

Kinetics of surfactant adsorption: the free energy approach

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Abstract

We review the free energy approach to the kinetics of surfactant adsorption at fluid–fluid interfaces. The formalism is applied to several systems. For non-ionic surfactant solutions, the results coincide with earlier models while indicating their limits of validity. We study the case of surfactant mixtures, focusing on the relation between the mixture kinetics and the properties of its individual constituents. Strong electrostatic interactions in salt-free ionic surfactant solutions drastically modify the adsorption kinetics. In this case the theory accounts for experimental results, which could not be earlier understood. The effect of screening by added salt is studied as well. Our theoretical predictions are compared with available experiments. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The kinetics of surfactant adsorption is a fundamental problem of interfacial science playing a key role in various processes and phenomena, such as wetting, foaming and stabilization of liquid films. For example, the wetting rate of a substrate by surfactant solutions was shown to be correlated with the dynamic surface tension of the solution, rather than its equilibrium surface tension [1]. Since the pioneering theoretical work of Ward and Tordai in the 1940s [2], the kinetics of

surfactant adsorption has been the object of thorough experimental and theoretical research [3–5].

The problem of adsorption kinetics, poses several theoretical difficulties. One question concerns the adsorption mechanism at the interface and its coupling to the kinetics in the bulk solution. Another important question is related to the definition and calculation of the time-dependent interfacial tension as measured in experiments. Earlier theoretical works have addressed these questions by adding appropriate assumptions to the theory. Such models can be roughly summarized by the following scheme. (i) Consider a diffusive transport of surfactant molecules from a semi-infinite bulk solution (following Ward and Tordai); (ii) introduce a certain adsorption equation as a boundary condition at the interface; (iii) solve for the time-dependent surface coverage; (iv) assume that the equilibrium equation of state is

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valid also out of equilibrium and calculate the dynamic surface tension. While certain models take an equilibrium adsorption isotherm as the interfacial boundary condition [6–8], others use a kinetic equation [9–12].

The purpose of this article is to review a theoretical approach based on a free-energy formalism [13–16]. The main advantage of the free-energy approach is that all the equations are derived from a single functional, thus yielding a more complete and consistent description of the kinetics in the entire system. The definition and calculation of the dynamic surface tension results naturally from the formalism itself, and extension to more complicated interactions can then follow. In this review, we summarize the essence of the free-energy approach and its application to various systems while skipping most of the technical calculations. More details can be found in previous publications [13–16].

The next section presents the general theoretical framework and basic considerations of our formalism. In the sections that follow we apply this general scheme to three examples. First, the simplest case of a single-component, non-ionic surfactant solution is considered. We analyze the various stages and characteristic time scales of the adsorption process. Results of earlier models are recovered as special cases, and their limits of validity are defined. In the second example, the treatment of the non-ionic case is extended to surfactant mixtures. Experiments portray a large variety of phenomena specific to mixed systems [8,17–21]. For instance, more complex dynamic surface tension is observed due to competition between different species. We focus on the relation between the adsorption behavior of the mixture and the properties of its individual constituents. Certain cases are found, where mixing several surfactant species may lead to significant differences in the kinetics. The third example concerns ionic surfactant solutions. In salt-free systems, strong electrostatic interactions are found to drastically modify the adsorption kinetics and yield interesting time dependence [22–24]. Using our approach, we point out the problems in earlier models as applied to such systems and account for the experimentally observed behavior.

Electrostatic screening caused by added salt is shown to lead to a kinetic behavior much similar to the non-ionic case.

Our theoretical predictions are compared with available experiments. However, specific experimental techniques, as can be found in [3], are not covered. Since a considerable body of theoretical work is summarized in this review, derivations are not given in full detail; further details can be found in [13–16].

2. Theoretical framework

This section outlines the general free energy formalism, which is used extensively in the sections that follow [13].

In this review we assume that the aqueous solution has a sharp, flat interface with another non-polar fluid phase (an oil or air phase), as is illustrated in Fig. 1. We are concerned with a surfactant solution below its critical micelle concentration (cmc), i.e. containing only monomers. In such a dilute solution there are two important energy scales – the thermal energy, T (throughout this review we take the Boltzmann constant as unity), and the energy of molecular transfer to the water–oil or water–air interface, α . In common surfactant systems α is much larger than T (typically in the range $10\text{--}20T$). As a result, a very compact monolayer is formed at the interface with an interfacial volume fraction close to unity.

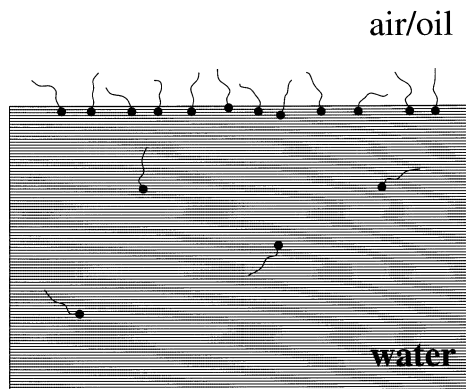


Fig. 1. Schematic view of the system. A sharp, flat interface separates a dilute surfactant solution from an air or oil phase.

Since the bulk volume fraction in such dilute solutions is very low (typically 10^{-6} – 10^{-4}), the surfactant attains a step-like profile having a sharp decrease within a molecular distance from the interface. It is unjustified in these circumstances to employ a continuum, gradient-expansion formalism for the entire system, as is done in many other interfacial problems. A more appropriate approach is to treat the interface as a distinct sub-system being in thermal and diffusive contact with the bulk solution. (For an earlier discussion of such a distinction, see [25]). Consequently, the excess free energy of the system is divided into a bulk contribution and an interfacial one.

We write the excess free energy per unit area as a functional of the various degrees of freedom $\{\phi_i\}_{i=1,2,\dots}$ required to describe the system (e.g. the surfactant volume fraction profile, electrostatic potential, etc.),

$$\Delta\gamma[\{\phi_i\}] = \int_0^\infty \Delta f[\{\phi_i(x, t)\}] dx + f_0[\{\phi_{i0}(t)\}]. \quad (2.1)$$

In the first term, Δf denotes the local excess in free energy density over the bulk, uniform solution, x being the distance from the interface and t the time. The second term, f_0 , describes the contribution from the interface itself, $\{\phi_{i0}\}$ being the interfacial values of the various degrees of freedom. A coupling term is to be included in f_0 to account for the contact between the interface and the bulk. Note that in order to correctly model the kinetics, the coupling should be made with the layer in contact, namely the sub-surface layer of solution ($x \rightarrow 0$), since it is generally not in equilibrium with the rest of the bulk during the process. It has been implicitly assumed in Eq. (2.1) that lateral inhomogeneities are negligible, i.e. the time scale of lateral kinetics is assumed very short compared with the adsorption process. This assumption is usually justified for fluid–fluid interfaces and allows a reduction of the problem to a single spatial dimension, namely the distance from the interface, x . (There are certain cases, however, where lateral diffusion seems to play an important role; see [26,27]).

Apart from T and α , another energy parameter, β , is usually required to quantitatively account for equilibrium, as well as kinetic experimental measurements [28]. It is associated with lateral attraction between surfactant molecules at the interface, which usually cannot be neglected due to the large interfacial coverage. Values of β may amount to several T , the thermal energy.

Once a free energy functional in the form of Eq. (2.1) has been formulated, the equilibrium relations and kinetic equations are easily derived. Equilibrium relations, such as the equilibrium profile and adsorption isotherm are found by setting the variation of the free energy with respect to the various degrees of freedom to zero,

$$\frac{\delta\Delta\gamma}{\delta\phi_i(x)} = 0, \quad \text{equilibrium.} \quad (2.2)$$

The corresponding extremum of the free energy yields the equilibrium equation of state, relating $\Delta\gamma$ with the equilibrium values of $\{\phi_i\}$. First-order kinetic equations can be derived as well from the variation of the free energy. Since the degrees of freedom relevant to the adsorption problem are conserved quantities (e.g. concentration profiles), the scheme for deriving the kinetic equation for a conserved order parameter should be employed (see, e.g. [29]),

$$\frac{\partial\phi_i}{\partial t} = \frac{a_i^2}{T} \frac{\partial}{\partial x} \left[D_i(\{\phi_i\}) \phi_i \frac{\partial}{\partial x} \left(\frac{\delta\Delta\gamma}{\delta\phi_i} \right) \right], \quad (2.3)$$

where a_i is a molecular size and $D_i(\{\phi_i\})$ a diffusion coefficient. Due to the step-like profile discussed above, a similar dependence may be assumed for the diffusion coefficient as well, i.e. having a constant value, D_i , in the dilute bulk and possibly a different value, D_{i0} , at the interface. The kinetic equations derived by this procedure do not account for convective transport. Convection is found to play a significant role in certain practical cases and experimental setups [30]. More recent experimental techniques, however, seem to exclude convective effects [3], and they will be neglected in the current review.

