

Kinetics of Surfactant Adsorption at Fluid–Fluid Interfaces: Surfactant Mixtures

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The adsorption at the interface between an aqueous solution of several surface-active agents and another fluid (air or oil) phase is addressed theoretically. We derive the kinetic equations from a variation of the interfacial free energy, solve them numerically, and provide an analytic solution for the simple case of a linear adsorption isotherm. Calculating asymptotic solutions analytically, we find the characteristic time scales of the adsorption process and observe the behavior of the system at various temporal stages. In particular, we relate the kinetic behavior of the mixture to the properties of its individual constituents and find good agreement with experiments. In the case of kinetically limited adsorption, the mixture kinetics is found to be considerably different from that of the single-surfactant solutions because of strong coupling between the species.

1. Introduction

The kinetics of surfactant adsorption plays an important role in various interfacial phenomena and has been an active field of research, both experimentally and theoretically, since the 40s.¹ Recently, a new theoretical approach based on a free-energy formalism was presented and applied to nonionic as well as ionic surfactant adsorption.² The main advantage of this approach is that all the equations are derived from a single functional. This feature facilitates generalizations of the model to more complicated situations.

Surfactant mixtures are used in numerous industrial applications, and are also encountered in many systems because of the presence of surface-active impurities. Experiments portray a large variety of phenomena specific to the kinetics of mixed systems.^{3–8} For instance, more complex dynamic surface tension is observed due to competition between the different species.

The equilibrium behavior of mixed-surfactant solutions was studied in detail in previous works.^{9–13} One of the important results, both theoretically and from the application point of view, is the ability to relate the mixed-surfactant behavior to that of the better understood, single-

surfactant one. In the current work we focus on kinetic aspects, deriving equilibrium results merely for completeness and comparison with previous models. 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 to the single-surfactant systems.

In this paper we extend our previously introduced model to describe the competition between two nonionic adsorbing species. In section 2 we present the model and derive the equilibrium relations and kinetic equations. The complete set of kinetic equations can be solved only numerically, as is done in section 3. We then discuss, in section 4, the asymptotic time dependence of diffusion-limited and kinetically limited adsorption and the corresponding characteristic time scales. We focus on the relation between the adsorption behavior of the mixture and the properties of its individual constituents. Good agreement is found between the experimental results and our predictions. In addition, we give an analytic solution for the kinetics in the simple case of a linear adsorption isotherm.

To make the formulation as transparent as possible, we have tried to minimize the number of symbols and used dimensionless forms whenever possible. To facilitate translation into experimentally useful, dimensional quantities, a nomenclature section is provided.

2. The Model

Our model is based on the free-energy formalism presented in detail in previous papers.² We consider a semi-infinite aqueous solution of nonionic surfactants having, at $x = 0$, a flat, sharp interface with a nonpolar fluid phase (such as air or oil). The solution is in contact with a bulk reservoir, at $x \rightarrow \infty$, containing two types of surfactant molecules, denoted by A and B. It is considered dilute, with the volume fraction of the two constituents well below their critical micelle concentration (cmc) values.¹⁴ At the interface, however, the surfactant volume

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(14) It should be noted, however, that industrial applications often involve surfactant solutions close to and above the cmc. For equilibrium theories of such surfactant mixtures, see refs 10 and 13.

fraction is usually much larger. Hereafter, we use ϕ to denote the volume fraction of surfactant A, ψ for the volume fraction of surfactant B, μ for the chemical potential, and D for the diffusion constant. The subscripts A and B distinguish between the two different surfactants. The subscripts 0, 1, and b are used to distinguish between different positions in the solution, corresponding respectively to the interface, subinterface layer, and bulk reservoir.

The excess interfacial free energy is equal to the reduction in surface tension,

$$\Delta\gamma[\phi, \psi] = \int_0^\infty \{\Delta f[\phi(x)] + \Delta f[\psi(x)]\} dx + f_0(\phi_0, \psi_0) \quad (2.1)$$

where Δf is the bulk contribution per unit volume of each species and f_0 the interfacial contribution per unit area. In dilute nonionic surfactant systems, the dominant contribution to the surface tension is usually the interfacial one, f_0 . Since the surfactant solution is considered dilute, the bulk free energy is taken to be the sum of $\Delta f(\phi)$ and $\Delta f(\psi)$. Each of these contributions contains the entropy of mixing in the ideal, dilute limit and a contact with the bulk reservoir. For species A we write

