentration is not extremely low, then the surface potential $\phi_s^{(e)}$ is high enough to have $\zeta \ll 1$; see

eq 2.26 and Figure 5 in ref 34. Having in mind that $\Gamma_2^{(e)}/\Gamma_1^{(e)} \leq 1$, we substitute $\zeta \ll 1$ in eq 4.8 and obtain $\lambda \approx 1$. Consequently, the values of t_i and τ_i are expected to be not so different. In other words, the adsorption relaxation times are not too sensitive to the initial condition: large or small deviation from equilibrium. Numerical results for an experimental system are shown in section 7.2 below.

Let us consider some special cases of eq 4.7. In the limiting case of *high concentration of added salt* one has $\eta \to 0$, $\zeta \to 1$, and $\lambda \to 1$; in this limit eq 4.6 reduces to

$$t_i = \tau_i = \left[\frac{2g_{i1} + g}{p}\left(\frac{1}{D_1}\right) + \frac{g_{i2}}{D_2} + \left(\frac{2}{D_2} + \frac{2}{D_3}\right)^{1/2}\right]^2 \tag{4.10}$$

$$i = 1, 2$$

where $p = 2 + g_{22} - g_{12}$. In the case of *nonionic* surfactant there are no counterions and counterion adsorption. Then $\Gamma_2 \equiv 0$ and consequently $g_{12} = g_{21} = g_{22} = g = 0$ and $p = 0$; see eqs 2.23 and 2.24. In such a case from eqs 2.23 and 4.10 one obtains the known expression for nonionic surfactants

$$t_1 = \tau_1 = \frac{1}{D_1}\left(\frac{\partial\Gamma_1}{\partial c_1}\right)^2 \tag{4.11}$$

cf. eq 1.2. The comparison between 4.10 and 4.11 shows that even for high salt concentrations the expressions for the relaxation of adsorption of *ionic* and *nonionic* surfactants are different. This is due to the fact that in the case of ionic surfactant there is (i) an interplay of surfactant adsorption and counterion binding (accounted for by g_{12}, g_{21}, and g_{22}) and (ii) the counterions and co-ions also take part in the diffusion process (not only D_1, but also D_2 and D_3 enter eqs 4.7 and 4.10).

In the limiting case of surfactant solution at *low concentration of added salt* one has $\eta \to 1$ (see eq 2.26) and then eq 4.7 reduces to

$$t_i = \frac{2\lambda^2}{\kappa^2 p^2}\left(\frac{1}{D_1} + \frac{1}{D_2}\right)(\zeta^2 g_{i1} + g_{i2} + \zeta g)^2 \tag{4.12}$$

$$i = 1, 2$$

In this case the counterion diffusion coefficient D_2 and the coefficients g_{12}, g_{21}, g_{22}, and g take place in eq 4.12 because the dissociation of the surfactant itself (in the absence of added salt) also gives counterions, which take part in the electrodiffusion process and bind to the surfactant adsorption layer.

5. Relaxation of Surface Tension after a Large Initial Deviation

5.1. Characteristic Relaxation Time. As noted in section 2.1, the surface tension of an ionic surfactant solution can be expressed as a sum of contributions from the adsorption and diffuse layers, $\sigma = \sigma_a + \sigma_d$, where σ_d is defined by eq 2.6 and σ_a is given by the equation[34]

$$\sigma_a = \sigma_0 - kTJ \tag{5.1}$$

σ_0 is the surface tension of the pure solvent (water) and J denotes the integral

$$J = \int_0^{c_{1s}}\Gamma_1(\hat{c}_{1s}, c_{2s})\frac{d\hat{c}_{1s}}{\hat{c}_{1s}} \tag{5.2}$$

which accounts for the effect of surfactant adsorption; c_{1s}

Table 2. Expressions for J Corresponding to Various Adsorption Isotherms

type of adsorption isotherm	expression for the integral J (eq 5.2)
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	$J = \Gamma_\infty \Gamma_1/(\Gamma_\infty - \Gamma_1) - \beta\Gamma_1^2/(kT)$

and c_{2s} are the subsurface concentrations of surfactant ions and counterions defined by eq 2.2. The integral J is solved analytically for various types of adsorption isotherms.[34] The results are summarized in Table 2, where m is an empirical parameter in the Freundlich isotherm and β is an interaction parameter in the Frumkin and van der Waals isotherms; see ref 34 for details.

Next, we consider deviations of the surface tension from its equilibrium value

$$\Delta\sigma(t) = \Delta\sigma_a(t) + \Delta\sigma_d(t) \qquad (5.3)$$

where

$$\Delta\sigma_a(t) = \sigma_a(t) - \sigma_a^{(e)}, \qquad \Delta\sigma_d(t) = \sigma_d(t) - \sigma_d^{(e)} \quad (5.4)$$

as before, the superscript "e" denotes equilibrium values. In particular, $\sigma_d^{(e)}$ can be obtained by a substitution of eq 3.19 into eq 2.6 and integration

$$\sigma_d^{(e)} = -8kT\frac{c_{2\infty}}{\kappa}[\cosh(\phi_s^{(e)}/2) - 1] \qquad (5.5)$$

Equation 5.5 gives the is the contribution of the electric double layer to the *equilibrium* surface tension.[54,44,34,30] In view of eqs 5.1 and Table 2, for small deviations from equilibrium one obtains

$$\Delta\sigma_a(t) = -kT\, J_{\Gamma_1}\Delta\Gamma_1(t) \qquad (5.6)$$

where

$$J_{\Gamma_1} \equiv \left(\frac{\partial J}{\partial\Gamma_1}\right)_T$$

see also eqs 4.1 and 5.4. One could verify that the differentiation of the expressions for J in Table 2, in accordance with eq 5.6, gives the same J_{Γ_1} as eq 2.31 and Table 1. In addition, for small deviations from equilibrium eq 2.6, along with the definitions of $\phi^{(e)}$ and Φ in eqs 2.12 and 3.2, yields

$$\Delta\sigma_d(t) = -\frac{4}{\kappa}kTc_{2\infty}\int_0^\infty \frac{d\phi^{(e)}}{dy}\frac{\partial\Phi}{\partial y}\,dy \qquad (5.7)$$

