

# Kinetics of Surfactant Adsorption at Fluid–Fluid Interfaces

Haim Diamant and David Andelman\*

School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel

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We present a theory for the kinetics of surfactant adsorption at the interface between an aqueous solution and another fluid (air, oil) phase. The model relies on a free-energy formulation. It describes both the diffusive transport of surfactant molecules from the bulk solution to the interface and the kinetics taking place at the interface itself. When applied to nonionic surfactant systems, the theory recovers results of previous models and justifies their assumptions. Common nonionic surfactants are predicted to undergo a diffusion-limited adsorption, in accord with experiments. For salt-free ionic surfactant solutions, electrostatic interactions are shown to drastically affect the kinetics. The adsorption in this case is predicted to be kinetically limited, and the theory accounts for unusual experimental results obtained recently for the dynamic surface tension of such systems. Addition of salt to an ionic surfactant solution leads to screening of the electrostatic interactions and to a diffusion-limited adsorption. In addition, the free-energy formulation offers a general method for relating the dynamic surface tension to surface coverage. Unlike previous models, it does not rely on equilibrium relations which are shown in some cases to be invalid out of equilibrium.

## 1. Introduction

Aqueous solutions of surface-active agents (*surfactants*) play a major role in various fields and applications, such as biological membranes, petrochemical processes, detergents, etc.<sup>1</sup> In some important cases, equilibrium properties of the surfactant adsorption at interfaces are not sufficient, and knowledge of the kinetics is required. Processes of fast wetting, foaming, and stability of thin soap films may serve as good examples. The kinetics of surfactant adsorption have been addressed by experimental and theoretical studies since the 1940s, and various experimental techniques have been devised, primarily aimed at the measurement of dynamic interfacial tensions.<sup>2</sup>

The pioneering theoretical work of Ward and Tordai<sup>3</sup> considered a diffusive transport of surfactant molecules from a bulk surfactant solution to an interface and formulated the time-dependent relation

$$\sigma(t) = \sqrt{\frac{D}{\pi}} \left[ 2c_b \sqrt{t} - \int_0^t \frac{c_1(\tau)}{\sqrt{t-\tau}} d\tau \right] \quad (1.1)$$

where  $c_b$  is the bulk concentration and  $D$  the surfactant diffusivity. This equation gives only one relation between  $\sigma(t)$ , the surface density of surfactants adsorbed at the interface, and  $c_1(t)$ , the surfactant concentration at the subsurface layer of solution.

Subsequent theoretical research has focused on providing the second closure relation between these two variables by introducing a certain adsorption mechanism at the interface. Various relations have been suggested, resembling equilibrium isotherms,<sup>4–6</sup> or having a kinetic differential form.<sup>7–10</sup> Such theories have been quite successful in describing the experimentally observed adsorption of common nonionic surfactants. Yet, they suffer from several drawbacks: (i) the closure relation between the surface density and subsurface concentration, which expresses the kinetics taking place at the interface, is introduced as an external boundary condition and does not uniquely arise from the model itself; (ii) the calculated dynamic surface tension

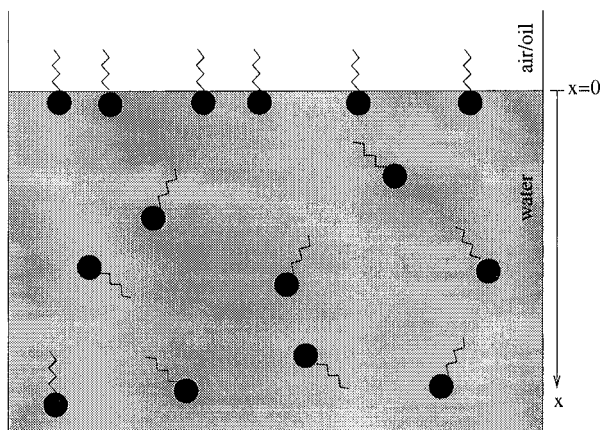
relies on an *equilibrium* equation of state, and assumes that it also holds out of equilibrium;<sup>11</sup> (iii) similar theories cannot be easily extended to describe more complicated systems, such as *ionic* surfactant solutions.<sup>12</sup>

In the current work we would like to present an alternative approach to the kinetics of surfactant adsorption, overcoming these drawbacks. In section 2 we lay the foundations of our model,<sup>13</sup> based on a free-energy formulation. Nonionic surfactants are considered, recovering results of previous models and justifying their assumptions. In particular, we show that the adsorption of common nonionic surfactants is limited by diffusion from the bulk solution. In section 3 we modify the theoretical framework and apply it to salt-free ionic surfactant solutions. A few models have been proposed for describing the kinetics of ionic surfactant adsorption,<sup>14–16</sup> yet none of them is able to account for recent experimental results for the dynamic surface tension of salt-free ionic surfactant solutions.<sup>12</sup> We show that the adsorption in such systems is limited by the kinetic processes at the interface. Consequently, we point out a problem common to all previous models. Using our model, we then account for the recent experimental findings. Section 4 considers ionic surfactant solutions with added salt. The adsorption is shown in this case to be limited again by diffusion, and the effect of salt concentration is examined. Finally, we present a few concluding remarks in section 5 and point out possible future prospects.

## 2. Nonionic Surfactants

Consider an interface between an aqueous solution of nonionic surfactants and an air or oil phase. The system is schematically illustrated in Figure 1. We assume that the width of the interface is much smaller, and its radius of curvature much larger, than any length scale relevant to the adsorption process. Hence, the interface can be regarded as sharp and flat, lying at the plane  $x = 0$ , and the problem is reduced to one dimension. At  $x \rightarrow \infty$ , the solution is in contact with a bulk reservoir of surfactant molecules, where the chemical potential and surfactant volume fraction are fixed to be  $\mu_b$  and  $\phi_b$ , respectively. We consider a dilute solution, i.e., the surfactant volume fraction is

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**Figure 1.** Schematic view of the system. A sharp, flat interface separates a dilute aqueous solution of nonionic surfactants from an air or oil phase.

much smaller than unity throughout the solution. The concentration is also smaller than the critical micelle concentration (cmc), so the surfactants are dissolved only as monomers. At the interface itself, however, the volume fraction may become large.

**2.1. Free Energy.** We write the excess in free energy per unit area due to the interface (i.e., the change in interfacial tension),  $\Delta\gamma$ , as a functional of the surfactant volume fraction in the bulk solution,  $\phi(x>0)$ , and its value at the interface,  $\phi_0$

$$\Delta\gamma[\phi] = \int_0^\infty \Delta f[\phi(x)] dx + f_0(\phi_0) \quad (2.1)$$

The first term is the contribution from the bulk solution,  $\Delta f$  being the excess in free energy per unit volume over the bulk, uniform state. The second is the contribution from the interface itself, where  $f_0$  is the free energy per unit area of the surfactant at the interface. The sharp, “steplike” profile considered has led us to treat the bulk solution and the interface as two coupled subsystems, rather than a single one.<sup>17</sup>

The bulk subsystem is considered as an ideal, dilute solution, including only the ideal entropy of mixing and the contact with the reservoir and neglecting gradient terms

$$\Delta f(\phi) = (1/a^3) \{ T[\phi \ln \phi - \phi - (\phi_b \ln \phi_b - \phi_b)] - \mu_b(\phi - \phi_b) \} \quad (2.2)$$

where  $a$  denotes the surfactant molecular dimension and  $T$  the temperature (we set the Boltzmann constant to unity).

At the interface, however, since  $\phi_0$  may become much larger than  $\phi(x>0)$ , we must take into account the finite molecular size and the interactions between surfactant molecules,

$$f_0(\phi_0) = (1/a^2) \left\{ T[\phi_0 \ln \phi_0 + (1 - \phi_0) \ln (1 - \phi_0)] - \alpha \phi_0 - \frac{\beta}{2} \phi_0^2 - \mu_1 \phi_0 \right\} \quad (2.3)$$

The term in the square brackets is the entropy of mixing, this time in its complete form, since  $\phi_0$  is not necessarily small. The second term accounts for the energetic preference of the surfactants to lie at the interface,  $\alpha$  being positive by the definition of our molecules as surface active. The third is the energy of lateral interaction between neighboring surfactants at the interface, where  $\beta$  is assumed to be positive too, i.e., expressing an overall *attractive* interaction. The last term accounts for the contact with the solution adjacent to the interface, where the chemical potential is  $\mu_1 \equiv \mu(x \rightarrow 0)$ .<sup>18</sup>

Variation of  $\Delta\gamma$  with respect to  $\phi(x)$  yields the excess in chemical potential at a distance  $x$  from the interface,

$$\Delta\mu(x) = \mu(x) - \mu_b = a^2 \frac{\delta\Delta\gamma}{\delta\phi(x)} = T \ln \phi(x) - \mu_b; \quad x > 0 \quad (2.4)$$

$$\Delta\mu_0 = \mu_0 - \mu_1 = a^2 \frac{\delta\Delta\gamma}{\delta\phi_0} = T \ln \frac{\phi_0}{1 - \phi_0} - \alpha - \beta\phi_0 - \mu_1 \quad (2.5)$$

From eq 2.4 we can deduce, as expected,

$$\begin{aligned} \mu_b &= T \ln \phi_b \\ \mu_1 &= T \ln \phi_1 \end{aligned} \quad (2.6)$$

where  $\phi_1 \equiv \phi(x \rightarrow 0)$  denotes the surfactant volume fraction at the subsurface layer.