$$\Delta f(\phi) = \frac{1}{a^3} [\phi \ln \phi - \phi - (\phi_b \ln \phi_b - \phi_b) - \mu_{b,A}(\phi - \phi_b)] \quad (2.2)$$

and similarly for species B. As this is a lattice model, it is conveniently formulated using volume fractions as the degrees of freedom. The translation to mole fractions or concentrations requires specifying molecular sizes for the various species. Here, the surfactant molecular size, a , is assumed to have the same value for both species, on account of simplicity.¹⁵ All the energies, chemical potentials, and interaction parameters are expressed in units of $k_B T$ where k_B is the Boltzmann constant and T the temperature. At the interface, the surfactant volume fractions are usually much larger and we have to consider the full, nonideal entropy of mixing and additional interaction terms:

$$f_0(\phi_0, \psi_0) = \frac{1}{a^2} \left[\phi_0 \ln \phi_0 + \psi_0 \ln \psi_0 + \eta_0 \ln \eta_0 - (\alpha_A + \mu_{1,A})\phi_0 - (\alpha_B + \mu_{1,B})\psi_0 - \frac{\beta_A}{2}\phi_0^2 - \frac{\beta_B}{2}\psi_0^2 - \epsilon\phi_0\psi_0 \right] \quad (2.3)$$

where α is the energy gain of adsorption onto the interface, β the interaction energy between molecules of the same kind, ϵ the interaction between different surfactants,¹⁶ and $\eta_0 \equiv 1 - \phi_0 - \psi_0$ is the surface coverage of the solvent (water). The interface is in contact with the subsurface layer, having a chemical potential $\mu_1 \equiv \mu(x \rightarrow 0)$. Out of equilibrium μ_1 may differ from the bulk chemical potential, μ_b . Although both α and μ_1 are linearly coupled with the surface coverage, their physical origin is quite different. The former is constant in time, characterizing the surface activity of the specific surfactant and mainly dependent

(15) Generalization of a lattice model to the case of different molecular sizes is, at least approximately, quite straightforward. See, for example, Zelman, D.; Kozlov, M. M.; Helfrich, W. *Europhys. Lett.* **1994**, *25*, 231. On the effect of different molecular sizes on the adsorption, see: Fainerman, V. B.; Miller, R. *Langmuir* **1997**, *13*, 409.

(16) 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 ϵ).

on the molecular structure (number of hydrocarbon groups in the surfactant tail). The latter is a time-dependent function participating in the surface kinetics. Variation of $\Delta\gamma$ with respect to ϕ and ψ yields the excess chemical potential at distance x from the interface:

$$\begin{aligned} \Delta\mu_A(x) &= \ln \phi(x) - \mu_{b,A} \\ \Delta\mu_B(x) &= \ln \psi(x) - \mu_{b,B} \end{aligned} \quad (2.4)$$

and at the interface itself,

$$\begin{aligned} \Delta\mu_{0,A} &= \ln \frac{\phi_0}{\eta_0} - \alpha_A - \beta_A \phi_0 - \epsilon\psi_0 - \mu_{1,A} \\ \Delta\mu_{0,B} &= \ln \frac{\psi_0}{\eta_0} - \alpha_B - \beta_B \psi_0 - \epsilon\phi_0 - \mu_{1,B} \end{aligned} \quad (2.5)$$

2.1. Equilibrium. At equilibrium the chemical potentials are equal to their bulk values throughout the solution, leading to two uniform profiles, $\phi(x > 0) \equiv \phi_b$ and $\psi(x > 0) \equiv \psi_b$. At the interface we obtain a Frumkin adsorption isotherm,¹⁷ generalized for the A/B mixture case:

$$\begin{aligned} \phi_0 &= \frac{\phi_b(1 - \psi_0)}{\phi_b + e^{-(\alpha_A + \beta_A \phi_0 + \epsilon\psi_0)}} \\ \psi_0 &= \frac{\psi_b(1 - \phi_0)}{\psi_b + e^{-(\alpha_B + \beta_B \psi_0 + \epsilon\phi_0)}} \end{aligned} \quad (2.6)$$

The adsorption of species A depends on species B because of the entropy of mixing (steric effect) and surfactant–surfactant interactions. The corresponding generalized Langmuir isotherm is obtained in the limit of no interactions, $\beta_A = \beta_B = \epsilon = 0$. Finally, the equilibrium equation of state, $\Delta\gamma = \Delta\gamma(\phi, \psi)$, takes the form

$$\Delta\gamma = \frac{1}{a^2} \left(\ln \eta_0 + \frac{\beta_A}{2}\phi_0^2 + \frac{\beta_B}{2}\psi_0^2 + \epsilon\phi_0\psi_0 \right) \quad (2.7)$$

which is equivalent to Lucassen–Reynders' result,⁹ when differences in molecular sizes are neglected.