The distinction between bulk and interface results in separate (though coupled) kinetic equations for the two sub-systems. Correspondingly, two limiting cases naturally arise. *Diffusion-lim-*

ited adsorption occurs when the interfacial kinetics is much faster than the transport from the bulk. In this case the interfacial layer may be assumed to maintain quasi-equilibrium with the sub-surface layer throughout the process. Consequently, the interfacial kinetic equations are reduced to equilibrium-like isotherms relating the surface coverage and sub-surface volume fraction. They thus serve merely as static boundary conditions for the kinetic equations in the bulk. The other limiting case is *kinetically limited adsorption*, where the interfacial kinetics becomes the slow limiting process, and the bulk may be assumed throughout the process as maintaining quasi-equilibrium with the changing interface. Deriving all the kinetic equations from a single functional allows a more rigorous determination of the conditions under which such limiting cases hold. This will be demonstrated in the following sections.

One of the important points in our formalism is that the excess free energy per unit area (Eq. (2.1)) is *identified* with the measurable reduction in interfacial tension. Furthermore, assuming that this definition holds at equilibrium, as well as out of equilibrium, readily solves the problem of calculating the *dynamic* surface tension, which is a fundamental obstacle in adsorption kinetics. Earlier works dealt with this obstacle by simply assuming that the equilibrium equation of state can be used for the dynamic surface tension as well [31]. Since the equation of state is merely the extremum of the functional in Eq. (2.1), using it out of equilibrium is valid only when the free energy is not too far from its minimum value. Noting that the dominant term in Eq. (2.1) is usually the interfacial one, f_0 , this requirement is fulfilled when the interface is close to equilibrium with the sub-surface layer. In other words, the scheme employed by earlier works is valid only for diffusion-limited adsorption. This observation becomes particularly important in kinetically limited systems, such as salt-free ionic surfactant solutions, where our general Eq. (2.1), rather than the equation of state, must be used in order to correctly calculate the dynamic surface tension.

3. Non-ionic surfactants

We start with the simplest case of an aqueous solution containing a single type of non-ionic surfactant [13]. The excess free energy (Eq. (2.1)) can be rewritten in this case as a functional of a single degree of freedom — the volume fraction profile of the surfactant, $\phi(x, t)$,

$$\Delta\gamma[\phi] = \int_0^\infty \Delta f[\phi(x, t)]dx + f_0[\phi_0(t)], \quad (3.1)$$

where ϕ_0 is the volume fraction at the interface (surface coverage). We assume a contact with a reservoir, where the surfactant has fixed volume fraction and chemical potential, ϕ_b and μ_b , respectively. Since the solution is dilute, steric and other short-range interactions between surfactant molecules are assumed to take place only at the interfacial layer itself. Hence, the two contributions to the excess free energy are written as

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

$$a^2f_0(\phi_0) = T[\phi_0 \ln \phi_0 + (1 - \phi_0) \ln(1 - \phi_0)] - (\alpha + \mu_1)\phi_0 - (\beta/2)\phi_0^2, \quad (3.3)$$

where a denotes the surfactant molecular size. The contribution from the bulk contains only the entropy in the ideal-solution limit and contact with the reservoir. In the interfacial contribution, however, we have included the entropy of mixing accounting for the finite molecular size, a linear term accounting for the surface activity and contact with the adjacent solution ($\mu_1 \equiv \mu(x \rightarrow 0)$ being the chemical potential at the sub-surface layer), and a quadratic term describing short-range lateral attraction between surfactant molecules at the interface. Although both α and μ_1 are linearly coupled with the surface coverage, their physical origin is quite different — α is constant in time, characterizing the surface activity of the specific surfactant, whereas μ_1 is a time-dependent function participating in the interfacial kinetics. By using a quadratic term for lateral attraction, we restrict to the simplest short-range pair interactions. This simplification is sufficient for describing the thermodynamics of monolayers in the gaseous and liquid states. It is

merely a second order term of an expansion in ϕ_0 , and generalization to more complicated situations can be made.

3.1. Equilibrium relations

Setting the variation of the free energy with respect to $\phi(x)$ and ϕ_0 to zero yields a uniform profile in the bulk, $\phi(x > 0) \equiv \phi_b$, and recovers the Frumkin adsorption isotherm (or the Langmuir one, if $\beta = 0$) at the interface [32],

$$\phi_0 = \frac{\phi_b}{\phi_b + e^{-(\alpha + \beta\phi_0)/T}}. \quad (3.4)$$

Substituting these results in the free energy functional recovers also the equilibrium equation of state,

$$a^2 \Delta \gamma = T \ln(1 - \phi_0) + (\beta/2) \phi_0^2. \quad (3.5)$$

3.2. Kinetic equations

Using the scheme of Eq. (2.3) to derive the kinetic equations, an ordinary diffusion equation is obtained in the bulk,

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}, \quad (3.6)$$

where D is the surfactant diffusion coefficient, assumed constant in the dilute bulk. In addition, we get a conservation condition at the sub-surface layer,

$$\frac{\partial \phi_1}{\partial t} = \frac{D}{a} \frac{\partial \phi}{\partial x} \Big|_{x=a} - \frac{\partial \phi_0}{\partial t}, \quad (3.7)$$

where $\phi_1 \equiv \phi(x \rightarrow 0)$ is the local volume fraction in the sub-surface layer, to be distinguished from the interfacial volume fraction, ϕ_0 . Finally, at the interface itself, we get

$$\frac{\partial \phi_0}{\partial t} = \frac{D_0}{a^2} \phi_1 \left[\ln \frac{\phi_1(1 - \phi_0)}{\phi_0} + \frac{\alpha}{T} + \frac{\beta\phi_0}{T} \right], \quad (3.8)$$

where D_0 may differ from D . Applying the Laplace transform with respect to time to Eqs. (3.6) and (3.7), we obtain a relation similar to that of Ward and Tordai [2],

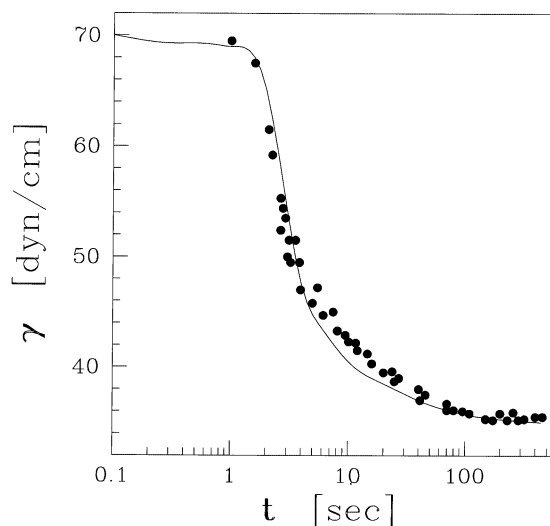


Fig. 2. Typical dynamic surface tension curve of a non-ionic surfactant solution. (Adapted from [28]). The solution contains 1.586×10^{-4} M 1-decanol. The solid line is a theoretical fit using the following parameters: $a = 4.86$ Å, $\alpha = 11.6T$, $\beta = 3.90T$ (all three parameters were fitted from independent equilibrium measurements), and $D = 6.75 \times 10^{-6}$ cm² s⁻¹.

$$\phi_0(t) = \left(\frac{D}{\pi a^2} \right)^{1/2} \left[2\phi_b \sqrt{t} - \int_0^t \frac{\phi_1(\tau)}{\sqrt{t-\tau}} d\tau \right] + 2\phi_b - \phi_1. \quad (3.9)$$

The system of two equations, Eqs. (3.8) and (3.9), with appropriate initial conditions, completely determines the adsorption kinetics and equilibrium state. Full solution of the equations can be obtained only numerically. Several numerical schemes have been proposed for solving the Ward–Tordai equation with various boundary conditions [3,4,11,16]. An example for a numerical solution fitted to experiment is given in Fig. 2.

Our formalism has led to a diffusive transport in the bulk (Eq. (3.9)) coupled to an adsorption mechanism at the interface (Eq. (3.8)). Let us examine the characteristic time scales associated with these kinetic equations. The diffusive transport from the bulk solution (Eq. (3.9)) relaxes like [7]

$$\frac{\phi_1(t \rightarrow \infty)}{\phi_b} \simeq 1 - \left(\frac{\tau_1}{t} \right)^{1/2}, \quad \tau_1 \equiv \frac{a^2}{\pi D} \left(\frac{\phi_{0,\text{eq}}}{\phi_b} \right)^2, \quad (3.10)$$

where $\phi_{0,\text{eq}}$ denotes the equilibrium surface coverage. The molecular diffusion time scale, a^2/D , is of order 10^{-9} s, but the factor $\phi_{0,\text{eq}}/\phi_b$ in surfactant monolayers can be very large (typically 10^5 – 10^6), so the diffusive transport to the interface may require minutes. On the other hand, the kinetic process at the interface (Eq. (3.8)) relaxes like

$$\frac{\phi_0(t \rightarrow \infty)}{\phi_{0,\text{eq}}} \simeq 1 - e^{-t/\tau_k},$$

$$\tau_k \equiv \frac{a^2}{D_0} \left(\frac{\phi_{0,\text{eq}}}{\phi_b} \right)^2 e^{-(\alpha + \beta \phi_{0,\text{eq}})/T}. \quad (3.11)$$