Using the derived expressions for the long-time relaxation of the surfactant solution after an initially large deviation, one obtains (see Appendix B)

$$\Delta\sigma_d(t) = -kTJ_{\Gamma_1}w\left(\Delta\Gamma_1(t) - \Delta\Gamma_2(t) + \frac{2q\lambda\Gamma_1^{(e)}}{\kappa(\pi t)^{1/2}}\tanh\frac{\phi_s^{(e)}}{4}\right)$$
$$(5.8)$$
$$t \to \infty$$

where w and λ are defined by eqs 2.34 and 4.8. Further,

(54) Davies, J. T. *Proc. R. Soc. London, Ser. A* **1951**, *208*, 224.

we substitute eqs 5.6 and 5.8 into eq 5.3

$$\Delta\sigma(t) = -kTJ_{\Gamma_1}\Bigg((1 + w)\Delta\Gamma_1(t) - w\Delta\Gamma_2(t) + \frac{2qw\lambda}{\kappa(\pi t)^{1/2}}\Gamma_1^{(e)}\tanh\frac{\phi_s^{(e)}}{4}\Bigg) \quad (5.9)$$

for $t \to \infty$. Finally, we substitute eq 4.6 into eq 5.9 and use eqs 2.31 and 4.1 to derive

$$\Delta\sigma(t) \equiv \sigma(t) - \sigma^{(e)} = E_G\left(\frac{t_\sigma}{\pi t}\right)^{1/2} \qquad (5.10)$$
$$t \to \infty$$

where the characteristic *relaxation time of surface tension*, after a *large* initial deviation from equilibrium, is defined by the expression

$$t_\sigma^{1/2} = (1 + w)t_1^{1/2} - wt_2^{1/2} - \frac{2qw\lambda}{\kappa}\tanh\frac{\phi_s^{(e)}}{4} \quad (5.11)$$

large deviations

(explanations about the calculation of t_σ and $\sigma(t)$ can be found in section 7 below). Comparing eqs 2.33, 4.9, and 5.11, one obtains that the characteristic relaxation times of surface tension after *small* and *large* initial deviations from equilibrium, τ_σ and t_σ, are connected with the following simple relationship

$$\tau_\sigma = t_\sigma|_{\lambda=1} \qquad (5.12)$$

In the limiting case of *nonionic* surfactant ($\phi_s^{(e)} \to 0$) one obtains $t_\sigma \to t_1$, where t_1 is given by eq 4.11. Then combining eq 4.11 with the definition of E_G and the Gibbs adsorption eq 2.3, one can verify that the long-time asymptotics of surface tension, eq 5.10, reduces to the Hansen formula, eq 1.5, as should be expected.

5.2. Slope of the Experimental Plot σ vs $t^{-1/2}$. Experimentally, data about $\sigma(t)$ are usually obtained by measuring the relaxation of surface tension of an initially disturbed surfactant solution. The data are then plotted as σ vs $t^{-1/2}$; if t is large enough, the latter plot represents a straight line whose intercept gives the equilibrium surface tension, $\sigma^{(e)}$, and whose slope characterizes the kinetics of adsorption. Equations 2.32 and 5.10 show that the *slope* of the experimental plot σ vs $t^{-1/2}$ for $t \to \infty$ is to be identified with

$$S_s = [\sigma(0) - \sigma^{(e)}]\left(\frac{\tau_\sigma}{\pi}\right)^{1/2} \qquad \text{(small deviations)} \quad (5.13)$$

$$S_l = E_G\left(\frac{t_\sigma}{\pi}\right)^{1/2} \qquad \text{(large deviations)} \quad (5.14)$$

Here S_s and S_l denote the slope in the case of small and large initial deviations from equilibrium, respectively. Usually E_G is between 1 and 500 mN/m.[55,56] On the other hand, the difference $[\sigma(0) - \sigma^{(e)}]$ is expected to be much smaller insofar as eq 5.13 corresponds to small initial deviations from equilibrium. As discussed in section 4.2 one could expect that $\lambda \approx 1$ and then eq 5.12 yields $\tau_\sigma \approx t_\sigma$. Hence the main quantitative difference between S_s

(55) Li, B.; Joos, P.; Horozov, T. *Colloids Surf., A* **1995**, *94*, 85.
(56) Tian, Y.; Holt, R. G.; Apfel, R. *J. Colloid Interface Sci.* **1997**, *187*, 1.

and S_1 originates from the fact that $E_G \gg [\sigma(0) - \sigma^{(e)}]$; consequently, one could expect that $S_1 \gg S_s$.

It is worthwhile noting that in view of eqs 5.6–5.11 one can represent eq 5.14 as a sum of two contributions

$$S_1 = S_1^{(a)} + S_1^{(d)} \tag{5.15}$$

where

$$S_1^{(a)} + E_G(t_1/\pi)^{1/2} \tag{5.16}$$

is the contribution of the adsorbed surfactant ions and counterions, and

$$S_1^{(d)} = 2\Gamma_1^{(e)}kT\left(\left(\frac{t_1}{\pi}\right)^{1/2} - \left(\frac{t_2}{\pi}\right)^{1/2} - \frac{2q\lambda}{\kappa}\tanh\frac{\phi_s^{(e)}}{4}\right)\tanh\frac{\phi_s^{(e)}}{2} \tag{5.17}$$

is the contribution of the diffuse electric double layer (see Figure 1). The numerical values of $S_1^{(a)}$ and $S_1^{(d)}$ are compared in section 7 below.

In summary, there are two parameters, which characterize the relaxation rate of surface tension. These are τ_σ and S_s in the case of small initial deviations and t_σ and S_1 in the case of large initial deviations. The parameters τ_σ, t_σ, and S_1 are related to diffusion coefficients and equilibrium thermodynamic properties of the solution, whereas S_s depends also on the value of the dynamic surface tension in the initial moment, $\sigma(0)$; the latter can be different in different measurements with the same solution. The values of τ_σ and t_σ are close to each other (insofar as $\lambda \approx 1$), which means that the relaxation time is not sensitive to the magnitude of the initial perturbation. On the other hand, S_1 is expected to be much larger than S_s. In section 7 below we present values of τ_σ, t_σ, and S_1 calculated from experimental equilibrium surface tension isotherms.

6. Elasticity of Adsorption Monolayers from Ionic Surfactants

6.1. Gibbs Elasticity for Soluble Surfactants. The definition of Gibbs (surface) elasticity of adsorption monolayers from *ionic* surfactants deserves a special discussion. The physical concept of surface elasticity is the most transparent for monolayers of *insoluble* surfactants, for which it has been initially introduced by Gibbs.[57] The increments $\Delta\sigma$ and $\Delta\Gamma_1$ in the definition of Gibbs elasticity

$$E_G = -\Gamma_1 \lim_{\Delta\Gamma_1 \to 0} \frac{\Delta\sigma}{\Delta\Gamma_1} = \Gamma_1\left(\frac{\partial\sigma}{\partial\Gamma_1}\right)_T \tag{6.1}$$

correspond to variations in surface tension and adsorption during a real process of interfacial dilatation.