2.2. Out of Equilibrium. We apply the procedure presented in ref 2, where the kinetic equations are derived from the variation of the free energy. The procedure is generalized for the present case of a two nonionic surfactant mixture. Since the bulk solution is dilute, two independent diffusion equations for the two surfactants are obtained, leading to two Ward–Tordai equations,¹⁸ similar to previous models:⁴

$$\begin{aligned} \phi_0(t) &= \frac{1}{a} \sqrt{\frac{D_A}{\pi}} \left[2\phi_b \sqrt{t} - \int_0^t \frac{\phi_1(\tau)}{\sqrt{t-\tau}} d\tau \right] + 2\phi_b - \phi_1 \\ \psi_0(t) &= \frac{1}{a} \sqrt{\frac{D_B}{\pi}} \left[2\psi_b \sqrt{t} - \int_0^t \frac{\psi_1(\tau)}{\sqrt{t-\tau}} d\tau \right] + 2\psi_b - \psi_1 \end{aligned} \quad (2.8)$$

At the interface, however, the two species are correlated

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and the procedure yields two coupled kinetic equations:

$$\begin{aligned} \frac{\partial \phi_0}{\partial t} &= \phi_1 \frac{D_A}{a^2} \left[\ln \left(\frac{\phi_1}{\phi_0} \eta_0 \right) + \alpha_A + \beta_A \phi_0 + \epsilon \psi_0 \right] \\ \frac{\partial \psi_0}{\partial t} &= \psi_1 \frac{D_B}{a^2} \left[\ln \left(\frac{\psi_1}{\psi_0} \eta_0 \right) + \alpha_B + \beta_B \psi_0 + \epsilon \phi_0 \right] \quad (2.9) \end{aligned}$$

As can be seen from the equation above, the coupling between the kinetics of the two species arises from an interaction term as well as an entropic one (via the η_0 term). It should be mentioned that this form of interfacial kinetic equations is particular to our free-energy approach. Close enough to equilibrium, however, it coincides with the usual adsorption–desorption form, as discussed in ref 2. The system of four equations, (2.8 and 2.9), with the appropriate initial conditions, completely determines the mixture kinetics and equilibrium state. Several limits, such as diffusion-limited and kinetically limited adsorption, can be treated analytically, as presented in section 4. The full solution of the mixed-kinetics case is obtained numerically.

3. Numerical Solution of the Full Equations

Several numerical schemes have been proposed for solving the Ward–Tordai equation with various boundary conditions.^{19–21} We generalized the recursive scheme suggested by Miller et al.¹⁹ to a surfactant mixture having time-dependent boundary conditions. The complete set of integro-differential equations were solved, as is explained in the Appendix.

The time dependence of ϕ_0 , ψ_0 , and their sum $\phi_0 + \psi_0$ can be seen in Figure 1. The mixture parameters are 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 the adsorption process, surfactant A has a higher surface affinity and dominates the later stages of adsorption. We note that, because of this competition, surfactant A not only takes over the adsorption at the later time stages but also forces surfactant B to desorb from the interface. In Figure 2 the dynamic surface tension is shown for the same time scales and adsorption parameters as those of Figure 1. The competition between the A and B surfactants results in a more complex decrease of the surface tension at intermediate times.

4. Limiting Time Behavior

The asymptotic time behavior close to equilibrium of the kinetic equations provides a means for comparing theoretical predictions to experimental results.³ Two limiting cases of adsorption can be distinguished and treated separately for long and short times: *Diffusion-limited adsorption* (DLA) occurs when the kinetics at the interface is much faster than the diffusion from the bulk to the subsurface layer. Equation 2.9 then equals zero,² since the interface is taken to be at equilibrium with the subsurface layer. The profiles in the bulk, $\phi(x > 0)$ and