**2.2. Thermodynamic Equilibrium.** In equilibrium, the chemical potential is equal to  $\mu_b$  throughout the entire system (the variations of  $\Delta\gamma$  vanish). From eq 2.4 we obtain the equilibrium profile

$$\phi(x) \equiv \phi_b; \quad x > 0 \quad (2.7)$$

and from eq 2.5, the equilibrium adsorption isotherm

$$\phi_0 = \frac{\phi_b}{\phi_b + e^{-(\alpha + \beta\phi_0)/T}} \quad (2.8)$$

We have recovered the *Frumkin adsorption isotherm*, which reduces to the well-known *Langmuir adsorption isotherm*<sup>19</sup> when the interaction term is neglected ( $\beta = 0$ ). From eqs 2.3, 2.5, and 2.7 one also obtains the equilibrium equation of state

$$\Delta\gamma = \frac{1}{a^2} \left[ T \ln (1 - \phi_0) + \frac{\beta}{2} \phi_0^2 \right] \quad (2.9)$$

which was previously derived from other, though equivalent considerations (integration of the Gibbs equation).<sup>9</sup>

**2.3. Out of Equilibrium.** Throughout our analysis we assume proportionality between velocities and the potential gradient<sup>20</sup> and take the surfactant mobility to be  $D/T$  according to the Einstein relation ( $D$  being the surfactant diffusivity). At positions not adjacent to the interface this leads to the following surfactant current density,

$$j(x) = -\phi \frac{D}{T} \frac{\partial\mu}{\partial x} = -D \frac{\partial\phi}{\partial x} \quad (2.10)$$

Applying the continuity condition,  $\partial\phi/\partial t = -\partial j/\partial x$ , we get the ordinary *diffusion equation*

$$\frac{\partial\phi}{\partial t} = D \frac{\partial^2\phi}{\partial x^2} \quad (2.11)$$

The proximity of the interface requires a more careful treatment. First, we discretize expression (2.1) on a lattice with cells of size  $a$

$$\Delta\gamma[\phi] = a \sum_{i=1}^{\infty} \Delta f(\phi_i) + f_0(\phi_0)$$

where  $\phi_i \equiv \phi(x=ia)$ . Discretized current densities,  $j_i$ , can be similarly defined. Since we do not allow molecules to leave the interface toward the other (air, oil) phase (i.e.,  $j_0 = 0$ ), we

have from the continuity condition

$$\frac{\partial \phi_0}{\partial t} = -\frac{j_1}{a}$$

and can therefore write

$$\frac{\partial \phi_1}{\partial t} = -\frac{j_2 - j_1}{a} = \frac{D}{a} \frac{\partial \phi}{\partial x} \Big|_{x=a} - \frac{\partial \phi_0}{\partial t} \quad (2.12)$$

Applying the Laplace transform to eqs 2.11 and 2.12 while assuming an initial uniform state,  $\phi(x, t=0) \equiv \phi_b$ , a relation is obtained between the surface and subsurface volume fractions,  $\phi_0$  and  $\phi_1$

$$\phi_0(t) = \frac{1}{a} \sqrt{\frac{D}{\pi}} \left[ 2\phi_b \sqrt{t} - \int_0^t \frac{\phi_1(\tau)}{\sqrt{t-\tau}} d\tau \right] + 2\phi_b - \phi_1 \quad (2.13)$$

This relation is similar to the classical result of Ward and Tordai,<sup>3</sup> eq 1.1, except for the term  $2\phi_b - \phi_1$ . This difference is due to the fine details we have considered near the interface and our initial condition. Ward and Tordai's analysis assumes a continuous profile up to the nonaqueous phase and hence replaces eq 2.12 with a simpler condition,  $\partial \phi_0 / \partial t = (D/a) \partial \phi / \partial x|_{x=0}$ . In addition, it requires an initial empty interface [ $\phi_0(t=0) = 0$ ], whereas we set  $\phi_0(t=0) = \phi_b$ . At any rate, the difference vanishes when the cell size,  $a$ , goes to zero. Finally, we find the equation governing the kinetics at the interface itself<sup>21</sup>

$$\frac{\partial \phi_0}{\partial t} = -\frac{j_1}{a} = \frac{\phi_1 D}{a T} \frac{\mu_1 - \mu_0}{a} = \frac{D}{a^2} \phi_1 \left[ \ln \frac{\phi_1(1-\phi_0)}{\phi_0} + \frac{\alpha}{T} + \frac{\beta \phi_0}{T} \right] \quad (2.14)$$

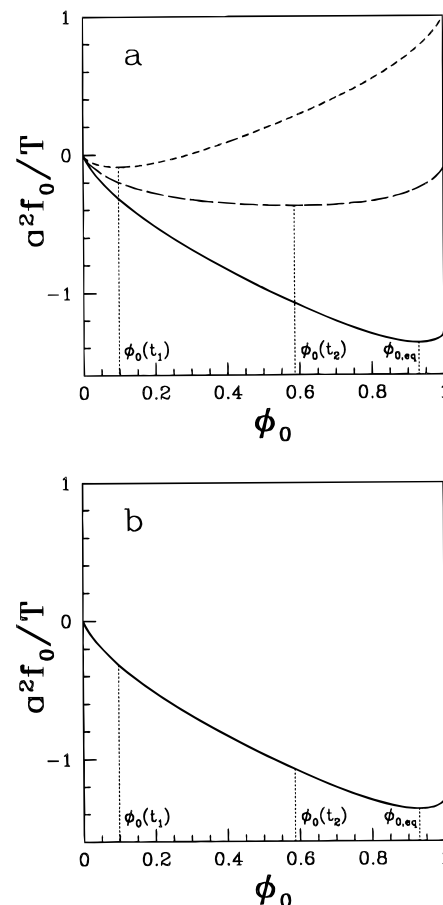
Simultaneous solution of eqs 2.13 and 2.14 yields the solution of the adsorption problem, *i.e.*, the time-dependent surface coverage,  $\phi_0(t)$ .

**2.4. Limiting Cases for the Adsorption.** In writing the above equations, we have separated the kinetics of the system into two coupled kinetic processes. The first takes place inside the bulk solution and is described by eqs 2.11 and 2.12 (or, alternatively, by eq 2.13), whereas the second takes place at the interface and is described by eq 2.14. Two important limiting cases correspond to the relative time scales of these two processes:

(i) *Diffusion-limited adsorption (DLA)* applies when the equilibration process inside the solution is much slower than the one at the interface. One can then assume that the interface is in equilibrium at all times with the adjacent solution; *i.e.*, the variation (2.5) vanishes, and  $\phi_0$  immediately responds to changes in  $\phi_1$  via the equilibrium isotherm.

(ii) *Kinetically limited adsorption (KLA)* takes place when the kinetic process at the interface is the slower one. In this case, the solution is assumed to be at all times in equilibrium with the bulk reservoir, *i.e.*, the variation (2.4) vanishes, and  $\phi_0$  changes with time according to eq 2.14.

One may suggest an alternative way of looking at the same limiting cases, the usefulness of which will become evident later on. Let us reexamine the expression for the interfacial contribution,  $f_0$  (eq 2.3). The DLA case corresponds to the following description (see Figure 2a). The interface is all the time at the minimum of the curve  $f_0(\phi_0)$ , yet the shape of the curve changes with time as  $\mu_1$  is changed by diffusion, until it attains the value of  $\mu_b$ . The surface coverage increases with time as the minimum of  $f_0$  is shifted to larger values of  $\phi_0$ . On the other hand, KLA corresponds to a different scenario (Figure 2b). The shape of



**Figure 2.** The two limiting cases for the time dependence of the adsorption: (a) Diffusion-limited adsorption (DLA)—the surface coverage,  $\phi_0$ , is determined by the minimum of the surface free energy,  $f_0$ , yet the shape of  $f_0$  changes with time. The curve is shown at three different times, corresponding to increasing values of the subsurface volume fraction,  $\phi_1$ : (i) at  $t_1$  close to the beginning of the process, when  $\phi_1 = 5 \times 10^{-7}$ , (ii) at a later time  $t_2$ , when  $\phi_1 = 1.5 \times 10^{-6}$ , and (iii) at equilibrium, when  $\phi_1 = \phi_b = 5 \times 10^{-6}$ . The energy constants are set to the (realistic) values  $\alpha = 12T$  and  $\beta = 3T$ . (b) Kinetically limited adsorption (KLA)—the shape of  $f_0$  is fixed and  $\phi_0$  increases with time until reaching equilibrium at the minimum of  $f_0$ .