In the case of a soluble *nonionic* surfactant the detected increase of σ in a real process of interfacial dilatation can be a pure manifestation of surface elasticity only if the period of dilatation, Δt, is much shorter than the characteristic relaxation time of surface tension, $\Delta t \ll t_\sigma$. Otherwise the adsorption and the surface tension would be affected by the diffusion supply of surfactant molecules from the bulk of solution toward the expanding interface. The diffusion transport tends to reduce the increase of

surface tension upon dilatation, thus apparently rendering the interface less elastic and more fluid. The initial condition for the problem of adsorption kinetics involves an "instantaneous" ($\Delta t \ll t_\sigma$) dilatation of the interface;[58] see eqs 2.19 and 3.1. This "instantaneous" dilatation decreases the adsorptions Γ_i and the subsurface concentrations c_{is} of the species (the subsurface is presumed to be always in equilibrium with the surface), but the bulk concentrations $c_{i\infty}$ remain unaffected.[1,3,12,17] This initially created difference between c_{is} and $c_{i\infty}$ further triggers the diffusion process. Now, let us inspect closer how this approach is to be extended to the case of ionic surfactants.

6.2. Gibbs Elasticity for Ionic Surfactants. As noted in section 2.1, in the case of *ionic* surfactant a nonuniform diffuse electric double layer (EDL) is formed in the vicinity of the interface. The main question is whether the electric field in the EDL should be affected by the "instantaneous" dilatation of the interface, $\Delta\Gamma_1$, which is involved in the definition of E_G; see eq 6.1. This problem has been examined in ref 39, and it has been established that a variation of the electric field during the initial instantaneous dilatation leads to results which are unacceptable from a theoretical viewpoint. This conclusion is related to the following two facts:

(i) The speed of propagation of the electric signals is much greater than the characteristic rate of diffusion.

(ii) Even a small initial variation in the surface charge density ρ_s immediately gives rise to an electric potential, which is linearly increasing with the distance from the interface (potential of a planar wall).

Thus a small initial perturbation of the interface would immediately affect the ions in the *whole* solution; of course, such an initial condition is physically unacceptable. In reality, a linearly growing electric field could not appear in an ionic solution, because a variation of the surface charge density would be immediately suppressed by exchange of counterions, which are abundant in the subsurface layer of the solution (see Figure 1). The theoretical equations suggest the same:[39] To have a mathematically meaningful initial condition of *small* perturbation for the diffusion problem, the initial dilatation must be carried out at constant surface charge density ρ_s (for details see the Appendix in ref 39). Thus we reach to the conclusion that the initial sudden interfacial dilatation, which is related to the definition of Gibbs elasticity of a soluble ionic surfactant, must be carried out at ρ_s = constant. From eq 2.7 one obtains

$$(\mathrm{d}\sigma)_{\rho_s} = (\mathrm{d}\sigma_a)_{\rho_s} + (\mathrm{d}\sigma_d)_{\rho_s} \tag{6.2}$$

where, as usual, σ_a and σ_d are the contributions of the adsorption and diffusion layers to the total interfacial tension, σ. An interfacial dilatation at constant ρ_s does not alter the diffuse part of the EDL, and consequently, $(\mathrm{d}\sigma_d)_{\rho_s} \equiv 0$; see eq 2.6. Since $\sigma_a = \sigma_0 - kTJ$ (see eq 5.1), the expressions for J in Table 2 show that σ_a depends only on Γ_1 at constant temperature. Then the definition of Gibbs elasticity of nonionic adsorption layers can be extended to ionic adsorption layers in the following way:

$$E_G \equiv -\Gamma_1\left(\frac{\partial\sigma}{\partial\Gamma_1}\right)_{T,\rho_s} = -\Gamma_1\left(\frac{\partial\sigma_a}{\partial\Gamma_1}\right)_T \tag{6.3}$$

ionic surfactant

The definition of Gibbs elasticity given by eq 6.3 corre-

(57) Gibbs, J. W. *The Scientific Papers of J. W. Gibbs*; Dover: New York, 1961; Vol. 1.

(58) Ozawa, A.; Minamisawa, A.; Sakai, K.; Takagi, K. *Jpn. J. Appl. Phys.* **1994**, *33*, L-1468.

sponds to an "instantaneous" ($\Delta t \ll t_\sigma$) dilatation of the *adsorption* layer (that contributes to σ_a) without affecting the *diffuse* layer and σ_d. The dependence of σ on Γ_1 for nonionic surfactants is the same as the dependence of σ_a on Γ_1 for ionic surfactants (see eq 5.1 and Table 2). Then eq 6.3 and Table 2 show that the expressions for E_G in Table 1 are valid for *both* nonionic and ionic surfactants. The effect of the surface electric potential on the Gibbs elasticity E_G of an ionic adsorption monolayer is implicit, through the equilibrium surfactant adsorption Γ_1, which depends on the electric properties of the interface. To illustrate this let us consider the case of a Langmuir adsorption isotherm for an *ionic* surfactant[34]

$$Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}, \qquad K \equiv K_1 + K_2 c_{2s} \qquad (6.4)$$

where K_1 and K_2 are constants (note that the constant in the Stern equation, eq 2.28, is $K_{st} = K_2/K_1$, see ref 34). Note that the above linear dependence of the adsorption parameter K on the subsurface concentration of counterions, c_{2s}, can be deduced from the equilibrium exchange reactions, which describe the adsorption of surfactant ions and counterions; see ref 38. Combining the respective expression from Table 1 with eq 6.4, we obtain $E_G = \Gamma_\infty kTKc_{1s}$. Further, with the help of eqs 2.2, 2.11, and 6.4, we derive

$$E_G = \Gamma_\infty kTKc_{1\infty}[K_1 \exp(-\phi_s^{(e)}) + K_2 c_{2\infty}] \qquad (6.5)$$

(for Langmuir isotherm)