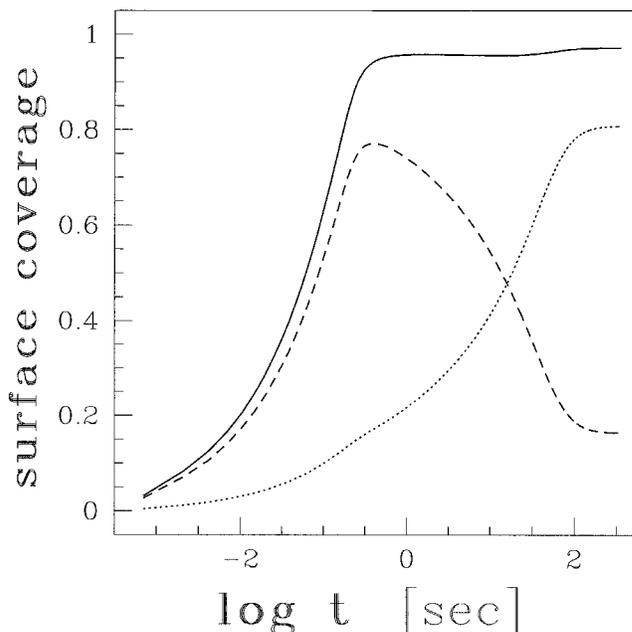


Figure 1. Surface coverage in a mixture of interacting surfactants. The dotted, dashed and solid lines are the surface coverages of surfactants A (ϕ_0), B (ψ_0), and the total coverage ($\phi_0 + \psi_0$), respectively. The assigned parameters are $\phi_b = 1 \times 10^{-4}$, $\psi_b = 2 \times 10^{-4}$,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

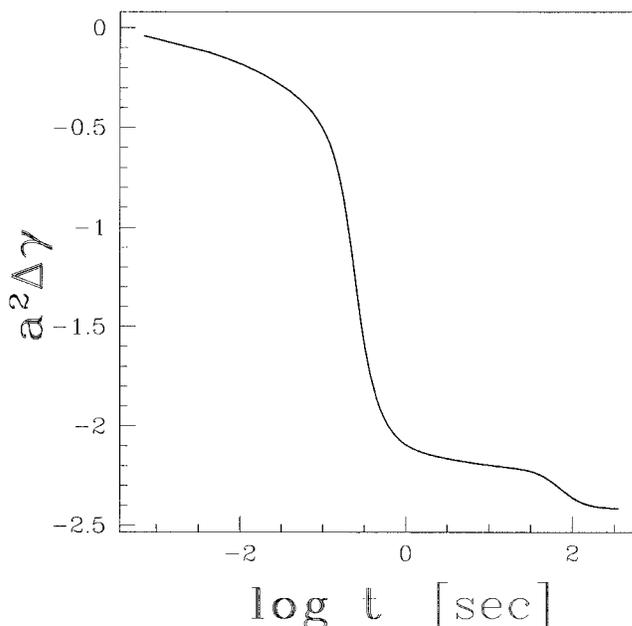


Figure 2. Dynamic surface tension for the system of Figure 1.

$\psi(x > 0)$, depend on the diffusion and evolve in time. On the other hand, *Kinetically limited adsorption* (KLA) takes place in the opposite limit, for which $\phi_1 = \phi_b$ and $\psi_1 = \psi_b$ throughout the process, implying that the bulk is constantly at equilibrium with the reservoir but not with the interface.

4.1. DLA Process at Long Times. Diffusion-limited processes such as the DLA considered here have a characteristic asymptotic $t^{-1/2}$ dependence as t goes to infinity. This is demonstrated in Figure 3. The asymptotic time dependence of all variables can be written in a generic

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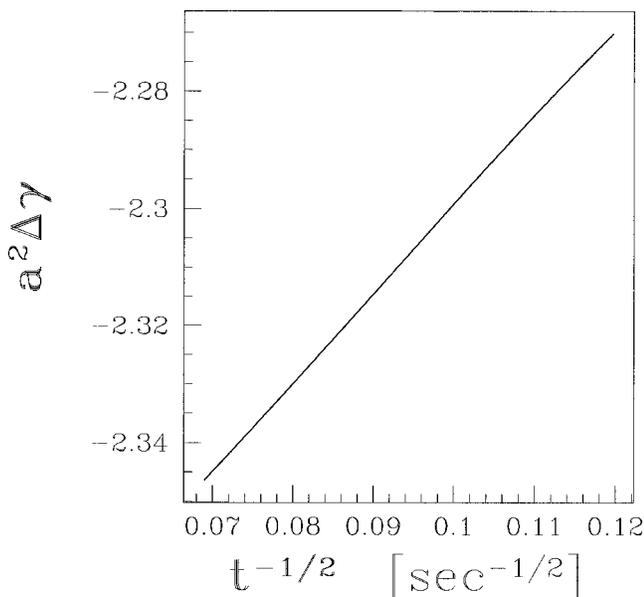