Typical values of α for common surfactants are much larger than T . In the absence of barriers hindering the kinetics at the interface, D_0 is not expected to be drastically smaller than D , and τ_k , therefore, is much smaller than τ_1 . In other words, the adsorption of common non-ionic surfactants is expected to be diffusion-limited. The asymptotic time dependence found in Eq. (3.10) gives a

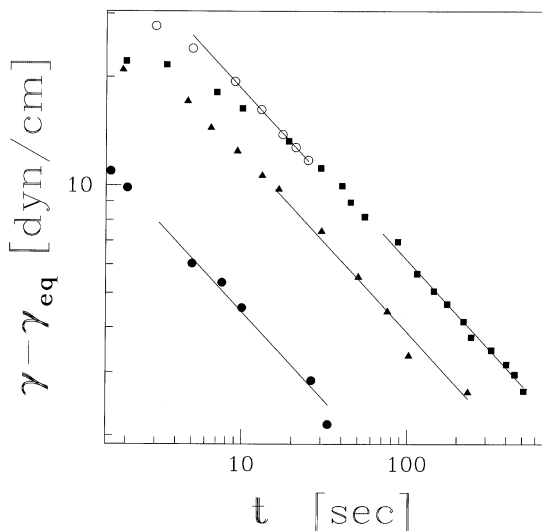


Fig. 3. Diffusion-limited adsorption exhibited by non-ionic surfactants. Four examples for dynamic surface tension measurements are shown. Open circles — decal alcohol, 9.49×10^{-5} M. (Adapted from [33].) Squares — Triton X-100, 2.32×10^{-5} M. (Adapted from [11].) Triangles — $C_{12}EO_8$, 6×10^{-5} M. (Adapted from [34].) Solid circles — $C_{10}PY$, 4.35×10^{-4} M. (Adapted from [34].) The asymptotic $t^{-1/2}$ dependence shown by the solid fitting lines is a ‘footprint’ of diffusion-limited adsorption.

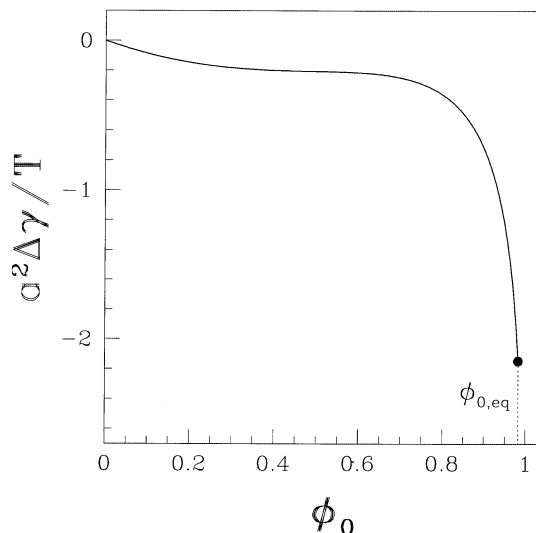


Fig. 4. Dependence of surface tension on surface coverage in diffusion-limited adsorption (Eq. (3.5)). The values taken for the parameters match the example in Fig. 2.

distinct ‘footprint’ for *diffusion-limited* adsorption, as demonstrated in Fig. 3.

One consequence of a diffusion-limited process is that the relation between ϕ_0 and ϕ_1 is given at all times by the equilibrium adsorption isotherm (Eq. (3.4) in our model). The solution of the adsorption problem in that case amounts, therefore, to the solution of the Ward–Tordai Eq. (3.9) with the adsorption isotherm as a boundary condition. An exact analytical solution exists only for the simplest, linear isotherm, $\phi_0 \propto \phi_1$ [30]. Such an approximation, however, is valid only for low surface coverage and, hence, not very useful for the description of the entire adsorption process [16]. For more realistic isotherms such as Eq. (3.4), one has to resort to numerical techniques, as mentioned above and demonstrated in Fig. 2. Another consequence of a diffusion-limited process, as explained in Section 2, is that the dynamic surface tension, $\Delta\gamma(t)$, approximately obeys the equilibrium equation of state (Eq. (3.5)). These results show that the validity of schemes employed by earlier theories is essentially restricted to diffusion-limited cases.

The dependence defined by the equilibrium equation of state (Eq. (3.5)) is depicted in Fig. 4. As a result of the competition between the en-

tropy and interaction terms in the equation, the surface tension changes very little for small surface coverages. As the coverage increases beyond about $1 - (\beta/T)^{-1/2}$, the surface tension starts decreasing until reaching equilibrium. This qualitatively explains the shape of dynamic surface tension curves found in experiments for non-ionic surfactants (see Fig. 2). When the adsorption is not diffusion-limited, this theoretical approach is no longer applicable, as will be demonstrated in the ionic case.

In a diffusion-limited process the various physical quantities all have the asymptotic characteristic $t^{-1/2}$ dependence, similar to Eq. (3.10). Yet, the relaxation times τ_0 , τ_1 and τ_γ , characterizing the temporal decay of ϕ_0 , ϕ_1 and γ , respectively, may differ

$$\frac{\phi_0}{\phi_{0,\text{eq}}} \simeq 1 - \left(\frac{\tau_0}{t}\right)^{1/2}, \quad \frac{\phi_1}{\phi_b} \simeq 1 - \left(\frac{\tau_1}{t}\right)^{1/2},$$

$$\frac{\Delta\gamma}{\Delta\gamma_{\text{eq}}} \simeq 1 - \left(\frac{\tau_\gamma}{t}\right)^{1/2}. \quad (3.12)$$

Experiments are usually concerned with surface coverage and surface tension, rather than sub-surface concentration. Substituting ϕ_1 of Eq. (3.10) in Eq. (3.4) and Eq. (3.5), we find

$$\tau_0 = \left[\frac{1 - \phi_{0,\text{eq}}}{1 - (\beta/T)\phi_{0,\text{eq}}(1 - \phi_{0,\text{eq}})} \right]^2 \tau_1,$$

$$\tau_\gamma = (\phi_{0,\text{eq}})^2 \tau_1. \quad (3.13)$$

Since $\phi_{0,\text{eq}}$ is usually very close to unity, the value of τ_γ extracted from dynamic surface tension measurements is practically identical to τ_1 of Eq. (3.10). (The possible divergence of τ_0 for $\beta > 4T$ is a consequence of the non-convexity of f_0 , Eq. (3.3), for these values of β , indicating a transition to a two-phase coexistence.)

3.3. Short time behavior

In order to provide a comprehensive description of the adsorption process, the time dependence during early stages is of interest as well. It should be first noted that diffusion-limited behavior cannot strictly start at $t=0$, since at that instance the interface and sub-surface layers are not at equilibrium with each other. Assuming a diffusion-limited time dependence of the form

$\phi_0(t) \simeq \text{const.} + (t/\tau_1)^{1/2}$ [7], the const. is found to be roughly equal to $2\phi_b$. (This can be obtained also from the analytic solution of the diffusion-limited problem in the linear adsorption limit; see [16]). In other words, only once the surface coverage has exceeded a value of $2\phi_b$, can one assume a process limited by diffusion. Prior to the onset of diffusion, a short stage takes place, when most of the molecules in the sub-surface layer rapidly adsorb onto the interface. Only when the sub-surface layer becomes almost completely depleted, do molecules from the bulk start migrating towards the interface by a diffusive mechanism. To address these very early time stages, the interfacial kinetics must be considered explicitly. Assuming that the bulk solution is still at its initial equilibrium state, unperturbed by the presence of the interface, the leading time behavior of the surface coverage is found from Eq. (3.8) to be linear,

$$\phi_0(t \rightarrow 0) \simeq \phi_b \left(1 + \frac{D_0\alpha}{a^2T} t \right). \quad (3.14)$$

A surface coverage of $2\phi_b$ is thus attained after a period of about $a^2T/(D_0\alpha)$. This time scale is typically extremely short (smaller than microseconds), unless the adsorption is hindered by barriers making D_0 drastically smaller than D . Hence, these very early time stages are usually of no experimental interest, and the measured initial time dependence is of a diffusion-limited form, i.e. proportional to $t^{1/2}$.

4. Non-ionic mixtures

In the next example we study the adsorption from a mixture of two non-ionic surfactants [16]. Surfactant mixtures are used in numerous industrial applications, and are also encountered in many systems because of the presence of surface-active impurities. The equilibrium behavior of mixed surfactant solutions was studied in detail in works [35–41]. One of the important results, both theoretically and from the application point of view, is the ability to relate the mixed-surfactant behavior with that of the better understood, single-surfactant one. One of our aims is to predict the mixture kinetics from the behavior of the single surfactants. A particularly

interesting question is whether mixing several species would lead in certain cases to a significant difference in the kinetics as compared with the single-surfactant systems.

We consider two surfactants denoted A and B. The same notation as in the earlier section is used, except for the following modifications. We use ϕ to denote volume fraction of surfactant A and ψ for that of surfactant B. Parameters characterizing the two surfactants, such as α , β , D etc., are distinguished by subscripts A and B. The subscripts 0, 1, b are used, as in the earlier section, to denote different positions in the solution (interface, sub-interface and bulk, respectively).