Equation 6.5 reveals the effect of salt on E_G: when the salt concentration increases, $c_{2\infty}$ also increases, whereas the (dimensionless) surface potential $\phi_s^{(e)}$ decreases (see Figure 5 in ref 34); then eq 6.5 predicts an increase of E_G with the rise of salt concentration (numerical illustration of this prediction is given in section 7.3).
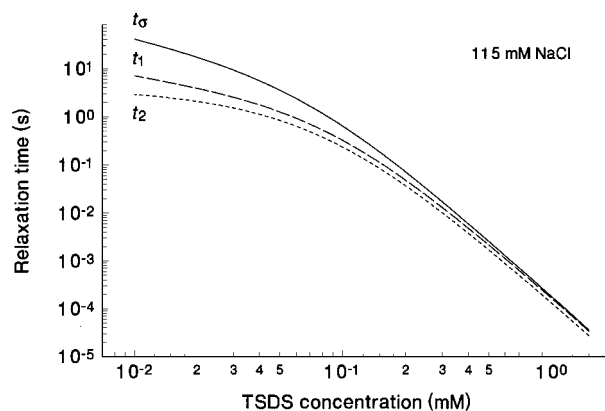
7. Numerical Results and Discussion

7.1. Parameters and Equations. The relaxation times of surfactant-ion adsorption, t_1, counterion binding, t_2, and surface tension, t_σ, as well as the Gibbs elasticity, E_G, and the slope parameter, S_l, are functions on the *equilibrium* thermodynamic parameters of the system. The latter can be determined from experimental surface tension isotherms, $\sigma = \sigma(c_{1\infty}, c_{2\infty})$, as demonstrated in ref 34. To examine and illustrate the numerical predictions of the theory, we will use the equilibrium parameters, determined in ref 34 from the data of Tajima et al.,[59,60] who measured the surface tension of aqueous solutions of tritiated sodium dodecyl sulfate (TSDS) for different concentrations of NaCl. The theoretical fits have been obtained with the help of the Frumkin adsorption isotherm for an *ionic* surfactant

$$Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT}\right) \qquad (7.1)$$

$$K \equiv K_1 + K_2 c_{2s}$$

in combination with eqs 2.7, 2.12, 5.1, and 5.5. The physical meaning of the parameters Γ_∞, β, K_1, and K_2 and the numerical procedure for data processing are described in ref 34, sections 6.1 and 9.2, respectively. The following

(59) Tajima, K.; Muramatsu, M.; Sasaki, T. *Bul. Chem. Soc. Jpn.* **1970**, *43*, 1991.
(60) Tajima, K. *Bul. Chem. Soc. Jpn.* **1970**, *43*, 3063.

Figure 2. Ionic surfactant solution with 0.115 M NaCl: relaxation times of surface tension, t_σ, of surfactant adsorption, t_1, and of counterion adsorption, t_2, calculated by means of eqs 4.7 and 5.11 as functions of surfactant (TSDS) concentration, $c_{1\infty}$, using parameters values determined from the best fit of data in ref 34.

values of the parameters of the model have been obtained from the fit:[34] $\Gamma_\infty = 4.42 \times 10^{-6}$ mol/m², $K_1 = 156$ m³/mol, $K_2 = 0.128$ m⁶/mol², and $2\beta\Gamma_\infty/(kT) = 0.80$; the temperature is $T = 293$ K. Knowing the values of the latter parameters, one can calculate the equilibrium values of Γ_1, Γ_2, c_{1s}, c_{2s}, and ϕ_s for every given surfactant and salt concentrations (for every couple of values of $c_{1\infty}$ and $c_{2\infty}$) from the set formed by eqs 2.2, 2.10, 2.28, and 7.1; note that $K_{st} = K_2/K_1$. As established in ref 34, the occupancy of the Stern layer, $\theta = \Gamma_2/\Gamma_1$, increases up to 0.74 for TSDS solutions. Therefore, the counterion adsorption (binding) must not be neglected. Further, we obtain the values of E_G (for Frumkin isotherm) J_{Γ_1} and g_{ij} ($i,j = 1, 2$) with the help of eqs 2.29−2.31 and Table 1. To calculate the relaxation times t_1 and t_2, we use values of the ionic diffusion coefficients reported in ref 39: $D_1 = 5.5 \times 10^{-10}$ m²/s, $D_2 = 6.06 \times 10^{-10}$ m²/s, and $D_3 = 6.61 \times 10^{-10}$ m²/s. Finally $\Gamma_1(t)$, $\Gamma_2(t)$, and $\sigma(t)$ can be computed by means of eqs 4.6, 5.10, and 5.11.