Figure 3. Dynamic surface tension for the system of Figure 1, redrawn for long times. The curve exhibits the $t^{-1/2}$ asymptotic behavior characteristic of DLA.

form as

$$\begin{aligned}\phi_0(t) &\approx \phi_{0,\text{eq}} (1 - \sqrt{\tau_0/t}) \\ \phi_1(t) &\approx \phi_b (1 - \sqrt{\tau_1/t}) \\ \Delta\gamma(t) &\approx \Delta\gamma_{\text{eq}} (1 - \sqrt{\tau_\gamma/t})\end{aligned}\quad (4.1)$$

where the subscript “eq” stands for equilibrium values. Note that the various time constants may generally depend on the surface coverages of both species. Taking the limit $t \rightarrow \infty$ of the Ward–Tordai relation 2.8 we get

$$\tau_{1,A} = \frac{a^2}{\pi D_A} \left(\frac{\phi_{0,\text{eq}}}{\phi_b} \right)^2 \quad (4.2)$$

The presence of surfactant B changes the equilibrium value of ϕ_0 (see eq 2.6). This is the *only* reason the relaxation time $\tau_{1,A}$ depends on surfactant B. For a DLA process, the surface and subsurface layers are considered at equilibrium with each other, and the coverage instantaneously follows any change in the subsurface concentration according to

$$\begin{aligned}\phi_0 &= \frac{\phi_1(1 - \psi_0)}{\phi_1 + e^{-(\alpha_A + \beta_A \phi_0 + \epsilon \psi_0)}} \\ \psi_0 &= \frac{\psi_1(1 - \phi_0)}{\psi_1 + e^{-(\alpha_B + \beta_B \psi_0 + \epsilon \phi_0)}}\end{aligned}\quad (4.3)$$

We now omit the subscript eq for brevity. Substituting (4.1) into (4.3) and comparing powers of t , we get two linear equations for $\tau_{0,A}$ and $\tau_{0,B}$:

$$\begin{aligned}\eta_0 \sqrt{\tau_{1,A}} &= (1 - \psi_0 - \beta_A \phi_0 \eta_0) \sqrt{\tau_{0,A}} + \psi_0 (1 - \eta_0 \epsilon) \sqrt{\tau_{0,B}} \\ \eta_0 \sqrt{\tau_{1,B}} &= (1 - \phi_0 - \beta_B \psi_0 \eta_0) \sqrt{\tau_{0,B}} + \phi_0 (1 - \eta_0 \epsilon) \sqrt{\tau_{0,A}}\end{aligned}\quad (4.4)$$

Let us consider a single-surfactant system (say the A) as a reference state. This is simply achieved by setting $\psi_{0,\text{eq}}$

Table 1. Comparison of the Predicted $\sqrt{\tau_\gamma}$ (eq 4.8) to Experimental Results^{4,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. 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 isotherms for the mixture, $\phi_{0,\text{eq}}$ and $\psi_{0,\text{eq}}$, were taken from the same reference. The values for $\Delta\gamma\sqrt{\tau_\gamma}$ (given in units of $\text{dyn s}^{1/2}/\text{cm}$) are obtained experimentally from the asymptotic slope of the γ vs $t^{-1/2}$ curves (see eq 4.1). The predicted values for $\Delta\gamma\sqrt{\tau_\gamma}$ 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.

and $\tau_{0,B}$ to zero, and denoting $\phi_0 \rightarrow \bar{\phi}_0$, $\eta_0 \rightarrow \bar{\eta}_0 = 1 - \phi_0$. Consequently,

$$\sqrt{\tau_{0,A}} = \frac{1 - \bar{\phi}_0}{1 - \beta_A(1 - \bar{\phi}_0)\bar{\phi}_0} \sqrt{\bar{\tau}_{1,A}} \quad (4.5)$$

where the “bars” throughout the paper denote values obtained for this single-component system.