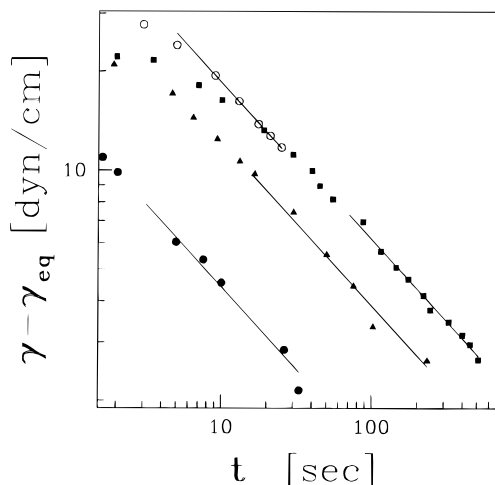
$f_0(\phi_0)$  remains fixed since  $\mu_1$  is constantly equal to  $\mu_b$ . The surface coverage,  $\phi_0$ , increases until finally reaching the value corresponding to the minimum of  $f_0$ .

In order to figure out whether one of the above limits applies to nonionic surfactant adsorption, the time scales of these two limiting cases must be compared. Let us start with the DLA case and look for the asymptotic time dependence of the process. We return to the Laplace transform of eqs 2.11 and 2.12 and let the conjugate variable of the transform approach zero.<sup>22</sup> In addition, since the DLA limit is currently considered, we neglect the kinetics at the interface and take  $\phi_0$  to be almost constant. After inverting back to  $t$ -space, this procedure leads to the following asymptotic time dependence, previously mentioned by Hansen<sup>5</sup>

$$\phi_b - \phi_1 \approx \frac{a\phi_{0,\text{eq}}}{\sqrt{\pi Dt}}, \quad t \rightarrow \infty \quad (2.15)$$

where  $\phi_{0,\text{eq}}$  is the equilibrium surface coverage. Looking at eq 2.15 we can identify the characteristic *time scale of diffusion*

$$\tau_d = \left( \frac{\phi_{0,\text{eq}}}{\phi_b} \right)^2 \frac{a^2}{D} \quad (2.16)$$



**Figure 3.** Nonionic surfactants experimentally found to exhibit DLA. Four examples of dynamic surface tension measurements are given:  $9.49 \times 10^{-5}$  M of decyl alcohol (open circles), as adapted from ref 27;  $2.32 \times 10^{-5}$  M of Triton X-100 (squares), adapted from ref 9;  $6 \times 10^{-5}$  M of  $C_{12}EO_8$  (triangles) and  $4.35 \times 10^{-4}$  M of  $C_{10}PY$  (solid circles), both adapted from ref 28. Note the asymptotic  $t^{-1/2}$  behavior, characteristic of DLA and shown by the solid fitting lines.

Typical values of  $a^2/D$  correspond to very short times (of order  $10^{-9}$  s), but the prefactor of  $(\phi_{0,eq}/\phi_b)^2$  is usually very large (of order, say,  $10^{11}$ ). Thus, the diffusion time scales may reach minutes.

In order to estimate the time scale of the kinetics taking place at the interface, we look at the asymptotic behavior of eq 2.14 and find<sup>23</sup>

$$\phi_{0,eq} - \phi_0(t) \sim e^{-t/\tau_k}$$

$$\tau_k \approx \left(\frac{\phi_{0,eq}}{\phi_b}\right)^2 \frac{a^2}{D} e^{-(\alpha+\beta\phi_{0,eq})/T} \quad (2.17)$$

Since the value of  $D$  at the interface is not expected to be drastically smaller than that inside the solution, comparison of eqs 2.16 and 2.17 leads to the conclusion that  $\tau_d > \tau_k$ . We thus expect that *common nonionic surfactants should exhibit diffusion-limited adsorption*. This is one of the conclusions of our study as applied to nonionic surfactants and has been observed for quite a large number of such surfactants.<sup>2,24</sup> It is somewhat expected, since we did not include in the interfacial free energy, eq 2.3, any potential barrier that might lead to kinetic limitations. The “footprint” of DLA is the asymptotic time dependence (see eq 2.15 and ref 5)

$$\phi_{0,eq} - \phi_0(t) \sim \sqrt{\tau_d/t}$$

For any reasonable dependence between the surface tension and surface coverage,  $\gamma(t) = \gamma[\phi_0(t)]$ , we expect the surface tension to also exhibit a similar asymptotic time dependence,  $\gamma(t) - \gamma_{eq} \sim \sqrt{\tau_d/t}$ . It should be compared with the asymptotic *exponential* time dependence in the case of KLA (eq 2.17). Four examples of experimental results are given in Figure 3, all exhibiting an asymptotic  $t^{-1/2}$  behavior, as expected for DLA.

Having realized that the adsorption is diffusion-limited, the mathematical solution of the problem amounts to the simultaneous solution of two equations: (i) the Ward–Tordai equation, (2.13), accounting for the diffusive transport; (ii) an isotherm, such as (2.8) (with  $\phi_1$  replacing  $\phi_b$ ), describing the (immediate) response of the surface coverage to changes in the subsurface layer of solution. Useful numerical schemes were suggested

for performing such a task,<sup>2,9</sup> yielding the time-dependent surface coverage,  $\phi_0(t)$ .

**2.5. Dynamic Surface Tension in a DLA Process.** Since most experiments measure dynamic surface tensions and not surface coverages, we still need a relation between these two variables in order to relate theoretical calculations to actual measurements. We return, therefore, to the evolution of the interfacial tension during a DLA process. As was stated above, in this limit the interfacial contribution,  $f_0(\phi_0)$ , is all the time at its minimum. We can, therefore, write

$$\Delta\gamma[\phi] = \int_0^\infty \Delta f[\phi(x)] dx + \frac{1}{a^2} \left[ T \ln(1 - \phi_0) + \frac{\beta}{2} \phi_0^2 \right]$$

If, in addition, the contribution from the bulk solution is neglected (recalling that it completely vanishes when equilibrium is reached), we are left with the equilibrium relation, eq 2.9. Hence, the equilibrium equation of state, relating the surface tension to the surface coverage, holds approximately also out of equilibrium. Note, that this conclusion is valid only in the case of *diffusion-limited adsorption*.

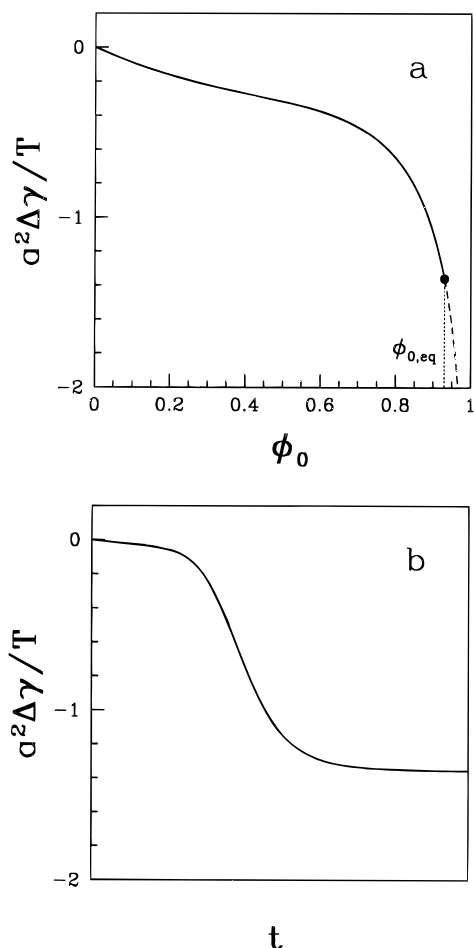
Practically all previous works assumed that the equilibrium relation between the surface tension and surface coverage holds for the *dynamic* surface tension as well. As we have just found, nonionic surfactants usually do undergo DLA. Hence, the assumption employed by previous works was justified, as far as nonionic surfactants were concerned. Indeed, satisfactory agreement with experimental findings is obtained when results of the numerical schemes mentioned above are related to the dynamic surface tension via the equilibrium equation of state.<sup>9,29</sup> However, this conclusion is drastically modified for *ionic* surfactants, as we show in the next section.