7.2. Calculated Relaxation Times. The adsorption relaxation times of surfactant ions, t_1, and counterions, t_2, are calculated from eqs 4.7 and 4.8, along with eqs 2.23−2.27. Next, the relaxation time of surface tension, t_σ, is calculated by means of eqs 2.34 and 5.11. Calculated dependencies of t_1, t_2, and t_σ on the bulk surfactant (TSDS) concentration, $c_{1\infty}$, are shown in Figure 2, for solutions with 0.115 M added NaCl, and in Figure 3, for solutions without added NaCl. Note that in Figures 2 and 3 and in all figures hereafter, the range of surfactant and salt concentrations correspond to the nonmicellar surfactant solutions studied experimentally in refs 59 and 60.
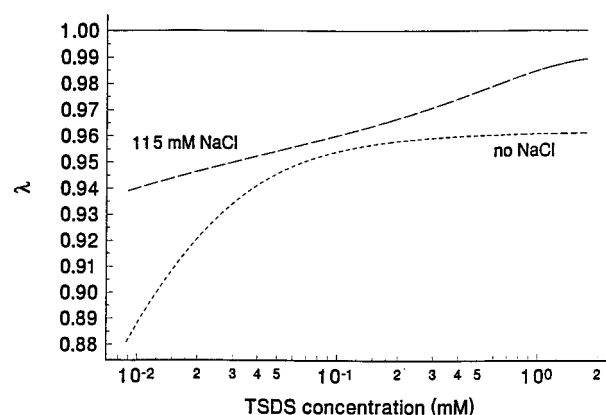
In Figures 2 and 3 one notices the wide range of variation of the relaxation times, which is from 2 to 6 orders of magnitude. For example, the relaxation time of surface tension, t_σ, drops from about 40 s for 0.01 mM surfactant (TSDS) concentration down to $\approx 4 \times 10^{-5}$ s for 1 mM TSDS (see Figure 2). In addition, one sees that systematically $t_2 < t_1 < t_\sigma$; the difference between these three relaxation times can be greater than 1 order of magnitude for the lower surfactant concentrations, especially in the case without added electrolyte (Figure 3). One can conclude that the terms proportional to w in eq 5.11, which give rise to the difference between t_1 and t_σ, play an important role, particularly for solutions of lower ionic strength. We recall that the terms of question originate from the relaxation of σ_d, which is the contribution of the diffuse electric double layer to the surface tension; see eqs 2.6 and 2.7. Figures 2 and 3 demonstrate that the ap-
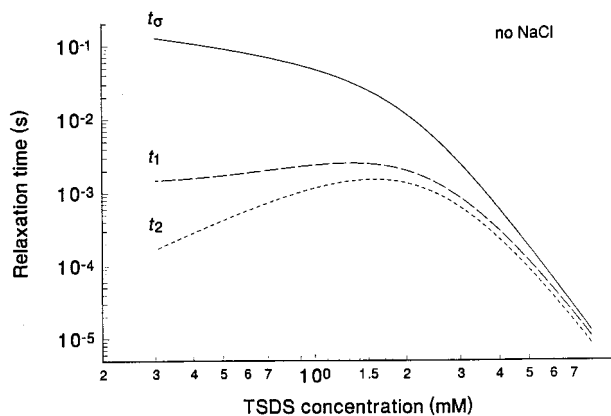
Figure 3. Ionic surfactant solution without added salt: relaxation times of surface tension, t_σ, of surfactant adsorption, t_1, and of counterion adsorption, t_2, calculated by means of eqs 4.7 and 5.11 as functions of surfactant (TSDS) concentration, $c_{1\infty}$, using parameters values determined from the best fit of data in ref 34.
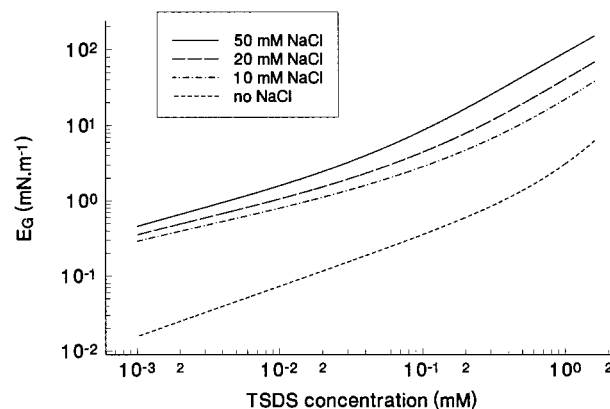

Figure 4. Plot of the parameter λ vs the surfactant (TSDS) concentration, $c_{1\infty}$. The two curves correspond to two fixed NaCl concentrations: 0 and 115 mM; λ is calculated by means of eq 4.8 using parameters values determined from the best fit of data in ref 34.

proximation $t_\sigma \approx t_1$, which is widely used in the literature, is applicable only for the higher surfactant concentrations, for which $t_\sigma \rightarrow t_1$. Note also that for a given surfactant concentration t_2 is always smaller than t_1 and t_σ; that is, the adsorption of counterions relaxes faster than does the adsorption of surfactant ions and the surface tension.

Qualitatively and quantitatively the results for the relaxation times after a *large* initial deviation, t_1, t_2, and t_σ, are similar to those obtained in ref 39 for the relaxation times after a *small* initial deviation, τ_1, τ_2, and τ_σ. In view of eqs 4.9 and 5.12, this result suggests that the parameter λ should be close to 1. Figure 4 shows that this is really the case; the plot of λ vs $c_{1\infty}$ is calculated with the help of eq 4.8 for the same NaCl concentrations used in Figures 2 and 3. One sees that $\lambda \geq 0.94$ in the examined range of concentrations and λ approaches 1 with the rise of surfactant concentration. Moreover, in the absence of NaCl the values of λ are greater and closer to 1 (Figure 4), which can be attributed to the greater surface potential, $\phi_s^{(e)}$, and the smaller $\zeta \equiv \exp(-\phi_s^{(e)}/2)$ in the absence of added electrolyte; see eq 4.8. The fact that $\lambda \approx 1$, and, consequently, $t_1 \approx \tau_1$, $t_2 \approx \tau_2$, and $t_\sigma \approx \tau_\sigma$, implies that the relaxation times are not so sensitive to the magnitude of the initial perturbation.

Figure 3 shows that in the absence of NaCl the counterionic relaxation time t_2 exhibits a pronounced

Figure 5. Plot of the Gibbs (surface) elasticity E_G vs the surfactant (TSDS) concentration, $c_{1\infty}$. The four curves correspond to four fixed NaCl concentrations: 0, 20, 50, and 115 mM; E_G is calculated by means of eq 7.2 using parameter values determined from the best fit of data in ref 34.

maximum when plotted vs the surfactant concentration, $c_{1\infty}$ (similar result is reported for τ_2 in ref 39). This fact can be attributed to the influence of electrostatic interactions.[39] Indeed, the supply of counterions to the relaxing interface is promoted by the gradient of the electric field, $\nabla\psi$, but opposed by the gradient of concentration, ∇c_2. The two effects compensate each other in such a way that the effect of $\nabla\psi$ is slightly predominant (otherwise there would not be supply of counterions from the bulk to the surface). The strong increase of the occupancy of the Stern layer, Γ_2/Γ_1, with the rise of surfactant concentration (see Figure 4 in ref 34) leads to a decrease of the surface charge density and a proportional decrease of the driving force of counterion supply, $\nabla\psi$. This can explain the initial increase in t_2 with the rise of the TSDS concentration (Figure 3). Since the ionic surfactant is also an electrolyte, at higher concentrations it suppresses the development of diffuse electric double layer and decreases the concentration gradient ∇c_2, which opposes the adsorption of counterions. This leads to acceleration of the adsorption process for the higher TSDS concentrations, which is manifested as a decrease of t_2; see Figure 3.

7.3. Gibbs Elasticity and Slope Parameter. Figure 5 shows the Gibbs (surface) elasticity of TSDS adsorption monolayers, E_G, plotted against the TSDS concentration for four different concentrations of NaCl. E_G is calculated by means of the expression in Table 1 stemming from the Frumkin isotherm

$$E_G = kT\Gamma_1\left(\frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}\right) \qquad (7.2)$$

we recall that the Frumkin isotherm has been used to fit the experimental data (see section 7.1). As seen in Figure 5, E_G increases with the rise of surfactant (TSDS) concentration. Moreover, for a fixed surfactant concentration one observes a strong increase of E_G with the increase of NaCl concentration. To understand this behavior of E_G, we notice that according to eq 7.2 E_G depends explicitly only on Γ_1 at fixed temperature T. Hence the influence of surfactant and salt on E_G can be attributed to the increase of the surfactant adsorption Γ_1 with the rise of both surfactant and salt concentration.