In a DLA process, the equation of state (2.7) holds also out of equilibrium,² since the equilibration of the interface with the subsurface layer is very fast for both species. Substituting (4.1) into (2.7), the asymptotic behavior of the surface tension is obtained:

$$\begin{aligned}-a^2 \Delta\gamma \sqrt{\tau_\gamma} &= \left(\frac{\phi_0}{\eta_0} - \beta_A \phi_0^2 - \epsilon \phi_0 \psi_0 \right) \sqrt{\tau_{0,A}} + \\ &\left(\frac{\psi_0}{\eta_0} - \beta_B \psi_0^2 - \epsilon \phi_0 \psi_0 \right) \sqrt{\tau_{0,B}}\end{aligned}\quad (4.6)$$

Without surface interactions ($\beta_A = \beta_B = \epsilon = 0$) only steric effects and surface activity terms are taken into account. The Frumkin-like isotherm (4.3) is simplified in this approximation to a Langmuir-like isotherm, and eq 4.4 takes the form

$$\begin{aligned}\sqrt{\tau_{0,A}} &= (1 - \phi_0) \sqrt{\tau_{1,A}} - \psi_0 \sqrt{\tau_{1,B}} \\ \sqrt{\tau_{0,B}} &= (1 - \psi_0) \sqrt{\tau_{1,B}} - \phi_0 \sqrt{\tau_{1,A}}\end{aligned}\quad (4.7)$$

Using eqs 4.5–4.7, we obtain a simple expression, relating τ_γ of the mixture with those of each species separately, $\bar{\tau}_{\gamma,A}$ and $\bar{\tau}_{\gamma,B}$:

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

where $\Delta\bar{\gamma}_A$ and $\Delta\bar{\gamma}_B$ are the equilibrium reduction in interfacial tension of the single-surfactant solutions. This correspondence relates the time scale of the surface tension relaxation in the mixture with the time scales corresponding to the individual species. As was pointed out previously, most common nonionic surfactants usually undergo DLA. Thus, the above result provides a convenient way of predicting the behavior of multicomponent surfactant mixtures based on single-surfactant data. In Table 1, we compare the predicted $\sqrt{\tau_\gamma}$ of eq 4.8 with experimental results obtained by Fainerman and Miller⁴ for a sequence of Triton X mixtures. On the basis of 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 the X-165 coverage in the presence of the X-405,⁴ implying strong interfacial interactions between the species. The deviation in the predicted kinetics in Table 1 probably arises from those interactions, which are not taken into account by eq 4.8. It is possible to treat also the general case, including interactions between surfactants, by using the full equations (4.4)–(4.6) instead of the simplified one (4.8). Such a procedure, however, involves three additional fitting parameters (β_A , β_B , and ϵ). Nevertheless, as demonstrated in Table 1, the simple prediction (4.8) may be applicable to various experimental systems.

4.2. KLA Process at Long Times. Although most nonionic surfactants undergo a DLA process, the adsorption of some nonionic surfactants as well as ionic ones is found to be kinetically limited. For a KLA process, the bulk of the mixture is assumed to be at equilibrium, $\phi(x) = \phi_b$ and $\psi(x) = \psi_b$. The equations governing the kinetics are now the interfacial ones, (2.9).

Asymptotic solutions at $t \rightarrow \infty$ of first-order equations such as (2.9) have an exponential form characteristic of KLA. Linearizing eq 2.9 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 between A and B ($\beta_A = \beta_B = \epsilon = 0$, yet keeping steric and surface activity effects), the expressions for τ_\pm are

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

where τ_A and τ_B are the KLA time scales of the single-surfactant case, defined as

$$\begin{aligned} \tau_A &= \frac{\bar{a}^2 (\phi_0)^2}{D_A (\phi_b)} e^{-\alpha_A} \\ \tau_B &= \frac{\bar{a}^2 (\psi_0)^2}{D_B (\psi_b)} e^{-\alpha_B} \end{aligned} \quad (4.11)$$

yet ϕ_0 and ψ_0 are the equilibrium values for 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 some simple cases.

For the case where the interfacial kinetics of surfactant A is much slower than that of B, $\tau_A \gg \tau_B$, eqs 4.9 and 4.10 are simplified to

$$\begin{aligned} (1 - \phi_{0,\text{eq}}) \Delta \phi_0 - \psi_{0,\text{eq}} \Delta \psi_0 &\sim e^{-t/\tau_-}; \quad \tau_- = \tau_A (1 - \phi_0) / \eta_0 \\ \Delta \psi_0 &\sim e^{-t/\tau_+}; \quad \tau_+ = \tau_B (1 - \phi_0) \end{aligned} \quad (4.12)$$

In the other limiting case, where the two species have similar time scales, $\tau_A \approx \tau_B$, we get

$$\begin{aligned} \Delta \phi_0 - \Delta \psi_0 &\sim e^{-t/\tau_-}; \quad \tau_- = \tau_A / \eta_0 \\ \phi_{0,\text{eq}} \Delta \phi_0 + \psi_{0,\text{eq}} \Delta \psi_0 &\sim e^{-t/\tau_+}; \quad \tau_+ = \tau_A \end{aligned} \quad (4.13)$$

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 KLA may lead to a significant reduction in adsorption rate. In this regime the mixture behavior may differ considerably from that of its individual constituents. Because of the relatively large factor of $1/\eta_0$, the KLA time scale may exceed the DLA one and the adsorption would become kinetically limited.