The dependence of  $\Delta\gamma$  on  $\phi_0$ , as defined by eq 2.9, is shown in Figure 4a. Note the moderate slope in the beginning of the process; the surface coverage significantly changes without a corresponding change in the surface tension. It is a result of the competition between the entropy and interaction terms in eq 2.9. As the surface coverage increases, the surface tension starts falling until it reaches its equilibrium value. Since  $\phi_0$  monotonically increases with time during the adsorption, we expect the *time* dependence of  $\Delta\gamma$  to resemble the schematic curve depicted in Figure 4b: a slow change in the beginning, then a rapid drop, and eventually a relaxation toward equilibrium. This is, indeed, in agreement with dynamic surface tension measurements (e.g., ref 9). Returning to Figure 4a, the surface tension will start its rapid fall roughly when the second derivative of  $\Delta\gamma$  with respect to  $\phi_0$  changes sign, i.e., when

$$1 - \phi_0 \sim (\beta/T)^{-1/2}$$

As one examines surfactant solutions of increasing bulk concentrations (but always below the cmc), the surface coverage corresponding to the beginning of the drop in surface tension will be reached earlier along the process. The initial period of slow change in the tension will shrink, until finally vanishing behind the finite experimental resolution. This trend is observed experimentally.<sup>29</sup>

The need for an interaction between surfactant molecules in order to account for such a time dependence of surface tensions was previously realized by Lin et al.<sup>29</sup> They even suggested the existence of a transition from a gaseous to a liquid phase as being responsible for the initial period of almost constant tension. In fact, the form of  $f_0$  as defined in eq 2.3 may account for a two-phase region, but only if  $\beta > 4T$ . As demonstrated



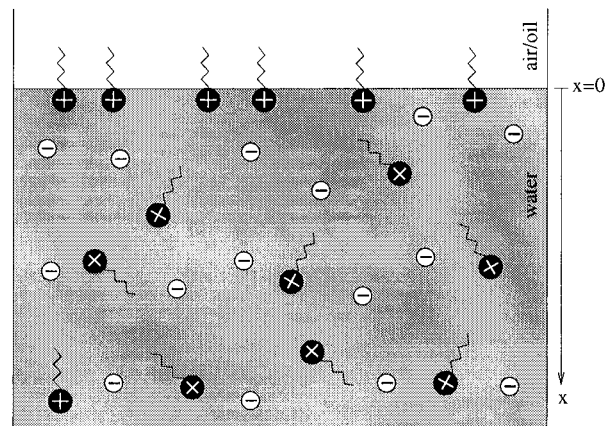
**Figure 4.** (a) Dependence between the surface tension and surface coverage in a DLA case (the parameters are the same as in Figure 2). (b) Schematic time dependence of the surface tension expected from a dependence  $\Delta\gamma(\phi_0)$  such as in (a): an initial slow change, then a rapid drop, and finally a relaxation toward equilibrium.

above in Figure 4 (where  $\beta = 3T$ ), this is not necessary, however, for recovering the experimentally observed time dependence.

### 3. Ionic Surfactants without Added Salt

We now consider the problem of *ionic* surfactant adsorption. The main difference compared to the previous, nonionic case is the introduction of electrostatic interactions. The kinetics of the system include, apart from the diffusive transport of molecules and their adsorption at the interface, the formation of an electric double layer due to the increasing surface charge. We start with the case of a salt-free solution, where the only charges present are those of the surfactant ions and their balancing counterions. The system is schematically illustrated in Figure 5. In such a case the electrostatic interactions are unscreened, and thus, as we shall see, have a drastic effect on the adsorption process. Instead of the single degree of freedom we have specified in the nonionic case, namely the surfactant profile,  $\phi(x,t)$ , we should consider here three degrees of freedom: the surfactant ion profile,  $\phi^+(x,t)$ , the counterion profile,  $\phi^-(x,t)$ , and the local mean electric potential,  $\psi(x,t)$  (without loss of generality, we take the surfactant ions as the positive ones).

For simplicity, we assume the following: (i) the surfactant molecules are fully ionized; (ii) the surfactant ions and counterions are monovalent (extension to general valencies, however,



**Figure 5.** Schematic view of the ionic salt-free system. A dilute solution containing surfactant ions and their counterions has a sharp, flat interface with an air or oil phase.

is quite straightforward within our mean-field formulation); (iii) as in the previous section, the solution is assumed to be dilute. In the current context this last assumption also allows us to treat the surfactant and counterion volume fractions as independent variables, as the probability for an ion and a counterion to overlap at the same spatial position is negligible.

The extension of the model to ionic surfactants evidently demonstrates the benefits of the free-energy formulation we have employed. We just repeat the scheme of section 2 while adding terms for the counterions and electrostatic interactions. Unlike previous models and due to its simplicity, this formulation will allow us to clarify the complex problem of ionic surfactant adsorption and reach novel conclusions concerning it.

**3.1. Free Energy.** Following the analysis of section 2, we write the change in interfacial tension in the form

$$\Delta\gamma[\phi^+, \phi^-, \psi] = \int_0^\infty \{ \Delta f^+[\phi^+] + \Delta f^-[\phi^-] + f_{el}[\phi^+, \phi^-, \psi] \} dx + f_0(\phi_0^+, \psi_0) \quad (3.1)$$

The first two terms are the contributions from the bulk solution, depending on the surfactant and counterion volume fractions. The third term is the electrostatic energy stored in the bulk solution. The last term is the contribution from the interface itself, depending on the interfacial values of the surfactant volume fraction,  $\phi_0^+$ , and the electric potential,  $\psi_0$ . The counterions are assumed to be surface-inactive, and their contribution to this term is neglected.<sup>30</sup> As in the previous discussion, the two types of ions dissolved in the bulk solution have contributions coming from their entropy of mixing and chemical potentials,

$$\Delta f^\pm(\phi^\pm) = \frac{1}{(a^\pm)^3} \{ T[\phi^\pm \ln \phi^\pm - \phi^\pm - (\phi_b^\pm \ln \phi_b^\pm - \phi_b^\pm)] - \mu_b^\pm(\phi^\pm - \phi_b^\pm) \} \quad (3.2)$$

where  $a^\pm$  are the molecular dimensions of the two ions and  $\phi_b^\pm$  and  $\mu_b^\pm$  their volume fractions and chemical potentials, respectively, at the bulk reservoir. Our assumption of monovalent ions implies

$$\frac{\phi_b^+}{(a^+)^3} = \frac{\phi_b^-}{(a^-)^3} = c_b$$

where  $c_b$  is the bulk concentration.

The electrostatic term contains the interaction between the ions and the electric field and the energy associated with the field itself

$$f_{el} = e \left( \frac{\phi^+}{(a^+)^3} - \frac{\phi^-}{(a^-)^3} \right) \psi - \frac{\epsilon}{8\pi} \left( \frac{\partial \psi}{\partial x} \right)^2 \quad (3.3)$$

where  $e$  is the electronic charge and  $\epsilon$  the dielectric constant of the solvent (water). Finally, the modified expression for the interfacial contribution,  $f_0$ , is obtained from eq 2.3 just by adding an electrostatic term

$$f_0(\phi_0^+, \psi_0) = \frac{1}{(a^+)^2} \left\{ T[\phi_0^+ \ln \phi_0^+ + (1 - \phi_0^+) \ln (1 - \phi_0^+)] - \alpha \phi_0^+ - \frac{\beta}{2} (\phi_0^+)^2 - \mu_1^+ \phi_0^+ + e \phi_0^+ \psi_0 \right\} \quad (3.4)$$

When the interface is still almost uncharged, another electrostatic contribution should be considered, namely that of the interaction between the ions and their “image” charges beyond the interface, as was pointed out by Onsager and Samaras.<sup>31</sup> This force decays like  $1/x^2$ , and since the dielectric constant of the other phase (air, oil),  $\epsilon_o$ , is smaller than that of the solvent,  $\epsilon$ , it is repulsive. The “image” force is comparable to the repulsion from the surface charge for distances

$$x < \sqrt{\frac{1}{16\pi\phi_0^+} \frac{\epsilon - \epsilon_o}{\epsilon + \epsilon_o}} a^+$$

Obviously, when the right-hand side of this expression becomes smaller than the molecular dimension,  $a^+$ , this force is irrelevant. For a water–air or water–oil interface this happens when  $\phi_0^+ \sim 0.02$ , i.e., very soon along the adsorption process. We allow ourselves, therefore, to disregard such early stages of adsorption and neglect this interaction altogether (it should be mentioned, however, that in the case of surface-*inactive* electrolytes, the “image” interaction has a significant contribution to the interfacial tension).