If the contribution of the attraction between the hydrocarbon tails of the adsorbed surfactant molecules can be neglected (set $\beta = 0$ in eq 7.2), the Frumkin isotherm reduces to the Langmuir isotherm, which also predicts an
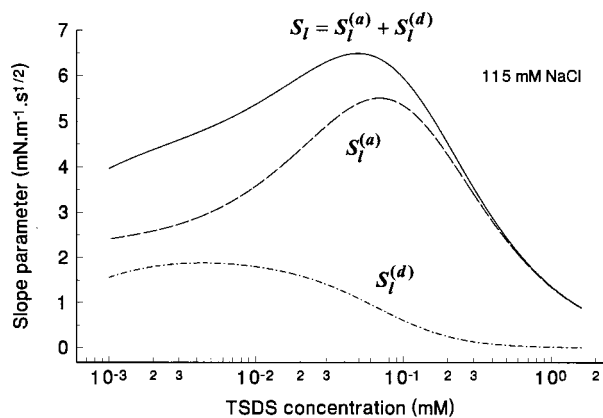
Figure 6. Ionic surfactant solution with 0.115 M NaCl: plots of the slope parameter, S_l, and its components due to the adsorption and diffuse layers, $S_l^{(a)}$ and $S_l^{(d)}$, calculated by means of eqs 5.15−5.17 as functions of surfactant (TSDS) concentration, $c_{1\infty}$; parameter values determined from the best fit of data in ref 34 are used.
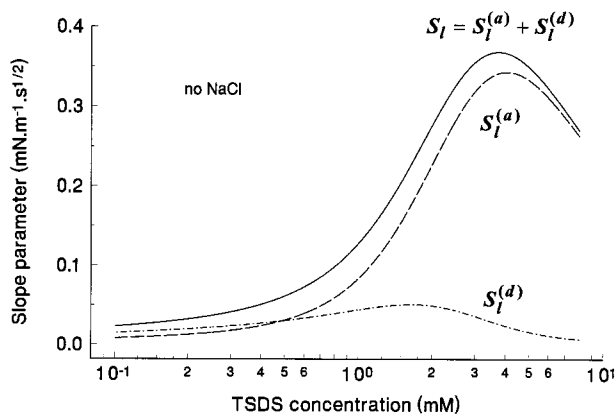

Figure 7. Ionic surfactant solution without added salt: plots of the slope parameter, S_l, and its components due to the adsorption and diffuse layers, $S_l^{(a)}$ and $S_l^{(d)}$, calculated by means of eqs 5.15−5.17 as functions of surfactant (TSDS) concentration, $c_{1\infty}$; parameter values determined from the best fit of data in ref 34 are used.

increase of the Gibbs elasticity E_G with the rise of the salt concentration $c_{2\infty}$; see eq 6.5 and the discussion after it.

Figures 6 and 7 show the calculated slope S_l of the dependence σ vs $t^{-1/2}$ for $t \to \infty$ after a large initial perturbation; see eq 3.1. The slope parameter S_l, and its components $S_l^{(a)}$ and $S_l^{(d)}$ due to the adsorption and diffuse layers, respectively, are calculated by means of eqs 5.14, 5.16, and 5.17. Note that $S_l = S_l^{(a)} + S_l^{(d)}$. In both Figures 6 and 7 the plot of S_l vs the surfactant (TSDS) concentration, $c_{1\infty}$, exhibits a maximum. This is due to the fact that $S_l \propto E_G t_\sigma^{1/2}$ with E_G and $t_\sigma^{1/2}$ being, respectively, increasing and decreasing function of $c_{1\infty}$; see eq 5.14 and Figures 2, 3 and 5.

Note also that in the presence of 0.115 M NaCl the maximum value of S_l is about 20 times greater than that in the absence of added NaCl; cf. Figures 6 and 7. This is a consequence of the fact that E_G is higher in the presence of 0.115 M NaCl; see Figure 5. Physically, this is due to the increase of the equilibrium surfactant adsorption Γ_1 caused by the added NaCl.

Figures 6 and 7 show also that the contributions of the diffuse and adsorption layers, $S_l^{(d)}$ and $S_l^{(a)}$, are comparable for the lower surfactant concentrations, whereas S_l is dominated by the contribution of the adsorption layer, $S_l^{(a)}$, for the higher surfactant concentrations. This find-
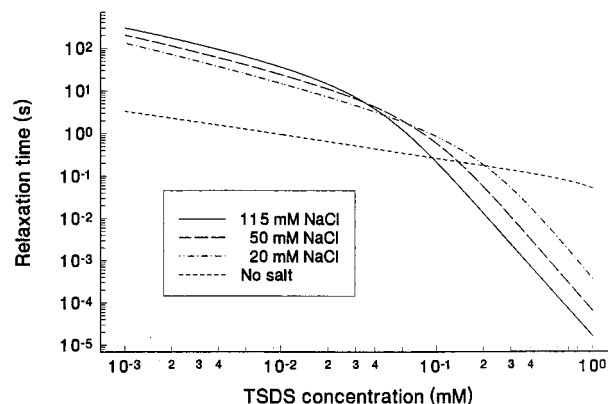
Figure 8. Relaxation time of surface tension, t_σ, plotted vs the surfactant (TSDS) concentration, $c_{1\infty}$. The four curves correspond to four fixed NaCl concentrations: 0, 20, 50, and 115 mM; t_σ is calculated by means of eq 5.11 using parameter values determined from the best fit of data in ref 34.

ing can be attributed to the fact that the increase of the ionic-surfactant concentration simultaneously suppresses the electric double layer (owing to the rise of the ionic strength) and increases the density of the surfactant adsorption monolayer.

7.4. Effect of Salt on the Surface-Tension Relaxation. Figure 8 shows calculated plots of the surface tension relaxation time t_σ vs the surfactant concentration $c_{1\infty}$ for four concentrations of NaCl. As seen in Figure 8, the theory predicts that the addition of salt (NaCl) accelerates the relaxation of the surface tension for the higher surfactant concentrations but decelerates it for the lower surfactant concentrations. Similar behavior of τ_σ vs $c_{1\infty}$ was reported in ref 39 for the case of small initial deviations from equilibrium. This curious inversion of the tendency can be interpreted in the following way.