4.3. Short Time Behavior. DLA Regime. Here, we assume that the surface and subsurface layers are already at equilibrium and examine the system at short time scales compared to the diffusion mechanism.

Note that the DLA behavior cannot strictly start at $t = 0$, since at that instance the interface and subsurface layers are not at equilibrium with each other. Assuming a DLA time dependence of the form $\phi_0(t) \approx \text{const.} + \sqrt{t/\tau_A}$, the const. is found to be roughly equal to $2\phi_b$. In other words, only once the surface coverage has exceeded a value of $2\phi_b$, indicating an almost complete depletion of the subsurface layer,¹⁸ can one assume a process limited by diffusion (the same argument applies to the second surfactant). Figure 4 shows the surface coverage and surface tension at this DLA stage plotted as a function of $t^{1/2}$. The linear dependence of the surface coverages is evident, whereas the dynamic surface tension, having contributions from both species, exhibits a small deviation from the $t^{1/2}$ behavior. Since surfactant A has been taken to be much slower than surfactant B, the $t^{1/2}$ behavior of the two surfactants overlaps only for a very short period of time.

Beyond the DLA Regime. At the very early time stages of the process, most of the molecules in the subsurface layer migrate rapidly to the interface. Only when the subsurface layer becomes nearly depleted do molecules from the bulk start migrating toward the interface by a diffusive mechanism. Before diffusion sets in, the DLA assumption is invalid and the interfacial kinetics must be considered explicitly. To address these very early time stages, we assume 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 (2.9) to be linear, as can be seen in Figure 5:

$$\begin{aligned} \phi_0(t \rightarrow 0) &\approx \phi_b + \frac{D_A}{\bar{a}^2} \phi_b \alpha_A t \\ \psi_0(t \rightarrow 0) &= \psi_b + \frac{D_B}{\bar{a}^2} \psi_b \alpha_B t \end{aligned} \quad (4.14)$$

Any correlation between the two species vanishes during this initial stage since the surfactants at the interface are dilute and noninteracting. We would like to emphasize that those very early time scales (10^{-11} – 10^{-7} s) are of no