We now take the variation of  $\Delta\gamma$  with respect to  $\phi^\pm(x)$  to get the excess in electrochemical potentials

$$\Delta\mu^\pm(x) = \mu^\pm(x) - \mu_b^\pm = (a^\pm)^2 \frac{\delta\Delta\gamma}{\delta\phi^\pm} = T \ln \phi^\pm \pm e\psi - \mu_b^\pm; \quad x > 0 \quad (3.5)$$

$$\Delta\mu_0^+ = \mu_0^+ - \mu_1^+ = (a^+)^2 \frac{\delta\Delta\gamma}{\delta\phi_0^+} = T \ln \frac{\phi_0^+}{1 - \phi_0^+} - \alpha - \beta\phi_0^+ + e\psi_0 - \mu_1^+ \quad (3.6)$$

We require that the electric potential vanish far away from the interface, that is,  $\psi(x \rightarrow \infty) = 0$ , and hence deduce from eq 3.5, as expected

$$\begin{aligned} \mu_b^\pm &= T \ln \phi_b^\pm \\ \mu_1^\pm &= T \ln \phi_1^\pm \pm e\psi_1 \end{aligned} \quad (3.7)$$

where  $\phi_1^+$  and  $\psi_1$  denote, respectively, the subsurface values of the surfactant volume fraction and electric potential. When we take the variation of  $\Delta\gamma$  with respect to  $\psi(x)$  and set it to zero (since only electrostatic effects are considered), the *Poisson equation* is obtained

$$\frac{\partial^2 \psi}{\partial x^2} = - \frac{4\pi e}{\epsilon} \left( \frac{\phi^+}{(a^+)^3} - \frac{\phi^-}{(a^-)^3} \right) \quad (3.8)$$

Finally, variation with respect to  $\psi(x=0) \equiv \psi_0$  yields the expected boundary condition

$$\left. \frac{\partial \psi}{\partial x} \right|_{x=0} = - \frac{4\pi e}{\epsilon (a^+)^2} \phi_0^+ \quad (3.9)$$

which is equivalent to the requirement of overall charge neutrality (only surfactant ions, and no counterions, are allowed to be adsorbed at the interface).

**3.2. Thermodynamic Equilibrium.** In equilibrium, the variations (3.5) and (3.6) vanish, and we recover the *Boltzmann distributions*

$$\phi^\pm(x) = \phi_b^\pm e^{\mp e\psi(x)/T}; \quad x > 0 \quad (3.10)$$

and the adsorption isotherm,

$$\phi_0^+ = \frac{\phi_b^+}{\phi_b^+ + e^{-(\alpha + \beta\phi_b^+ - e\psi_0)/T}} \quad (3.11)$$

We have recovered the *Davies adsorption isotherm* for ionic surfactants.<sup>32</sup> Combining eqs 3.8 and 3.10 leads to the well-known *Poisson–Boltzmann equation*

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{8\pi e c_b}{\epsilon} \sinh \frac{e\psi}{T} \quad (3.12)$$

which determines the equilibrium double-layer potential.<sup>33,34</sup> Integrating this equation once and using the boundary condition (3.9) yield the surface potential

$$\psi_0 = \frac{2T}{e} \sinh^{-1}(\lambda\phi_0^+) \quad (3.13)$$

where

$$\lambda \equiv \kappa a^+ / 4\phi_b^+$$

and  $\kappa^{-1} \equiv (8\pi c_b e^2 / \epsilon T)^{-1/2}$  is the *Debye–Hückel screening length*. Substituting  $\psi_0$  from eq 3.13, the Davies isotherm can be expressed in terms of  $\phi_0^+$  alone

$$\phi_0^+ = \frac{\phi_b^+}{\phi_b^+ + \left[ \lambda\phi_0^+ + \sqrt{(\lambda\phi_0^+)^2 + 1} \right]^2 e^{-(\alpha + \beta\phi_b^+)/T}} \quad (3.14)$$

From eqs 3.10, 3.12, and 3.9 one can calculate the contribution of the bulk solution to the interfacial free energy at equilibrium,

$$\begin{aligned} f_{\text{bulk}}^{\text{eq}} &\equiv \int_0^\infty (\Delta f^+ + \Delta f^- + f_{el}) dx \\ &= - \frac{2T}{(a^+)^2 \lambda} \left( \cosh \frac{e\psi_0}{2T} - 1 \right) = - \frac{2T}{(a^+)^2 \lambda} \left[ \sqrt{(\lambda\phi_0^+)^2 + 1} - 1 \right] \end{aligned} \quad (3.15)$$

From eqs 3.4, 3.6, and 3.15 we then get the *equilibrium equation of state*

$$\Delta\gamma = \frac{1}{(a^+)^2} \left[ T \ln(1 - \phi_0^+) + \frac{\beta}{2} (\phi_0^+)^2 - \frac{2T}{\lambda} \left( \sqrt{(\lambda\phi_0^+)^2 + 1} - 1 \right) \right] \quad (3.16)$$

In the limit of weak electric fields ( $\lambda\phi_0^+ \ll 1$ ), the electrostatic repulsion between surfactant ions at the interface predominates. As a result, the electrostatic correction to the nonionic equation of state (2.9) is quadratic in  $\phi_0^+$  and effectively reduces the lateral attraction term. In the limit of strong electric fields ( $\lambda\phi_0^+ \gg 1$ ), however, the high concentration of counterions near the interface makes the electrostatic term become only linear in  $\phi_0^+$ .

**3.3. Out of Equilibrium.** We write the current densities as in the previous section

$$j^\pm(x) = -\phi^\pm \frac{D^\pm}{T} \frac{\partial \mu^\pm}{\partial x} = -D^\pm \left( \frac{\partial \phi^\pm}{\partial x} \pm \frac{e}{T} \phi^\pm \frac{\partial \psi}{\partial x} \right) \quad (3.17)$$

where  $D^\pm$  are the diffusivities of the two ions. Applying the continuity condition, the *Smoluchowski diffusion equations* are obtained

$$\frac{\partial \phi^\pm}{\partial t} = D^\pm \frac{\partial}{\partial x} \left( \frac{\partial \phi^\pm}{\partial x} \pm \frac{e}{T} \phi^\pm \frac{\partial \psi}{\partial x} \right) \quad (3.18)$$

As in section 2, we treat separately the positions adjacent to the interface by discretizing the expressions for the various contributions and considering the current densities near the interface. The condition (see section 2.3)

$$\frac{\partial \phi_0^+}{\partial t} = -\frac{j_1^+}{a^+}$$

leads in this case to

$$\frac{\partial \phi_1^\pm}{\partial t} = \frac{D\phi^\pm}{a^\pm} \left( \frac{\partial \phi^\pm}{\partial x} \Big|_{x=a^\pm} \pm \frac{e}{T} \phi_1^\pm \frac{\partial \psi}{\partial x} \Big|_{x=a^\pm} \right) - \frac{\partial \phi_0^\pm}{\partial t} \quad (3.19)$$

The kinetic equation for the surfactant adsorption at the interface turns out to be

$$\frac{\partial \phi_0^+}{\partial t} = \frac{D^+}{(a^+)^2} \phi_1^+ \left[ \ln \frac{\phi_1^+(1 - \phi_0^+)}{\phi_0^+} + \frac{\alpha}{T} + \frac{\beta\phi_0^+}{T} - \frac{e(\psi_0 - \psi_1)}{T} \right] \quad (3.20)$$

where the last term in the brackets may be viewed as an electrostatic barrier located at the edge before the interface. It can be also written, by means of eq 3.9, as

$$\frac{e(\psi_0 - \psi_1)}{T} \approx \frac{4\pi l}{a^+} \phi_0^+$$

where  $l \equiv e^2/\epsilon T$  is the Bjerrum length (about 7 Å for water at room temperature). The kinetic equation can then be expressed, like its nonionic parallel, eq 2.14, in terms of  $\phi_0^+$  and  $\phi_1^+$  alone. Finally, since we have assumed negligible adsorption of counterions at the interface, we may require

$$\partial \phi_0^- / \partial t = 0 \quad (3.21)$$

The Smoluchowski equations (3.18) together with the Poisson equation (3.8) make a set of three differential equations for the three unknown functions,  $\phi^+(x,t)$ ,  $\phi^-(x,t)$ , and  $\psi(x,t)$ . Equations 3.9, 3.19, 3.20, and 3.21 set the boundary conditions for these

functions at the interface. If we add appropriate boundary conditions at infinity (where the volume fractions converge to their bulk value and the electric potential vanishes) and initial conditions (say, a perfectly uniform initial state with a vanishing electric potential), the mathematical problem is well posed and, at least in principle, solvable. The task of solving this system of equations, nevertheless, seems rather formidable, though similar systems have recently been dealt with numerically by MacLeod and Radke.<sup>16</sup> Fortunately enough, in all practical cases one can avoid the elaborate mathematical treatment, as will be demonstrated below.