For the *lower* surfactant concentrations (in the region of Henry), the diffusion supply of surfactant is very slow and it controls the kinetics of adsorption. In the absence of salt, the equilibrium surfactant adsorption monolayer is comparatively diluted, so the diffusion flux from the bulk is able to quickly equilibrate the adsorption layer. The addition of salt at low surfactant concentrations strongly increases the equilibrium surfactant adsorption; consequently, much longer time is needed for the slow diffusion influx to equilibrate the interface.[39] This corresponds to the left-hand side branches of the curves in Figure 8.

The accelerating effect of NaCl for the *higher* surfactant concentrations can be attributed to the suppression of the electric double layer by the added salt. At such high surfactant concentrations the adsorption monolayer is dense and the equilibrium adsorption is very weakly dependent on the surfactant and salt concentrations. In such a case the shrinking of the electric double layer because of added salt gets the upper hand and accelerates the adsorption process.[39] This corresponds to the right-hand side branches of the curves in Figure 8.

Figure 9 presents the calculated slope parameter, S_l, as a function of the surfactant (TSDS) concentration; the curves correspond to different fixed concentrations of NaCl. One sees that S_l *increases* with the rise of NaCl concentration for fixed surfactant concentration, similarly to the Gibbs elasticity E_G; see Figure 5. This tendency is the opposite to that of the relaxation time t_σ for the higher surfactant concentration—see the right-hand side of Figure 8, where t_σ is seen to *decrease* with the rise of NaCl concentration. Since $S_l \propto E_G(t_\sigma)^{1/2}$, it turns out that in the
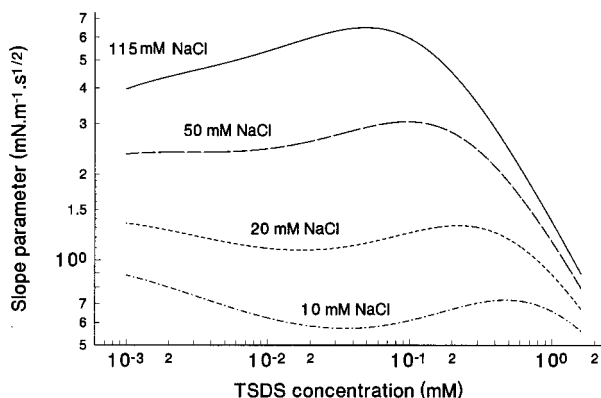
Figure 9. Slope parameter, S_1, plotted vs the surfactant (TSDS) concentration, $c_{1\infty}$. The four curves correspond to four fixed NaCl concentrations: 10, 20, 50, and 115 mM; S_1 is calculated by means of eq 5.14 using parameter values determined from the best fit of data in ref 34.

Figure 10. Numerical output of the asymptotic eq 5.10 for the dynamic surface tension $\sigma(t)$ (the continuous curves) tested against the computer solution of MacLeod and Radke[28] (the points) for two fixed NaCl concentrations: 0 and 115 mM; see the text for details.

latter concentration range the increase of E_G dominates the decrease of $(t_\sigma)^{1/2}$. These theoretical predictions (the curves in Figure 9) can be verified experimentally as discussed below.

7.5. Experimental Determination of the Slope Parameter. It was mentioned that S_1 is liable to a direct experimental determination from the relaxation (long-time asymptotics) of dynamic surface tension $\sigma(t)$ after a *large* initial deviation from equilibrium

$$\sigma(t) \approx \sigma^{(e)} + S_1 t^{-1/2} \qquad (t \gg t_\sigma) \qquad (7.3)$$

Such experiments are now under way; the results will be reported in a subsequent paper. Here we note only that the experimental data for $\sigma(t)$ must satisfy the following two requirements in order to give S_1 as defined by eq 5.14:

(I) One should be certain that the condition $t \gg t_\sigma$ is satisfied and eq 7.3 can be applied; an indication is the linearity of the respective portion of the plot σ vs $t^{-1/2}$.

(II) One should be certain that a *large* initial deviation from equilibrium is experimentally realized; i.e., eq 3.1 is satisfied in the initial moment when the adsorption of surfactant is to be (approximately) zero.

For example, a relatively simple experiment on measurement of $\sigma(t)$ and determination of S_1 may involve pouring of the experimental solution in the experimental cell and a subsequent detection of the variation (relaxation) of surface tension by means of the conventional Wilhelmi-plate method. In such a case requirement I could be violated for very low surfactant concentrations, for which the relaxation time is too long and linear plot of σ vs $t^{-1/2}$ is difficult to be achieved experimentally. On the other hand, it is difficult to satisfy requirement II for concentrations just below the critical micelle concentration (cmc), for which the surfactant adsorption is rather quick. For that reason we anticipate that the best surfactant concentration range for comparison of the present theory with the experiment is the interval $0.01 \times \text{cmc} \leq c_{1\infty} \leq 0.1 \times \text{cmc}$.

7.6. Verification of the Theory against Numerical Data. To test the derived equations and the numerical procedure, we compare the output of our analytical expressions with the numerical results of MacLeod and Radke,[28] who have also imposed the initial condition for large deviation from equilibrium, eq 3.1. These authors make use of the thermodynamic theory by Borwankar and Wasan,[24] which differs from our theoretical approach in the following two aspects: (i) The counterion binding (the existence of Stern layer) is neglected, i.e., $K_2 = 0$ and
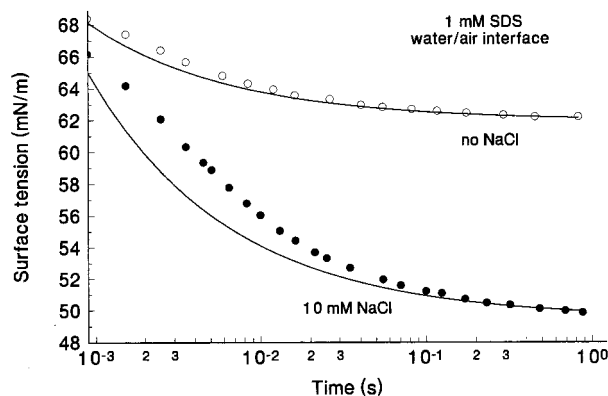
$\Gamma_2 = 0$. (ii) The electric contribution to the surface tension is calculated by means of the equilibrium expression, eq 5.5, which leads to neglecting the difference between t_σ and t_1. In such a case it is pertinent to compare the numerical results from ref 28 with the corresponding long time asymptotics

$$\sigma - \sigma_e = \left(\frac{\partial \sigma}{\partial \Gamma_1}\right)^{(e)} (\Gamma_1 - \Gamma_1^{(e)}) = -\left(\frac{\partial \sigma}{\partial \ln \Gamma_1}\right)^{(e)} \left(\frac{t_1}{\pi t}\right)^{1/2} \quad (7.4)$$