The excess free energy of Eq. (2.1) is written in the mixture case as

$$\Delta\gamma[\phi, \psi] = \int_0^\infty \{\Delta f[\phi(x)] + \Delta f[\psi(x)]\} dx + f_0(\phi_0, \psi_0). \quad (4.1)$$

Since the solution is dilute, the two species are assumed to be uncorrelated in the bulk. The bulk free energy is taken, therefore, as a sum of single-surfactant contributions, given by Eq. (3.2). The surfactant molecular size, a , is assumed to have the same value for both species, on account of simplicity. (On the effect of differing molecular sizes, see [42]). At the interface, due to the high surface coverage, coupling terms must be considered,

$$\begin{aligned} a^2 f_0(\phi_0, \psi_0) &= T(\phi_0 \ln \phi_0 + \psi_0 \ln \psi_0 + \eta_0 \ln \eta_0) \\ &\quad - (\alpha_A + \mu_{1,A})\phi_0 - (\alpha_B + \mu_{1,B})\psi_0 - (\beta_A/2)\phi_0^2 \\ &\quad - (\beta_B/2)\psi_0^2 - \chi\phi_0\psi_0 \end{aligned} \quad (4.2)$$

where additional interaction between different surfactants has been introduced, having a characteristic energy χ . Note that this is a tertiary system (two solutes in a solvent), requiring three parameters for a complete description of the interactions (in our case β_A , β_B and χ). For brevity we use $\eta_0 \equiv 1 - \phi_0 - \psi_0$ as the surface coverage of the solvent (water).

The uncorrelated contributions of the two species, $\Delta f(\phi)$ and $\Delta f(\psi)$, result in decoupled equilibrium and kinetic equations in the bulk. Any correlation between the surfactants in this model originates, therefore, from interfacial interactions.

4.1. Equilibrium relations

Following the scheme of Eq. (2.2) to derive equilibrium relations, two uniform profiles are obtained in the bulk, $\phi(x > 0) \equiv \phi_b$ and $\psi(x > 0) \equiv \psi_b$. At the interface we get a Frumkin adsorption isotherm, generalized for the A–B mixture case,

$$\begin{aligned} \phi_0 &= \frac{\phi_b(1 - \psi_0)}{\phi_b + e^{-(\alpha_A + \beta_A\phi_0 + \chi\psi_0)/T}}, \\ \psi_0 &= \frac{\psi_b(1 - \phi_0)}{\psi_b + e^{-(\alpha_B + \beta_B\psi_0 + \chi\phi_0)/T}}. \end{aligned} \quad (4.3)$$

The adsorption of species A depends on species B through the entropy of mixing (steric effect) and surfactant–surfactant interactions. Finally, the equilibrium equation of state, $\Delta\gamma = \Delta\gamma(\phi_0, \psi_0)$, takes the form,

$$a^2\Delta\gamma = T \ln \eta_0 + (\beta_A/2)\phi_0^2 + (\beta_B/2)\psi_0^2 + \chi\phi_0\psi_0. \quad (4.4)$$

4.2. Kinetic equations

Applying the scheme of Eq. (2.3) to the current free-energy functional yields two single-surfactant diffusion equations like Eq. (3.6) for the two species. Consequently, two decoupled Ward–Tordai equations like Eq. (3.9) are obtained as well. At the interface, however, the two species are correlated and the scheme yields two coupled kinetic equations,

$$\begin{aligned} \frac{\partial\phi_0}{\partial t} &= \frac{D_A}{a^2} \phi_1 \left[\ln\left(\frac{\phi_1\eta_0}{\phi_0}\right) + \frac{\alpha_A}{T} + \frac{\beta_A\phi_0}{T} + \frac{\chi\psi_0}{T} \right] \\ \frac{\partial\psi_0}{\partial t} &= \frac{D_B}{a^2} \psi_1 \left[\ln\left(\frac{\psi_1\eta_0}{\psi_0}\right) + \frac{\alpha_B}{T} + \frac{\beta_B\psi_0}{T} + \frac{\chi\phi_0}{T} \right]. \end{aligned} \quad (4.5)$$

As can be seen from Eq. (4.5), the coupling between the kinetics of the two species arises from an interaction term, as well as from an entropic one (via η_0). The system of four equations (two Ward–Tordai equations like Eq. (3.9) and the two equations, Eq. (4.5)), with the appropriate initial conditions, completely determines the mixture kinetics and equilibrium state.

The set of equations can be fully solved numerically. We generalized the recursive scheme of

Miller et al. [4] to a surfactant mixture having time-dependent boundary conditions. An example for the resulting time dependence of the various quantities is given in Fig. 5. The mixture parameters were specifically chosen to show the interesting case of competition between the two species. While surfactant B diffuses more rapidly and is more abundant at the interface during the initial stages of adsorption, surfactant A has a higher surface affinity and dominates the later stages. We note that due to this competition, not only does surfactant A take over the adsorption at the later time stages, but it also forces surfactant B to desorb from the interface. As shown in Fig. 5(b), the competition between surfactants leads to a more complex decrease of the surface tension at intermediate times.

As in the previous section, we are interested in the characteristic time scales of the mixture kinetics. Assuming a diffusion-limited adsorption, the relaxation time scales of the two sub-surface concentrations, $\tau_{1,A}$ and $\tau_{1,B}$ are found to be identical to the single-surfactant result, Eq. (3.10). They are still inter-dependent, however, since the presence of each species changes the equilibrium surface coverage of the other. The coupling appears more

explicitly in the time scales of the surface coverages, $\tau_{0,A}$ and $\tau_{0,B}$ and surface tension, τ_γ . Two coupled linear equations are obtained for $\tau_{0,A}$ and $\tau_{0,B}$,

$$\begin{aligned} \eta_0 \sqrt{\tau_{1,A}} &= \left(1 - \psi_0 - \frac{\beta_A}{T} \phi_0 \eta_0\right) \sqrt{\tau_{0,A}} \\ &\quad + \psi_0 \left(1 - \frac{\chi}{T} \eta_0\right) \sqrt{\tau_{0,B}} \\ \eta_0 \sqrt{\tau_{1,B}} &= \left(1 - \phi_0 - \frac{\beta_B}{T} \psi_0 \eta_0\right) \sqrt{\tau_{0,B}} \\ &\quad + \phi_0 \left(1 - \frac{\chi}{T} \eta_0\right) \sqrt{\tau_{0,A}}, \end{aligned} \quad (4.6)$$

where the subscript ‘eq’ has been omitted for brevity. The expression for τ_γ also combines contributions from both species,

$$\begin{aligned} -a^2 \Delta \gamma \sqrt{\tau_\gamma} &= \left(\frac{\phi_0}{\eta_0} - \frac{\beta_A}{T} \phi_0^2 - \frac{\chi}{T} \phi_0 \psi_0\right) \sqrt{\tau_{0,A}} \\ &\quad + \left(\frac{\psi_0}{\eta_0} - \frac{\beta_B}{T} \psi_0^2 - \frac{\chi}{T} \phi_0 \psi_0\right) \sqrt{\tau_{0,B}} \end{aligned} \quad (4.7)$$

If we ‘turn off’ interactions ($\beta_A = \beta_B = \chi = 0$), Eq. (4.7) is reduced to a simple expression, relating τ_γ of the mixture with those of each species separately, $\bar{\tau}_{\gamma,A}$ and $\bar{\tau}_{\gamma,B}$ (given each by Eq. (3.13)),

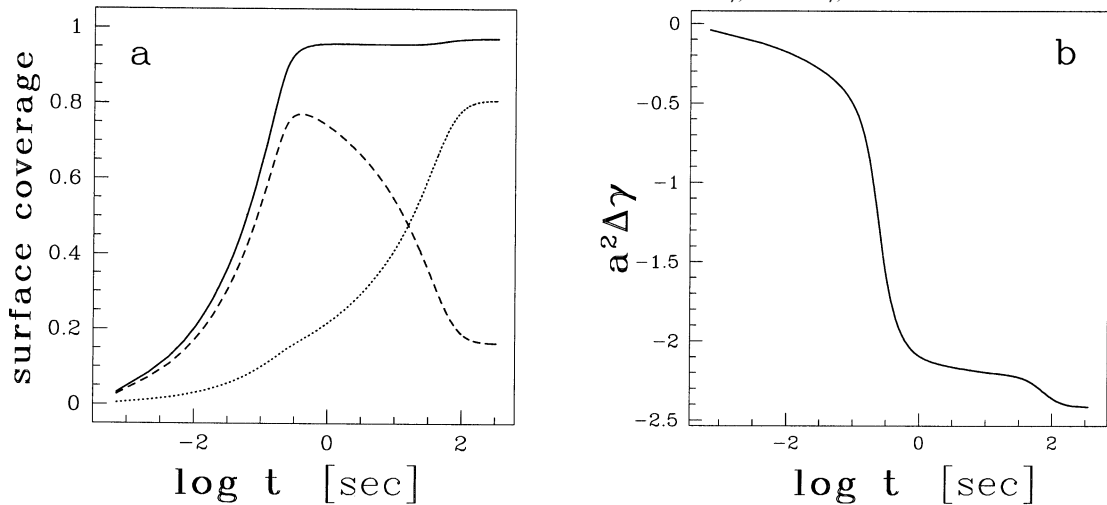


Fig. 5. (a) Surface coverage in a mixture of interacting surfactants. The dotted, dashed and solid lines are the surface coverages of surfactants A (ϕ_0), B (ψ_0), and the total coverage ($\phi_0 + \psi_0$), respectively. The assigned parameters are: $\phi_b = 10^{-4}$, $\psi_b = 2 \times 10^{-4}$, $\alpha_A = 10T$, $\alpha_B = 9T$, $\beta_A = \beta_B = 3T$, $\chi = T$, $D_A^{1/2}/a = 300 \text{ s}^{-1/2}$, and $D_B^{1/2}/a = 900 \text{ s}^{-1/2}$. This implies that surfactant A diffuses more slowly but is more surface active. (b) Dynamic surface tension of the same system.