**3.4. Limiting Cases for the Adsorption.** As in section 2, we are interested again in the distinction between *diffusion-limited adsorption*, where the kinetics are controlled by the diffusive transport inside the solution, and *kinetically limited adsorption*, where the process is controlled by the kinetics at the interface. The kinetics inside the solution are governed now by eqs 3.18. In order to identify the corresponding time scale, let us assume for simplicity that the ions have equal diffusivities,  $D^+ = D^- \equiv D$ , and that the electric field is weak,  $e\psi/T \ll 1$ . If we add the two equations (3.18) and recall the Poisson equation (3.8), the sum  $\phi^+(x,t) + \phi^-(x,t)$  is found, to first order in the electric field, to undergoes a *free* diffusion. Since both at  $t = 0$  and  $t \rightarrow \infty$  this sum is  $\phi_b^+ + \phi_b^-$  for any  $x$ , it follows that it remains unchanged during the entire process. Keeping this conclusion in mind and again making use of the Poisson equation (3.8), we now subtract the two equations (3.18) and obtain a linear diffusion equation for the electric potential,  $\psi$ ,

$$\frac{\partial \psi}{\partial t} = D \left( \frac{\partial^2 \psi}{\partial x^2} - \kappa^2 \psi \right) \quad (3.22)$$

This equation describes the kinetics of relaxation of the electric double layer. Its characteristic length scale is, as expected, the Debye–Hückel screening length,  $\kappa^{-1}$ , and the resulting time scale is

$$\tau_e = (\kappa^2 D)^{-1} \quad (3.23)$$

More rigorously, we can calculate the asymptotic solution of eq 3.22, obtaining the following interesting time dependence

$$\psi(x, t \rightarrow \infty) \approx \psi_0 \left( t - \frac{x}{2\kappa D} \right) \Theta \left( t - \frac{x}{2\kappa D} \right) e^{-\kappa x} \quad (3.24)$$

where  $\Theta(t)$  is the step (Heaviside) function. This potential may be viewed as a “retarded equilibrium potential”: a point  $x$  in the solution is in some sense in equilibrium with the interface (hence the exponential profile), but with the interface as it was some time  $(x/2\kappa D)$  ago. The information propagates from the interface to the solution with the velocity  $2\kappa D$ . From eq 3.24 it is clearly verified that the length scale is  $\kappa^{-1}$ , and the time scale is  $\tau_e$  as defined in eq 3.23.

Equation 3.23 states the time scale needed for the electric double layer to adjust and attain equilibrium with the interface. Yet, in a salt-free solution, the surfactant and counterion profiles themselves construct the electric double layer, and therefore,  $\tau_e$  is also the time scale of relaxation of the surfactant profile.

Typical values for  $D$  are about  $10^{-6}$  cm<sup>2</sup>/s, and  $\kappa^{-1}$  in salt-free ionic surfactant solutions amounts to hundreds of angstroms. This yields very small values for  $\tau_e$  (on the order of microseconds). The relaxation of the profile, therefore, is much faster in the case of ionic surfactants (without added salt) than in the case of nonionic ones. This effect is due to the strong electrostatic interactions which drastically accelerate the kinetics inside the solution. In other words, the diffusion inside a salt-

free ionic surfactant solution is an *ambipolar diffusion*<sup>35</sup> rather than a regular one. If the ion diffusivities are not assumed to be equal, one should replace  $D$  in eq 3.23 with some effective diffusivity. If the electric field is not weak, as is practically always the case in salt-free surfactant solutions, then the time scale of profile relaxation will be even *shorter*, and the above conclusion, obtained for weak electric fields, will not change.

Turning to the kinetics which take place at the interface, we treat eq 3.20 similar to eq 2.14 of section 2, expand it close to equilibrium, and find the time scale

$$\begin{aligned}\tau_k &\simeq \left(\frac{\phi_{0,\text{eq}}^+}{\phi_b^+}\right)^2 \frac{(a^+)^2}{D^+} \exp\{-[\alpha + \beta\phi_{0,\text{eq}}^+ - e(\psi_{0,\text{eq}} + \psi_{1,\text{eq}})/T]\} \\ &= \tau_k^{(0)} \exp[e(\psi_{0,\text{eq}} + \psi_{1,\text{eq}})/T]\end{aligned}\quad (3.25)$$

where  $\tau_k^{(0)}$  denotes the kinetic time scale found in the absence of electrostatics (eq 2.17). As expected, the electrostatic repulsion of surfactant ions from the charged interface slows down the adsorption process. The sum  $\psi_0 + \psi_1$  may also be written as  $2\psi_1 + (\psi_0 - \psi_1)$ , where the first term expresses the slowing down due to the subsurface concentration (which is lowered because of  $\psi_1$ ), and the second accounts for a further slowing effect due to the edge electrostatic barrier. If the electric field is strong, as is practically the case in salt-free surfactant solutions, the duration of the process may become longer by orders of magnitude. This can be verified experimentally when the electrostatic interactions are screened by added salt.<sup>12</sup> Using eq 3.13 in the limit of strong fields, together with eq 3.9, we can estimate the slowing factor by

$$\exp[e(\psi_{0,\text{eq}} + \psi_{1,\text{eq}})/T] \simeq \left(\frac{\kappa a^+ \phi_{0,\text{eq}}^+}{2 \phi_b^+}\right)^4 \exp\left(-\frac{4\pi l \phi_{0,\text{eq}}^+}{a^+ \phi_{0,\text{eq}}^+}\right)\quad (3.26)$$

This factor is typically very large. For example, in the experimental system of ref 12 one finds  $\kappa a^+ \sim 10^{-2}$ ,  $\phi_{0,\text{eq}}^+/\phi_b^+ \sim 10^5$  and  $l/a^+ \sim 1$ , so the slowing factor amounts to about  $10^7$ .<sup>37</sup>

We see that the strong electrostatic interactions present in salt-free ionic surfactant solutions drastically shorten the time scale of diffusion inside the solution and drastically lengthen the time scale of kinetics at the interface. We expect, therefore, that *ionic surfactants in salt-free solutions should exhibit kinetically limited adsorption*. On the one hand, this conclusion greatly simplifies the mathematical treatment of the problem: we can safely assume that the electric double layer is in quasi-equilibrium with the changing interface (*i.e.*, it obeys the Poisson–Boltzmann theory) and deal with the kinetics at the interface alone. On the other hand, the conclusion of kinetic control invalidates some of the assumptions employed by previous models. It implies that the relevant adsorption scenario of the two described in section 2.4 is the second one, illustrated in Figure 2b. We recall that according to this limiting scenario, the interfacial contribution to the free energy,  $f_0(\phi_0^+)$ , retains the same shape throughout the process and reaches its minimum only at equilibrium. Hence, one cannot use in this case the equilibrium equation of state, such as eq 3.16, to calculate dynamic surface tensions.

Having realized that the adsorption is limited by the kinetics at the interface, we can take the ion profiles and electric double layer to be in quasi-equilibrium. The Poisson–Boltzmann theory, therefore, can be implemented, and the kinetic equation, (3.20), is rewritten as

$$\begin{aligned}\frac{\partial \phi_0^+}{\partial t} &= \left(\frac{D^+ \phi_b^+}{(a^+)^2}\right) \frac{\exp[(4\pi l/a^+) \phi_0^+]}{[\lambda \phi_0^+ + \sqrt{(\lambda \phi_0^+)^2 + 1}]^2} \times \\ &\left\{ \ln \left[ \frac{\phi_b^+(1 - \phi_0^+)}{\phi_0^+} \right] + \frac{\alpha}{T} + \frac{\beta \phi_0^+}{T} - 2 \sinh^{-1}(\lambda \phi_0^+) \right\}\end{aligned}\quad (3.27)$$

The mathematical problem of finding the time-dependent surface coverage,  $\phi_0^+(t)$ , is thus reduced to a single integration.

**3.5. Dynamic Surface Tension in a KLA Process.** In order to relate calculated surface coverages to measured surface tensions, we need, as in section 2, an appropriate relation between these two variables. As we have just concluded, the equilibrium equation of state will not do in the case. Since kinetically limited adsorption is considered, the contribution to the free energy from the bulk solution has the equilibrium dependence on the surface coverage, *i.e.*,  $f_{\text{bulk}}^{\text{eq}}(\phi_0^+)$  of eq 3.15. Hence, we can write the free energy (or equivalently, the dynamic surface tension) as a function of the surface coverage alone,

$$\begin{aligned}\Delta\gamma[\phi_0^+(t)] &= f_0(\phi_0^+) + f_{\text{bulk}}^{\text{eq}}(\phi_0^+) \\ &= \frac{1}{(a^+)^2} \left\{ T \left[ \phi_0^+ \ln \phi_0^+ + (1 - \phi_0^+) \ln(1 - \phi_0^+) - \phi_0^+ \ln \phi_b^+ - \right. \right. \\ &\quad \left. \left. \frac{2}{\lambda} \left( \sqrt{(\lambda \phi_0^+)^2 + 1} - 1 \right) + 2\phi_0^+ \sinh^{-1}(\lambda \phi_0^+) \right] - \right. \\ &\quad \left. \alpha \phi_0^+ - \frac{\beta}{2} (\phi_0^+)^2 \right\}\end{aligned}\quad (3.28)$$