(see eq 4.6) where t_1 is to be calculated by means of our eq 4.7 for $K_2 = 0$ and $\Gamma_2 = 0$. Moreover, we have to use the same values of the parameters $K \equiv K_1$ and Γ_∞, which have been originally determined in ref 24 by fitting experimental data for 1 mM solution of SDS, with 10 mM NaCl and without NaCl. The continuous lines in Figure 10 represent the numerical output of our eq 7.4 obtained with these parameters values. Numerical data from Figure 17 in the paper by MacLeod and Radke[28] are presented with the full and empty symbols for the solutions with and without NaCl, respectively. Figure 10 shows that our theoretical curve coincides with the numerical results in ref 28 for the *longer* times. This is an excellent agreement because eq 7.4 is in fact a long-time asymptotics and it really behaves in this way, as seen in Figure 10.

Finally, it should be noted that eq 7.4 has been used for the sake of comparison with available numerical data (Figure 10). For comparison with *experimental* data it is advisable to use eq 5.10 (along with eqs 4.7 and 5.11), which takes into account the contribution of the counterion binding and the relaxation of the diffuse electric double layer.

8. Concluding Remarks

In this article we consider the theoretical problem about the adsorption kinetics and the relaxation of surface tension of an *ionic* surfactant solution. The effects of added nonamphiphilic electrolyte and counterion binding are taken into account and examined. We consider a *large* initial deviation from equilibrium, which is defined as the formation of a new interface: there is no adsorbed surfactant and electric double layer at the initial moment. Next, the surfactant solution is allowed to relax without any subsequent perturbation. In principle, the time dependence of σ can be obtained by solving a set of differential equations, which describe the electrodiffusion, adsorption, and the distribution of electric field inside the solution; see eqs 2.14–2.16. The main problem is that the

electrodiffusion equations are nonlinear, and it is impossible to find a general analytical solution, especially for large initial deviations from equilibrium. Nevertheless, it turns out that the problem can be linearized in the asymptotic case of long times ($t \rightarrow \infty$); see eqs 3.12 and 3.13 and the related discussion. As a result we obtain explicit expressions for the characteristic relaxation times of surfactant-ion and counterion adsorptions, t_1 and t_2, in terms of ionic diffusivities and thermodynamic parameters of the adsorption layer; see eqs 4.6–4.8.

Next we determine the characteristic relaxation time of surface tension, t_σ, which is different from the adsorption relaxation times, t_1 and t_2, because of a specific contribution from the relaxation of the perturbed diffuse electric double layer; see eqs 5.10–5.11 and their derivation. The results show that the relaxation times in the case of *large* initial perturbation, t_1, t_2, and t_σ, become equal to the relaxation times in the case of *small* initial perturbation, τ_1, τ_2, and τ_σ, when the parameter λ is equal to 1; see eqs 4.8, 4.9, and 5.12. The calculations show that really $\lambda \approx 1$ for an experimental system (Figure 4), and consequently, the relaxation times are not too sensitive to the magnitude of the initial perturbation. From this viewpoint t_1, t_2, and t_σ can be considered as general kinetic properties of the ionic surfactant solution.

Another parameter, characterizing the rate of relaxation of surface tension, is the slope, S_l, of the asymptotic dependence σ vs $t^{-1/2}$ for $t \rightarrow \infty$; note that S_l is liable to experimental determination. It was established that in the case of large initial perturbation the slope parameter is simply related to the Gibbs (surface) elasticity E_G and the relaxation time: $S_l = E_G (t_\sigma / \pi)^{1/2}$; see eq 5.14. The definition of Gibbs elasticity of an adsorption monolayer from soluble ionic surfactant is discussed in detail; see section 6. It is concluded that despite the presence of a diffuse electric double layer, the thermodynamic definition of E_G for *ionic* surfactants is analogous to that for *nonionic* surfactants, cf. eqs 6.1 and 6.3; in particular, the expressions in Table 1 hold for both types of surfactants. The calculations based on experimental data for an ionic surfactant show that E_G increases strongly with the rise of electrolyte (NaCl) concentration; see eq 6.5 and Figure 5.

As an illustrative example we used the best fit from ref 34 of the data by Tajima et al.[59,60] for TSDS solutions with added NaCl. The fit gives the parameters of the theoretical model, K_1, K_2, Γ_∞, and β. Then the corresponding relaxation times of adsorption and surface tension, as well as the Gibbs elasticity and the slope parameter S_l, are calculated as functions of the surfactant and salt concentrations; see Figures 2–9. The numerical results show that the relaxation times satisfy the relationship $t_2 < t_1 < t_\sigma$; for some concentrations the difference between these three relaxation times can be greater than 1 order of magnitude. The theory predicts that the addition of salt accelerates the relaxation of the surface tension for the higher surfactant concentrations but decelerates it for the lower surfactant concentrations (Figure 8). On the other hand, the Gibbs elasticity E_G and the slope parameter S_l increase with the rise of salt concentration for all submicellar surfactant concentrations (Figures 5 and 9). The possibilities for comparison of theory and experiment are discussed in sections 5.2 and 7.5. The derived asymptotic expressions are verified against an exact computer solution of the electrodiffusion problem, and an excellent agreement is found (Figure 10).

The results can be applied to interpret experimental data for surface tension relaxation in the concentration range below the cmc, for various surfactant and salt concentrations (such a systematic experimental study is now under way). The results could be useful for the theoretical analysis of dynamic processes in foams, emulsions and suspensions, which are accompanied by adsorption of ionic surfactants. In particular, the coalescence of bubbles or drops at the early highly dynamic stages of foam or emulsion production is expected to be sensitive to the degree of saturation of the newly created interfaces with surfactant and, correspondingly, to the relaxation time of surfactant adsorption.

Supporting Information Available: Appendix A "Relaxation of adsorption" and Appendix B "Relaxation of surface tension" contain mathematical derivations of some equations in the main text of the paper. This material is available free of charge via the Internet at http://pubs.acs.org.