Table 1
Comparison of the predicted τ_γ to experiment ^a

| A | B | $\phi_0/\bar{\phi}_0$ | $\psi_0/\bar{\psi}_0$ | $\Delta\bar{\gamma}_A\sqrt{\bar{\tau}_A}$ | $\Delta\bar{\gamma}_B\sqrt{\bar{\tau}_B}$ | $\Delta\gamma\sqrt{\tau_\gamma}$ (th) | $\Delta\gamma\sqrt{\tau_\gamma}$ (exp) | error |
|-------|-------|-----------------------|-----------------------|---|---|---------------------------------------|--|-------|
| X-405 | X-45 | 0.13 | 0.69 | 0.6 | 62 | 29.5 | 32 | 8% |
| X-405 | X-100 | 0.25 | 0.67 | 0.6 | 38 | 17.1 | 17 | 0.6% |
| X-405 | X-114 | 0.06 | 0.71 | 0.6 | 14 | 7.1 | 6.8 | 4% |
| X-405 | X-165 | 0 | 1.4 | 0.6 | 4.4 | 8.6 | 6.5 | 33% |

^a The materials used were sequences of Triton X mixtures [19]. The single-surfactant values, $\bar{\phi}_0$, $\bar{\psi}_0$, $\Delta\bar{\gamma}_A\sqrt{\bar{\tau}_A}$, $\Delta\bar{\gamma}_B\sqrt{\bar{\tau}_B}$ and equilibrium coverages for the mixture, $\phi_{0,\text{eq}}$ and $\psi_{0,\text{eq}}$, are taken from the same reference. The values for $\Delta\bar{\gamma}\sqrt{\tau_\gamma}$ (given in units of $\text{dyn s}^{1/2} \text{cm}^{-1}$) are obtained experimentally from the asymptotic slope of γ versus $t^{-1/2}$ curves (see Eq. (3.12)). The predicted values for $\Delta\bar{\gamma}\sqrt{\tau_\gamma}$ of the mixture and the corresponding experimental results are given in the columns indicated by ‘th’ and ‘exp’, respectively. The last column shows the respective error between theory and experiment.

$$\Delta\gamma\sqrt{\tau_\gamma} = \Delta\bar{\gamma}_A \left(\frac{\phi_0}{\bar{\phi}_0} \right)^2 \sqrt{\bar{\tau}_{\gamma,A}} + \Delta\bar{\gamma}_B \left(\frac{\psi_0}{\bar{\psi}_0} \right)^2 \sqrt{\bar{\tau}_{\gamma,B}}, \quad (4.8)$$

where $\bar{\phi}_0$ and $\bar{\psi}_0$ denote the surface coverages of the single-surfactant systems and $\Delta\bar{\gamma}_A$, $\Delta\bar{\gamma}_B$ the corresponding changes in equilibrium surface tension. Eq. (4.8) is a ‘weighting formula’ for relating the time scale of surface tension relaxation in the mixture with those of its individual constituents. It provides, therefore, a convenient tool for predicting the behavior of multi-component surfactant mixtures, based on single-surfactant data. In Table 1 the predicted τ_γ of Eq. (4.8) is compared with experimental results obtained by Fainerman and Miller [19] for a sequence of Triton X mixtures. Based on single-surfactant values and equilibrium isotherms for the mixture, the two terms of Eq. (4.8) are calculated separately. The agreement between theory and experiment is quite good, although experiments were limited to cases having one species dominating the adsorption. The last entry in the table corresponds to a mixture of Triton X-405 and Triton X-165. Here the predicted τ_γ deviates from the experimental one by 33%. Equilibrium measurements on this mixture reveal an *increase* in X-165 coverage upon addition of X-405 [19], indicating strong interfacial interactions between the species. The deviation in the predicted kinetics in Table 1 is attributed to those interactions, which are not taken into account by Eq. (4.8). (It is possible to treat also the general case, including interactions, by using the full Eq. (4.6) and Eq. (4.7) instead of the simplified Eq. (4.8). Such a procedure, how-

ever, involves three additional fitting parameters — β_A , β_B and χ .)

4.3. Kinetically limited adsorption

Although most non-ionic surfactants undergo a diffusion-limited process, as was discussed in the previous section, the adsorption of certain surfactants is found to be kinetically limited due to adsorption barriers. It is of interest, therefore, to examine the mixture kinetics in the kinetically limited case. The equations governing such a process are the two-coupled interfacial (Eq. (4.5)). Linearizing about the equilibrium state, $\phi_{0,\text{eq}}$ and $\psi_{0,\text{eq}}$, two time scales denoted τ_+ and τ_- emerge ($\tau_- > \tau_+$). These collective time scales correspond to the kinetics of a certain combination of surfactant coverages,

$$\begin{aligned} C_1\Delta\phi_0 + C_2\Delta\psi_0 &\sim e^{-t/\tau_-}, \\ C_3\Delta\phi_0 + C_4\Delta\psi_0 &\sim e^{-t/\tau_+}, \end{aligned} \quad (4.9)$$

where $\Delta\phi_0 \equiv \phi_0 - \phi_{0,\text{eq}}$, $\Delta\psi_0 \equiv \psi_0 - \psi_{0,\text{eq}}$, and $C_1 \dots C_4$ are constants. Since $\tau_- > \tau_+$, it is τ_- which limits the kinetics of the system.

In the simple case of no surface interactions ($\beta_A = \beta_B = \chi = 0$), the expressions for τ_\pm are

$$\begin{aligned} \frac{2}{\tau_\pm} &= \frac{1 - \psi_0}{\tau_A} + \frac{1 - \phi_0}{\tau_B} \\ &\pm \sqrt{\left(\frac{1 - \psi_0}{\tau_A} + \frac{1 - \phi_0}{\tau_B} \right)^2 - \frac{4\eta_0}{\tau_A\tau_B}}, \end{aligned} \quad (4.10)$$

where τ_A and τ_B are the time scales of the single-surfactant case, formulated in Eq. (3.11), yet with

ϕ_0 and ψ_0 of the mixture. The behavior of the mixed system combines the single-surfactant kinetics in a complicated manner. We can gain some insight on this coupling by considering two simple cases. In the limit where the interfacial kinetics of surfactant A is much slower than that of B, $\tau_A \gg \tau_B$, Eq. (4.9) and Eq. (4.10) are simplified to

$$(1 - \phi_{0,\text{eq}})\Delta\phi_0 - \psi_{0,\text{eq}}\Delta\psi_0 \sim e^{-t/\tau_-},$$

$$\Delta\psi_0 \sim e^{-t/\tau_+}, \quad \tau_- = \frac{1 - \phi_0}{\eta_0} \tau_A.$$

$$\tau_+ = \frac{1}{1 - \phi_0} \tau_B, \quad (4.11)$$

In the other limit, where the two species have similar time scales, $\tau_A \simeq \tau_B$, we get

$$\Delta\phi_0 - \Delta\psi_0 \sim e^{-t/\tau_-}, \quad \tau_- = \frac{\tau_A}{\eta_0} \quad (4.12)$$

$$\phi_{0,\text{eq}}\Delta\phi_0 + \psi_{0,\text{eq}}\Delta\psi_0 \sim e^{-t/\tau_+}, \quad \tau_+ = \tau_A$$

The factor $1/\eta_0$ in τ_- is quite interesting. Since the equilibrium surface coverage of the solvent, η_0 , is usually very small in surfactant systems, this factor implies that the coupling in a surfactant mixture undergoing kinetically limited adsorption may lead to a significant reduction in adsorption

rate. In this regime the mixture behavior may differ considerably from that of its individual constituents. Due to the relatively large factor of $1/\eta_0$, the time scale of interfacial kinetics may exceed the diffusive one and the adsorption would then become kinetically limited.