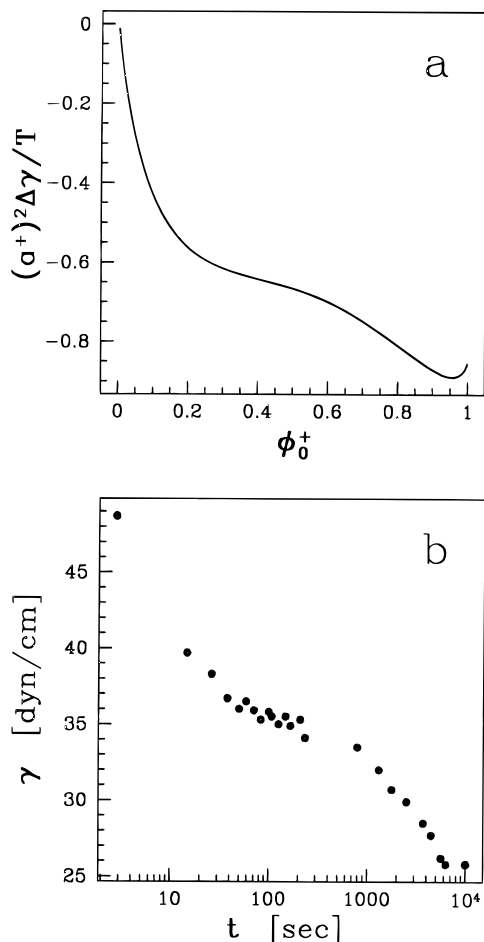
Expression 3.28 determines the behavior of the dynamic surface tension as the surfactant ions adsorb at the interface and the surface coverage increases. Note that it is very different from the equilibrium relation (3.16), and hence, using the equilibrium equation of state to relate  $\Delta\gamma$  to  $\phi_0^+$  is invalid in this case.

Assuming a strong electric field ( $\lambda \phi_0^+ \gg 1$ ), the function  $\Delta\gamma(\phi_0^+)$  can be shown to depart from the convex shape of a simple well, if  $\beta/T > 2(2 + \sqrt{3}) \simeq 7.5$ . For such high values of  $\beta$  we should expect, therefore, an interesting time dependence of the dynamic surface tension, as demonstrated in Figure 6. It should be stressed that the curve of Figure 6a is not presumed to exactly correspond to the experimental results reproduced in Figure 6b. Our claim is that an interfacial free energy of the form suggested by eq 3.28 may clearly account for the unusual, experimentally observed dynamic surface tension depicted in Figure 6b.

For values of parameters other than those chosen in Figure 6, the interfacial free energy may have a nonmonotonic, double-well shape. In such a case, we still expect the time dependence of the surface tension to schematically resemble the curve in Figure 6b, *i.e.*, to exhibit a period of almost constant tension as the system undergoes the transition from the first well to the second. Our current, diffusive formalism, however, cannot quantitatively describe the kinetics of such a process.<sup>20,36</sup>

**3.6. Effect of Counterion Adsorption.** An issue still to be addressed is whether such high values for the interaction constant,  $\beta$ , are reasonable for ionic surfactants. Measurements on nonionic surfactants yield typical values for  $\beta$  which are smaller than  $4T$ .<sup>29</sup> There is no obvious reason why ionic surfactants should exhibit, apart from the Coulombic repulsion, also much stronger lateral attraction at the interface. The answer lies in one of the assumptions we have used. Throughout the analysis above, it was assumed that the counterions are surface-inactive and hence not present at all at the interface itself. In fact, this assumption is inaccurate and was taken merely for





**Figure 6.** (a) Dependence between surface tension and surface coverage in the KLA case, according to eq 3.28, where the values taken for the parameters are  $a^+ = 12 \text{ \AA}$ ,  $\phi_b^+ = 3.6 \times 10^{-4}$ ,  $\alpha = 11.5T$  and  $\beta = 9T$ . (b) Experimentally observed dynamic surface tension of a salt-free  $3.5 \times 10^{-4} \text{ M}$  SDS solution against dodecane, adapted from ref 12. The time dependence is schematically consistent with a nonconvex dependence  $\Delta\gamma(\phi_0^+)$  such as the one in (a).

the sake of a clearer and simpler discussion. The high surface potentials involved in salt-free surfactant solutions should attract a certain amount of counterions to the interface. Our aim now is to calculate the correction introduced into the interfacial free energy as a result of the presence of a small amount of counterions at the interface.

For simplicity, we assume the counterions to be in quasi-equilibrium throughout the system, and therefore obey the Boltzmann distribution (3.10)

$$\phi_0^- = \phi_b^- e^{e\psi_0/T}$$

Since the surface charge consists now of both surfactant ions and counterions, expression 3.13 for the surface potential should be modified

$$\psi_0 = \frac{2T}{e} \sinh^{-1} \{ \lambda [\phi_0^+ - (a^+/a^-)^2 \phi_0^-] \} \quad (3.29)$$

In the limits of a strong field ( $\lambda\phi_0^+ \gg 1$ ) and a small density of adsorbed counterions [ $\phi_0^-/(a^-)^2 \ll \phi_0^+/(a^+)^2$ ], we find from eq 3.29 that the counterion surface coverage depends quadratically on the surfactant one,

$$\phi_0^- \approx 4\lambda^2 \phi_b^- (\phi_0^+)^2 \quad (3.30)$$

The adsorbed counterions introduce the following direct correction to the interfacial free energy as was formulated in section 3.1.

$$\delta(\Delta\gamma)_{\text{counter}} = \frac{1}{(a^-)^2} [T(\phi_0^- \ln \phi_0^- - \phi_0^-) - e\phi_0^- \psi_0 - \mu_1^- \phi_0^-]$$

In quasi-equilibrium this expression reduces to

$$\delta(\Delta\gamma)_{\text{counter}} = -\frac{T}{(a^-)^2} \phi_0^-$$

so the correction to  $(a^+)^2 \Delta\gamma/T$  takes the form

$$\delta\left(\frac{(a^+)^2 \Delta\gamma}{T}\right)_{\text{counter}} = -\left(2\lambda \frac{a^+}{a^-}\right)^2 \phi_b^- (\phi_0^+)^2 \quad (3.31)$$

In addition, the adsorbed counterions introduce *indirect* corrections into the free energy, through the terms  $e\phi_0^+ \psi_0$  and  $f_{\text{bulk}}^{\text{eq}}$  of eq 3.28. However, these two corrections turn out to exactly cancel each other. Note that apart from electrostatic interactions, we have neglected any other, short-range interactions between surfactant ions and counterions at the interface.

Looking at expression 3.31, we find that the effect of a small amount of adsorbed counterions is equivalent to an effective increase in the lateral attraction term,  $-\beta(\phi_0^+)^2/2$  of eq 3.4. The coefficient  $(2\lambda a^+/a^-)^2 \phi_b^-$  can be also written as  $2\pi\lambda a^-/(a^+)^2$ . Taking  $a^- \leq a^+ \sim l$  leads to a correction of order 1–10, i.e., the counterion adsorption may introduce, indeed, a significant addition to the attraction term. Note, that the increase in  $\beta$  is sensitive to molecular details (the dimensions of the two types of ions). This fact may be related to the experimental observation that some ionic surfactants do exhibit the unusual time dependence depicted in Figure 6b, while others do not.<sup>38</sup>

#### 4. Ionic Surfactants with Added Salt

In many practical cases, the solution contains, in addition to the surfactant ions and their counterions, also a certain amount of dissolved salt. The effect of adding mobile ions, whose concentration usually exceeds that of the surfactant, is to screen the electrostatic interactions. Since it was found in section 3 that strong electrostatic interactions drastically affect the nature of the adsorption process, we should expect the results in the presence of added salt to be significantly different from the case of salt-free ionic solutions.

In principle, adding salt introduces two additional degrees of freedom into our formalism, namely the profiles of the salt ions and their counterions. This should significantly complicate the already elaborate problem of ionic surfactant adsorption. In order to avoid such complications we adopt the following simplifying assumptions:

(i) The salt is surface-inactive and its concentration is much larger than that of the surfactant. This assumption allows us to separate the role played by the two types of ions: the surfactant ions adsorb at the interface and build up the surface charge, whereas the salt ions form the electric double layer inside the solution.

(ii) The salt ions are much more mobile than the surfactant ones. Relying on this assumption, the kinetics of the salt ions can be neglected, and the double layer they form can be assumed to maintain quasi-equilibrium with the changing surface charge.

(iii) For simplicity, we assume that the salt ions and counterions are monovalent as well, or more generally, have the same valency.<sup>39</sup>

Most of the formulation given in section 3 remains valid, in particular the equations governing the surfactant kinetics, eqs 3.18–3.20. The main difference is that the electric potential,  $\psi$ , is no longer regarded as an independent degree of freedom coupled to the surfactant profile,  $\phi$ . Instead, it is simply given by the potential of an equilibrium double layer, depending on the surface coverage and salt bulk concentration alone. The high salt concentration we have assumed allows us to take a screened double-layer potential in the linear, Debye–Hückel regime<sup>34</sup>

$$\psi(x,t) = \frac{4\pi e}{\epsilon\kappa a^2} \phi_0(t) e^{-\kappa x} \quad (4.1)$$

bearing in mind that in this section, the salt bulk concentration,  $c_s$ , replaces the surfactant one,  $c_b$ , in the definition of  $\kappa$ . Substituting this potential in eqs 3.18 and 3.19, we obtain the equations determining the kinetics inside the solution

$$\frac{\partial \phi}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial \phi}{\partial x} - \frac{\kappa^2}{2c_s a^2} \phi_0 e^{-\kappa x} \phi \right) \quad (4.2)$$

$$\frac{\partial \phi_1}{\partial t} = \frac{D}{a} \left( \frac{\partial \phi}{\partial x} \Big|_{x=a} - \frac{\kappa^2}{2c_s a^2} \phi_0 \phi_1 \right) - \frac{\partial \phi_0}{\partial t} \quad (4.3)$$

In the last equation we have also assumed that the Debye–Hückel screening length is much larger than the surfactant molecular dimension,  $\kappa a \ll 1$ . The equation describing the adsorption kinetics at the interface, eq 3.20, remains valid as it is.

As in the previous two sections, we are interested in the distinction between the two limits—diffusion-limited vs kinetically limited adsorption. In order to find the time scale of diffusion, we treat the electric field as a small perturbation and seek a solution to eqs 4.2 and 4.3 which is close to the one in the nonionic case. A procedure similar to the one given in section 2 is now employed, yielding the following asymptotic expression

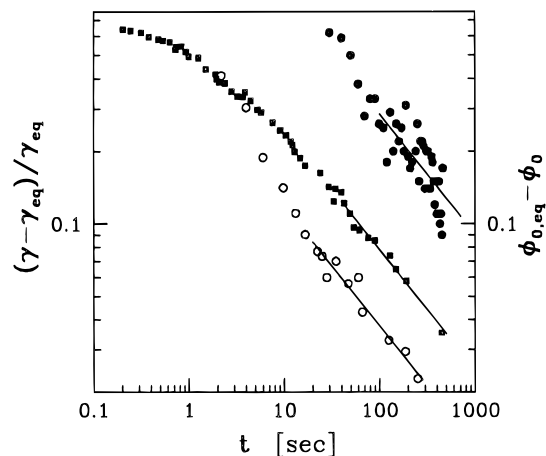
$$\phi_b - \phi_1 \approx \frac{\kappa \phi_b \phi_{0,\text{eq}}}{2c_s a^2} + \frac{a \phi_{0,\text{eq}}}{\sqrt{\pi D t}} \left[ 1 - \frac{c_b}{2c_s} - \frac{\kappa \phi_{0,\text{eq}}}{2c_s a^2} \left( 1 - \frac{3c_b}{2c_s} \right) \right] \quad (4.4)$$

When this result is compared to its nonionic parallel, eq 2.15, two observations are to be made. The first is that eq 4.4 contains an additional constant term, since the equilibrium subsurface concentration differs from the bulk one in the presence of an electric field. The second is that the diffusion time scale is slightly corrected, as expected, by the weak electrostatic interactions,

$$\tau_d = \tau_d^{(0)} \left[ 1 - \frac{c_b}{2c_s} - \frac{\kappa \phi_{0,\text{eq}}}{2c_s a^2} \left( 1 - \frac{3c_b}{2c_s} \right) \right]^2 \quad (4.5)$$

where  $\tau_d^{(0)}$  denotes the diffusion time scale found in the nonionic case (eq 2.16). The correction vanishes when we take very high salt concentrations, leading to a complete screening of electrostatic interactions.

Turning to the case of KLA, we find that the expression for the time scale of kinetics at the interface derived for salt-free solutions, eq 3.25, remains valid also in the presence of added salt. However, unlike the case of section 3, the electric field in this case is weak, and the resulting slowing factor is small, so that  $\tau_k \geq \tau_k^{(0)}$ . Since the time scales of both the diffusion inside the solution and the kinetics at the interface have been



**Figure 7.** DLA exhibited by ionic surfactants in the presence of added salt. Three examples are given: dynamic surface tension of  $4.86 \times 10^{-5}$  M SDS with 0.1 M NaCl against dodecane (open circles and left ordinate), adapted from ref 12; dynamic surface tension of  $2.0 \times 10^{-4}$  M SDS with 0.5 M NaCl against air (squares and left ordinate), adapted from ref 40; surface coverage deduced from second harmonic generation measurements on a saturated solution of SDNS with 2% NaCl against air (solid circles and right ordinate), adapted from ref 41. Note the asymptotic  $t^{-1/2}$  behavior, characteristic of DLA and shown by the solid fitting lines.

shown, in the presence of salt, to differ only slightly from those of the nonionic case, we conclude that *ionic surfactants with added salt, like nonionic surfactants, should exhibit diffusion-limited adsorption*. As in the case of nonionic surfactants, this conclusion is well supported by experiments, as illustrated in Figure 7. Indeed, measurements on ionic surfactant solutions with salt can be well fitted by theoretical curves, using the same schemes used for nonionic surfactants (see section 2).<sup>12</sup>

## 5. Concluding Remarks

In this work we have presented an alternative approach to the problem of the kinetics of surfactant adsorption. One of the advantages of this approach is that the diffusion inside the aqueous solution and the kinetics of adsorption at the interface are not introduced as two separate, independent processes, but both arise from the same model. This makes the model more complete than previous ones and allows us to point at the process limiting the kinetics of the entire system in various cases. We find the adsorption to be limited by the bulk diffusion in the cases of nonionic surfactants and ionic surfactants with added salt, and by the kinetics at the interface in the case of salt-free ionic surfactant solutions. Such conclusions lead to a significant mathematical simplification of the statement of the problem. They are also in agreement with experimental findings.

Another advantage is that the formulation can be readily extended to more complicated systems. We have used this to account for the kinetic adsorption of ionic surfactants with and without added salt. In particular, we have been able to explain the recently reported unusual time dependence of the surface tension in salt-free ionic surfactant solutions. In addition, our free-energy approach provides a general, straightforward method for calculating dynamic surface tensions from surface coverages, which does not rely on equilibrium relations. This feature turns out to be essential in the case of salt-free ionic surfactant solutions.

The adsorption of ionic surfactants behaves very differently in the presence or absence of salt: it is diffusion-limited in the former case, and kinetically limited in the latter case. This has been shown both experimentally and by our theory. In order to reach better understanding of the kinetics of surfactant

adsorption, additional experiments are required, particularly on ionic surfactants. All experiments until now have involved aqueous solutions which are either free of salt or containing high concentrations of it. It should be interesting to examine aqueous solutions with low salt concentrations and observe the crossover from one limiting behavior to another. Moreover, since the adsorption in the case of salt-free ionic surfactant solutions has been found to be kinetically limited, dynamic surface tension measurements may be used to “probe” the actual dependence of the interfacial free energy,  $f_0(\phi_0)$ , on the surface coverage,  $\phi_0$ . This, in turn, may help explain the equilibrium phase behavior of ionic surfactant monolayers under various conditions (e.g., under compression).

The theory presented in this work is incomplete in two main aspects. The first is that our diffusive formalism, as was mentioned in section 3, cannot fully describe the kinetics in cases where an energy barrier must be overcome before the interfacial free energy reaches its minimum. According to the analysis of section 3, actual dynamic surface tension measurements imply that the free energy in the case of certain ionic surfactant solutions probably does exhibit such a barrier. Quantitative treatment of the evolution of such systems should require, therefore, a more accurate (perhaps “Kramers-like”<sup>42</sup>) theory. The second aspect is the lateral diffusion at the interface, whose time scale has been completely neglected by this work. As was mentioned in section 2, cases where lateral diffusion is significant are encountered in practice, and a future, more complete theory cannot ignore its effect.

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- (22) This is the so-called Tauberian method for finding asymptotic expressions using the Laplace transform.
- (23) Close to equilibrium we can also write  $\partial\phi_0/\partial t \approx (D\phi_0/a^2\phi_{0,eq}) - [e^{\alpha+\beta\phi_0}/T\phi_1(1-\phi_0) - \phi_0]$ , which coincides with the adsorption–desorption form of the Frumkin (or Langmuir, when  $\beta = 0$ ) kinetic equation used by previous works.<sup>7–10</sup>
- (24) Note that in the discussion above we have completely neglected a third time scale—the time needed for lateral diffusion and molecular reorientation at the interface. If, however, due to certain molecular constraints, this time scale is no longer negligible, exceptions to the above conclusions are to be expected (see refs 25 and 26).
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- (37) This does not mean that adding salt will shorten the process by such an enormous factor. As we shall see in section 4, adding salt leads back to diffusion-limited adsorption on the time scale of  $\tau_0$ , which is much longer than  $\tau_k^{(0)}$ .
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