5. Ionic surfactants

We turn to the more complicated, yet important problem of ionic surfactant adsorption [14], and start with the salt-free case where strong electrostatic interactions are present. In Fig. 6, we have reproduced experimental results reported by Bonfillon et al. [22,23] and by Hua and Rosen [24]. The dynamic surface tension of the investigated ionic salt-free solutions exhibits much longer kinetics and richer behavior than in common non-ionic systems. A few theoretical models were suggested for the problem of ionic surfactant adsorption [43–46], yet none of them could produce such dynamic surface tension curves. Moreover, it is rather evident that a theoretical scheme for non-ionic surfactants, such as the one discussed in the previous sections, cannot fit the ionic results. On the other hand, as can be seen in Fig. 6, addition of salt to the solution leads to a

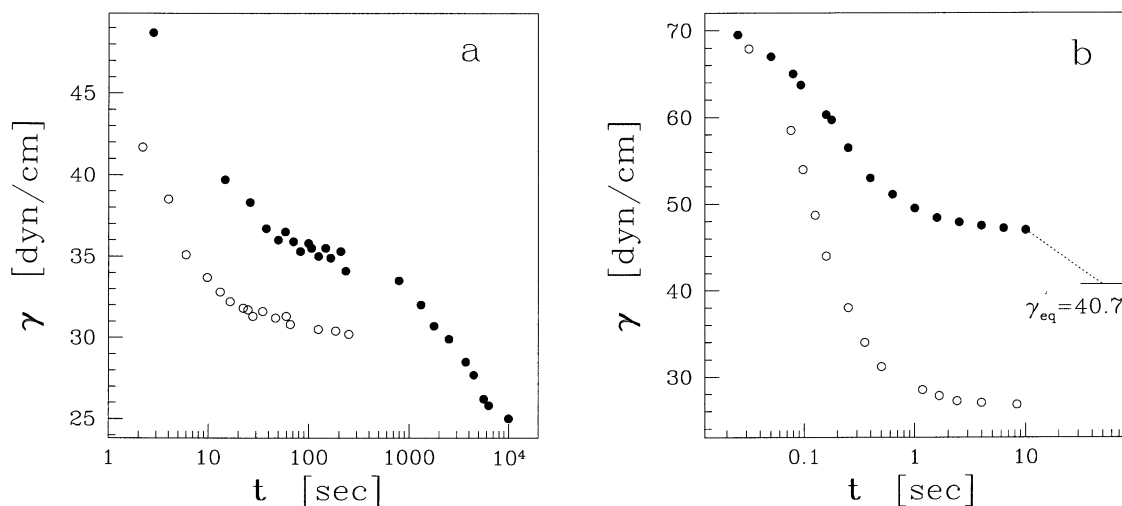


Fig. 6. (a) Dynamic interfacial tension between SDS aqueous solutions and dodecane. Filled circles — 3.5×10^{-4} M SDS without salt; open circles — 4.86×10^{-5} M SDS with 0.1M NaCl. (Adapted from [23]) (b) Dynamic surface tension between 5.84×10^{-4} M DESS solution and air. Filled circles — without salt; open circles — with 0.1 M NaCl. (Adapted from [24]; the authors did not provide details of the relaxation towards final equilibrium in the salt-free case.)

very similar behavior, as compared with the non-ionic case. It is thus inferred that the different kinetics observed for the salt-free solutions results from strong electrostatic interactions, which are screened upon addition of salt. Let us now study this effect in more detail. We follow the same line presented in the previous sections while adding appropriate terms to account for the additional interactions.

The free energy in the current case is written as a functional of three degrees of freedom – the surfactant profile, $\phi^+(x, t)$ (we arbitrarily take the surfactant as the positive ion), the counterion profile, $\phi^-(x, t)$, and a mean electric potential, $\Psi(x, t)$,

$$\begin{aligned} \Delta\gamma[\phi^+, \phi^-, \Psi] \\ = \int_0^\infty [\Delta f(\phi^+) + \Delta f(\phi^-) + f_{\text{el}}(\phi^+, \phi^-, \Psi)] dx \\ + f_0(\phi_0^+) + f_{\text{el},0}(\phi_0^+, \Psi_0). \end{aligned} \quad (5.1)$$

The bulk contributions coming from the two profiles, Δf^\pm , contain the same terms as in Eq. (3.2) of the non-ionic case. The interfacial contribution, f_0 , is identical to Eq. (3.3) and is taken as a function of the surfactant coverage alone, assuming that the counterions are surface-inactive. In addition, electrostatic contributions are introduced in the bulk free energy, as well as in the interfacial one, accounting for interactions between the ions and the electric field and the energy associated with the field itself,

$$f_{\text{el}} = e \left[\frac{\phi^+}{(a^+)^3} - \frac{\phi^-}{(a^-)^3} \right] \Psi - \frac{\varepsilon}{8\pi} \left(\frac{\partial \Psi}{\partial x} \right)^2 \quad (5.2)$$

$$f_{\text{el},0} = \frac{e}{(a^+)^2} \phi_0^+ \Psi_0, \quad (5.3)$$

where a^\pm are the molecular sizes of the two ions, e the electronic charge and $\varepsilon \simeq 80$ the dielectric constant of water. For simplicity, we have restricted ourselves to fully ionized, monovalent ions, implying that $\phi_b^+/(a^+)^3 = \phi_b^-/(a^-)^3 = c_b$, c_b being the bulk concentration. Ions in solution, apart from interacting with each other, are subject to an additional repulsion from the interface due to ‘image-charge’ effects [47]. It can be shown, however, that those effects become negligible in

our case as soon as the surface coverage exceeds about 2% [14].

5.1. Equilibrium relations

Employing the same scheme of Eq. (2.2), the variation with respect to $\phi^\pm(x)$ yields the Boltzmann ion profiles,

$$\phi^\pm(x > 0) = \phi_b^\pm e^{\mp e\Psi(x)/T}, \quad (5.4)$$

with respect to $\Psi(x)$ — the Poisson equation,

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi e}{\varepsilon} \left[\frac{\phi^+}{(a^+)^3} - \frac{\phi^-}{(a^-)^3} \right], \quad (5.5)$$

with respect to Ψ_0 — the electrostatic boundary condition,

$$\left. \frac{\partial \Psi}{\partial x} \right|_{x=0} = -\frac{4\pi e}{\varepsilon (a^+)^2} \phi_0^+, \quad (5.6)$$

and, finally, the variation with respect to ϕ_0^+ recovers the Davies adsorption isotherm [48],

$$\phi_0^+ = \frac{\phi_b^+}{\phi_b^+ + e^{-(\alpha + \beta \phi_0^+ - e\Psi_0)/T}}. \quad (5.7)$$

Combining Eqs. (5.4) and (5.5) leads to the well-known Poisson–Boltzmann equation for the equilibrium double-layer potential [49,50],

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{8\pi e c_b}{\varepsilon} \sinh \frac{e\Psi}{T}, \quad (5.8)$$

By means of the Poisson–Boltzmann equation, the Davies isotherm Eq. (5.7) can be re-expressed as

$$\phi_0^+ = \frac{\phi_b^+}{\phi_b^+ + [b\phi_0^+ + \sqrt{(b\phi_0^+)^2 + 1}]^2 e^{-(\alpha + \beta \phi_0^+)/T}}, \quad (5.9)$$

where $b \equiv a^+/(4\phi_b^+ \lambda)$, and $\lambda \equiv (8\pi c_b e^2/\varepsilon T)^{-1/2}$ is the Debye–Hückel screening length [51,52]. The equilibrium equation of state, relating surface tension and surface coverage, is

$$\begin{aligned} (a^+)^2 \Delta\gamma = T \ln(1 - \phi_0^+) + \frac{\beta}{2} (\phi_0^+)^2 \\ - \frac{2T}{b} \left(\sqrt{(b\phi_0^+)^2 + 1} - 1 \right). \end{aligned} \quad (5.10)$$

For weak fields the electrostatic correction to the equation of state (cf. Eq. (3.5)) is quadratic in the

coverage, thus merely modifying the lateral interaction term, whereas for strong fields it becomes linear in the coverage.

5.2. Kinetic equations

Applying the same scheme of Eq. (2.3) to the current case yields in the bulk the Smoluchowski diffusion equations,

$$\frac{\partial \phi^\pm}{\partial t} = D^\pm \frac{\partial}{\partial x} \left(\frac{\partial \phi^\pm}{\partial x} \pm \frac{e}{T} \phi^\pm \frac{\partial \Psi}{\partial x} \right), \quad (5.11)$$

where D^\pm are the diffusion coefficients of the two ions, assumed to be constant in the dilute bulk. At the sub-surface we find

$$\begin{aligned} \frac{\partial \phi_{\text{I}}^\pm}{\partial t} &= \frac{D^\pm}{a^\pm} \left(\frac{\partial \phi^\pm}{\partial x} \Big|_{x=a^\pm} \pm \frac{e}{T} \phi_{\text{I}}^\pm \frac{\partial \Psi}{\partial x} \Big|_{x=a^\pm} \right) \\ &- \frac{\partial \phi_{\text{O}}^\pm}{\partial t}, \end{aligned} \quad (5.12)$$

and, finally, at the interface itself,

$$\begin{aligned} \frac{\partial \phi_{\text{O}}^+}{\partial t} &= \frac{D_0^+}{(a^+)^2} \phi_{\text{I}}^+ \left[\ln \frac{\phi_{\text{I}}^+ (1 - \phi_{\text{O}}^+)}{\phi_{\text{O}}^+} + \frac{\alpha}{T} \right. \\ &\left. + \left(\frac{\beta}{T} - \frac{4\pi l}{a^+} \right) \phi_{\text{O}}^+ \right], \end{aligned} \quad (5.13)$$

where the diffusion coefficient at the interface, D_0^+ , may differ from its value in the bulk. The electrostatic boundary condition, Eq. (5.6), has been used in Eq. (5.13) to replace an electrostatic barrier term, $e(\Psi_0 - \Psi_1)/T$, with the approximate term $(4\pi l/a^+) \phi_{\text{O}}^+$, where $l \equiv e^2/\epsilon T$ is the Bjerrum length (about 7 Å for water at room temperature).

Neglecting electrodynamic effects, the Poisson equation holds out of equilibrium as well. The kinetic equations just derived, along with the Poisson, Eq. (5.5), the boundary condition of Eq. (5.6), another boundary condition for the counterion profile (e.g. $\phi_{\text{O}}^-(t) = 0$), and appropriate initial conditions, together determine the kinetics and equilibrium state of the adsorption problem. This set of equations can be fully solved only numerically (a similar set was solved in [46]).

The relaxation in the bulk solution, accounted for by the Smoluchowski Eq. (5.11), has the characteristic time scale $\tau_e = \lambda^2/D$, where D is an effective ambipolar diffusion coefficient [53]. This

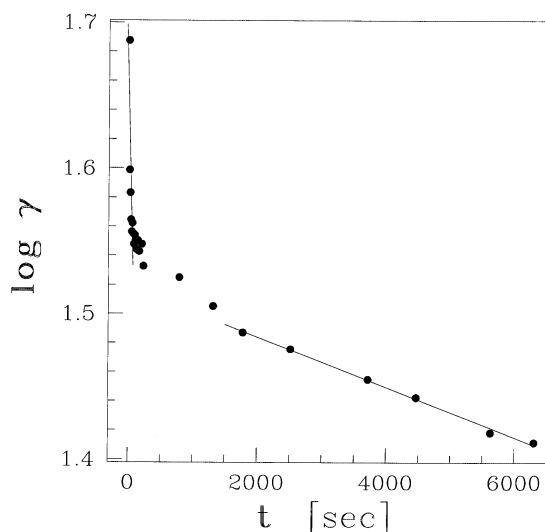


Fig. 7. Dynamic surface tension of the salt-free SDS solution of Fig. 6(a), redrawn on a semi-log plot. Two exponential relaxations are observed, indicating a kinetically limited process.

time scale is typically very short (of the order of microseconds), i.e. electrostatic interactions make the bulk relaxation much faster than in the non-ionic case. The relaxation at the interface (Eq. (5.13)) has an asymptotic exponential form like Eq. (3.11). It is dramatically slowed down, however, by electrostatic repulsion, having a time scale of

$$\begin{aligned} \tau_k &= \tau_k^{(0)} \exp\left(\frac{e\Psi_0 + e\Psi_1}{T}\right) \\ &\simeq \tau_k^{(0)} \left(\frac{a^+}{2\lambda} \frac{\phi_{\text{O,eq}}^+}{\phi_{\text{b}}^+}\right)^4 \exp\left[-\left(\frac{4\pi l}{a^+}\right) \phi_{\text{O,eq}}^+\right], \end{aligned}$$

where $\tau_k^{(0)}$ denotes the kinetic time scale in the absence of electrostatics (Eq. (3.11)). In salt-free surfactant solutions the surface potential reaches values significantly larger than T/e , and, hence, the interfacial relaxation is by orders of magnitude slower than in the non-ionic case.

The conclusion is that ionic surfactants in salt-free solutions should, in many cases, undergo kinetically limited adsorption. Due to the strong electrostatic repulsion, unlike the non-ionic case, the adsorption can become *kinetically limited* even if the diffusion coefficient at the interface is not significantly larger than that in the bulk. Indeed,

dynamic surface tension curves of such solutions exhibit an exponential asymptotic time dependence, rather than the diffusive $t^{-1/2}$ behavior, as is demonstrated in Fig. 7.

The scheme employed for non-ionic surfactants, focusing on the diffusive transport inside the solution, is no longer valid. By contrast, the diffusive relaxation in the bulk is practically immediate and we should concentrate on the interfacial kinetics, Eq. (5.13). In this case the sub-surface volume fraction, ϕ_1^+ , obeys the Boltzmann law (Eq. (5.4)) rather than the Davies adsorption isotherm (Eq. (5.7)), and the electric potential is given by the Poisson–Boltzmann theory. Using these results, Eq. (5.13) can be expressed as a function of the surface coverage alone,

$$\frac{\partial \phi_0^+}{\partial t} = \frac{D_0^+ \phi_b^+}{(a^+)^2} \frac{\exp[(4\pi l/a^+) \phi_0^+]}{[b\phi_0^+ + \sqrt{(b\phi_0^+)^2 + 1}]^2} \times \left\{ \ln \left[\frac{\phi_b^+ (1 - \phi_0^+)}{\phi_0^+} \right] + \frac{\alpha}{T} + \frac{\beta \phi_0^+}{T} - 2 \sinh^{-1}(b\phi_0^+) \right\} \quad (5.14)$$

thus reducing the problem to a single integration.

Not only does the scheme for solving the kinetic equations differ from the non-ionic case, but also the way to calculate the dynamic surface

tension has to change. In kinetically limited adsorption the variation of the free energy with respect to the surface coverage does not vanish, and, consequently, the equation of state Eq. (5.10) is strictly invalid out of equilibrium. The expression for the dynamic surface tension in the kinetically limited case can be derived from the general functional of Eq. (5.1) by assuming quasi-equilibrium inside the bulk solution (i.e. using Boltzmann profiles and the Poisson–Boltzmann equation),

$$(a^+)^2 \Delta \gamma [\phi_0^+(t)] = T \phi_0^+ \ln(\phi_0^+ / \phi_b^+) + T(1 - \phi_0^+) \ln(1 - \phi_0^+) - \alpha \phi_0^+ - (\beta/2)(\phi_0^+)^2 + 2T[\phi_0^+ \sinh^{-1}(b\phi_0^+) - (\sqrt{(b\phi_0^+)^2 + 1} - 1)/b] \quad (5.15)$$

Assuming high surface potentials ($b\phi_0^+ \gg 1$), the function defined in Eq. (5.15) becomes non-convex for $\beta/T > 2(2 + \sqrt{3}) \simeq 7.5$, as demonstrated in Fig. 8(a). In such cases an unusual time dependence for the dynamic surface tension results (Fig. 8(b)). We thus infer that the shape of experimental dynamic surface tension curves, such as those presented in Fig. 6, is a consequence of a kinetically limited adsorption brought about by strong electrostatic interactions. Physically, the non-con-

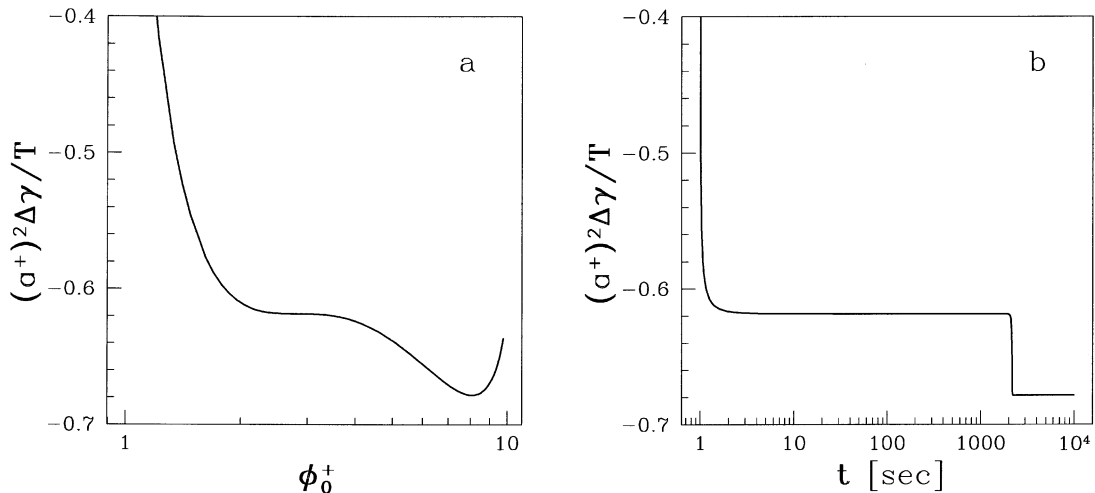


Fig. 8. (a) Dependence of surface tension on surface coverage in kinetically limited adsorption (Eq. (5.15)). The values taken for the parameters are: $a^+ = 17 \text{ \AA}$, $\phi_b^+ = 6 \times 10^{-5}$, $\alpha = 14.78T$ and $\beta = 8.5T$. The values were selected to yield a non-convex, yet decreasing curve (see text). (b) The corresponding dynamic surface tension, calculated using Eqs. (5.14) and (5.15) with the value $D_0^+ = 6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

vexity implies a sort of two-phase coexistence, suggesting the following scenario. As the surface coverage increases, the system reaches a local free-energy minimum leading to a pause in the adsorption (the intermediate plateau of the experimental curves). This metastable state lasts until domains of the denser, global-minimum phase are nucleated, resulting in further increase in coverage and a corresponding decrease in surface tension. In Fig. 8 we have exploited a special set of parameters in order to demonstrate the effect of non-convexity within our current formalism. A complete treatment of the scenario described above, however, cannot be presented within such a formalism, since it inevitably leads to a monotonically decreasing free energy as a function of time, and hence, cannot account for nucleation [29].

A value of $\beta > 7.5T$ required for non-convexity is somewhat large compared with the typical lateral attraction between surfactant molecules. Throughout the above calculations, we have assumed that no counterions are adsorbed at the interfacial layer. It can be shown that the presence of a small amount of counterions at the interface introduces a correction to the free energy, which is quadratic in the surfactant coverage, i.e. leading to an effective increase in lateral attraction [14]. The increase in β due to the counterions turns out to be $[2\pi la^-(a^+)^2]T$, which may amount to a few T . This contribution accounts for a larger β leading to non-convexity. (The peculiar dynamic surface tension behavior shown in Fig. 6 is not observed for every ionic surfactant. It has not been observed, for example, in salt-free DTAB solutions [54]).

5.3. Adding salt

Finally, let us consider the effect of adding salt to an ionic surfactant solution. For simplicity, and in accord with practical conditions, it is assumed that the salt ions are much more mobile than the surfactant and their concentration exceeds that of the surfactant. In addition, we take the salt ions to be monovalent and surface-inactive. Under these assumptions, the kinetics of the salt ions can be neglected, reducing their role to the formation of a thin electric double layer near the interface, which maintains quasi-equilibrium with the adsorbed sur-

face charge. The double-layer potential is taken in the linear, Debye-Hückel regime [50–52], $\Psi(x,t) = (4\pi e\lambda/\varepsilon a^2)\phi_0(t)e^{-x/\lambda}$, with a modified definition of the Debye-Hückel screening length, $\lambda \equiv (8\pi c_s l)^{-1/2}$, $c_s \gg c_b$ being the salt concentration (the superscript ‘+’ is omitted hereafter from the surfactant symbols).

Substituting the double-layer potential in Eq. (5.11) and Eq. (5.12), the kinetic equations in the bulk and sub-surface layer are obtained,

$$\frac{\partial \phi}{\partial t} = D \frac{\partial}{\partial x} \left(\frac{\partial \phi}{\partial x} - \frac{\phi_0 e^{-x/\lambda}}{2a^2 \lambda^2 c_s} \phi \right), \quad (5.16)$$

$$\frac{\partial \phi_1}{\partial t} = \frac{D}{a} \left(\frac{\partial \phi}{\partial x} \Big|_{x=a} - \frac{\phi_0}{2a^2 \lambda^2 c_s} \phi_1 \right) - \frac{\partial \phi_0}{\partial t}, \quad (5.17)$$

whereas the kinetic equation at the interface itself remains the same as Eq. (5.13). Considering the electric potential as a small perturbation, Eqs. (5.16) and (5.17) lead to the asymptotic expression

$$\begin{aligned} \phi_1(t \rightarrow \infty)/\phi_b &\simeq \frac{1 - \phi_{0,\text{eq}}}{2a^2 \lambda c_s} - \left(\frac{\tau_1}{t} \right)^{1/2} \\ \tau_1 &\equiv \tau_1^{(0)} \left[1 - \frac{c_b}{2c_s} - \frac{\phi_{0,\text{eq}}}{2a^2 \lambda c_s} \left(1 - \frac{3c_b}{2c_s} \right) \right]^2, \end{aligned} \quad (5.18)$$

where $\tau_1^{(0)}$ denotes the diffusion time scale in the non-ionic case (Eq. (3.10)). Due to surface charge, the equilibrium sub-surface concentration is smaller than that of the bulk reservoir. More important, though, is the correction to the diffusion time scale introduced by the screened electrostatic interactions. As expected, it decreases with increasing salt concentration.

Since the kinetic equation at the interface is identical to the one in the absence of salt, so is the expression for the corresponding time scale. In the case of added salt, however, the surface potential is much smaller than T/e , and the kinetic time scale, τ_k , becomes only slightly larger than the non-ionic one (Eq. (3.11)). Ionic surfactants with added salt are expected, therefore, to behave much like non-ionic surfactants, i.e. undergo diffusion-limited adsorption if no strong hindrance to adsorption exists. The departure from the non-ionic behavior depends on salt concentration and is described to first approximation by Eq. (5.18). The ‘footprint’ of diffusion-limited adsorption, i.e. a $t^{-1/2}$ asymp-

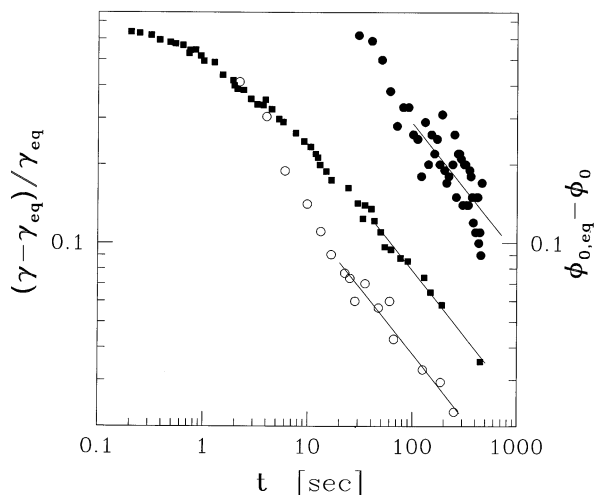


Fig. 9. Diffusion-limited adsorption exhibited by ionic surfactants with added salt. Open circles and left ordinate — dynamic interfacial tension between dodecane and an aqueous solution of 4.86×10^{-5} M SDS with 0.1 M NaCl. (Adapted from [23].) Squares and left ordinate — dynamic surface tension of an aqueous solution of 2.0×10^{-4} M SDS with 0.5 M NaCl. (Adapted from [55].) Filled circles and right ordinate — surface coverage deduced from second harmonic generation measurements on a saturated aqueous solution of SDNS with 2% NaCl. (Adapted from [56].) The asymptotic $t^{-1/2}$ dependence shown by the solid fitting lines is a ‘footprint’ of diffusion-limited adsorption.

otic time dependence, is observed in experiments, as is demonstrated in Fig. 9. Consequently, the scheme described in previous sections for solving the adsorption problem and calculating the dynamic surface tension in the non-ionic case is applicable also for ionic surfactants with added salt, and good fitting to experimental measurements can be obtained [23].

6. Summary

We have reviewed a theoretical approach to the fundamental problem of the adsorption kinetics of surfactants. The formalism is more general than previous ones as it yields the kinetics in the entire system, both in the bulk solution and at the interface, relying on a single functional and reducing the number of externally inserted assumptions previously employed.

Common non-ionic surfactants, not hindered by high adsorption barriers, are shown to undergo diffusion-limited adsorption, in agreement with experiments. In the non-ionic case our general formalism coincides with earlier ones and helps clarify the validity of their assumptions. The adsorption process can be roughly divided into three temporal stages. At extremely early times the surface coverage and surface tension change linearly with time because of interfacial kinetics. This stage, however, is in most practical cases too short to be observed experimentally (usually less than microseconds). Due to this fast adsorption stage, the sub-surface layer becomes nearly empty, which in turn drives a second, diffusion-limited stage, where the surfactant diffuses from the bulk with a $t^{1/2}$ time dependence. The final relaxation towards equilibrium is usually diffusion-limited, exhibiting an asymptotic $t^{-1/2}$ behavior.

In non-ionic surfactant mixtures, the initial adsorption stages are dominated by the more mobile species. In cases where the less mobile species is more surface-active, an intermediate stage is predicted — while one species undergoes desorption, the coverage gradually becomes dominated by the other, energetically favorable surfactant. The kinetic behavior of the mixture can be evaluated based on equilibrium isotherms and single-surfactant data, yielding good agreement with experiments. For surfactant mixtures exhibiting kinetically limited adsorption, we find a ‘synergistic’ effect, where the mixture kinetics may be considerably different from that of the individual species. In cases of high equilibrium surface coverage, a significant decrease in adsorption rate is predicted due to coupling between the two surfactants.

Strong electrostatic interactions in salt-free ionic surfactant solutions are found to have a dramatic effect. The adsorption becomes kinetically limited, which may lead to an unusual time dependence, as observed in dynamic surface tension measurements. Such a scenario could not be accounted for by previous models. Addition of salt to ionic surfactant solutions leads to screening of the electrostatic interactions, and the adsorption becomes similar to the non-ionic one, i.e. diffusion-limited. The departure from the non-

ionic behavior as the salt concentration is lowered has been described by a perturbative expansion.

A general method to calculate dynamic surface tension is obtained from our formalism. In the diffusion-limited case it coincides with previous results, which used the equilibrium equation of state. In the kinetically limited case it produces different expressions leading to novel conclusions.

Our kinetic model is restricted to simple relaxation processes, where the free energy monotonously decreases with time. In order to provide a quantitative treatment of more complicated situations, such as the ones described for salt-free ionic solutions, a more accurate theory is required, including, e.g. a nucleation mechanism.

Finally, as was demonstrated by the various cases treated in this review, the approach presented here can be easily extended to include additional components and interactions. This can be done by incorporating other terms in the excess free energy Eq. (2.1) and working out the kinetics using the same scheme as presented above. Examples for interesting extensions are adsorption from micellar solutions and the incorporation of lateral diffusion.

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