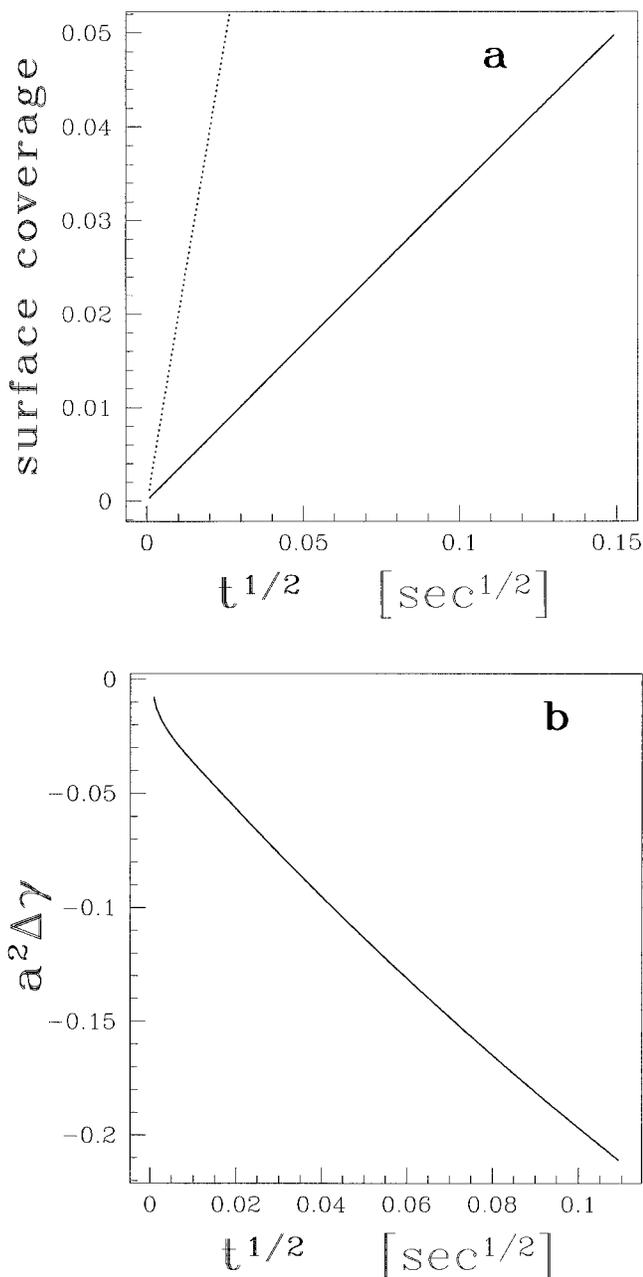


Figure 4. Surface coverage (a) and dynamic surface tension (b) for the system of Figure 1, redrawn for intermediate short times. The curve exhibits the expected $t^{1/2}$ behavior characteristic of DLA at short times.

experimental interest. We study them as an analytic limit of the general kinetic equations.

4.4. Linear Isotherm Limit: Weakly Adsorbing Surfactants. We present now a very simplified and restricted case which, nevertheless, is of interest since it has an analytic solution. The assumptions for which this case can be treated are (i) one of the surfactants (say A) has a low surface activity and undergoes a slow DLA process, (ii) the second surfactant (B) is assumed to be at equilibrium, and (iii) the two species do not interact. Since the surface coverage of surfactant A is always very low, its isotherm can be taken as linear in ϕ_1 (Henry's law):

$$\phi_0 = e^{\alpha_A} \phi_1 \quad (4.15)$$

as can be seen from taking the low-coverage limit of eq 2.6. With the above assumptions, the time-dependent

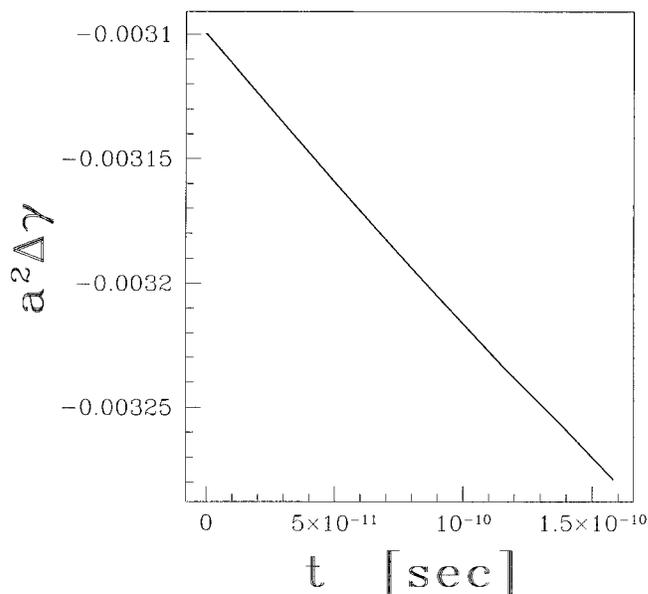


Figure 5. Dynamic surface tension for the system of Figure 1, redrawn for extremely short times. The curve exhibits the predicted linear behavior.

surface coverages of the two species can be explicitly calculated,^{20–22}

$$\begin{aligned} \phi_0(t) &= [1 - \tanh(\alpha_A/2)e^{\beta\tau} \operatorname{erfc}(\sqrt{t/\tau})]\phi_b e^{\alpha_A} \\ \psi_0(t) &= \frac{\psi_b[1 - \phi_0(t)]}{\psi_b + e^{\alpha_B}} \end{aligned} \quad (4.16)$$

where $\tau \equiv (a^2/D_A)(1 + e^{\alpha_A})^2$. Note that in the limit $t \rightarrow 0$, the DLA process starts at $\phi_0(t=0) = 2\phi_b/(e^{-\alpha_A} + 1)$ which is somewhat smaller than $2\phi_b$. This result is consistent with an early-stage dynamics, where the subsurface layer is entirely depleted, as was discussed in section 4.3. Furthermore, the linear relation (4.15) is always valid for short enough times, when the surface coverage is low (with no further limiting assumptions), as demonstrated in Figure 6.

5. Conclusions

We have examined the behavior of nonionic surfactant mixtures by solving numerically the governing kinetic equations, as well as deriving analytical limiting cases. A comprehensive description of the different adsorption stages is obtained. For mixtures of common, nonionic surfactants, the adsorption process can be divided into four temporal stages. At the very early times of the adsorption, the process begins with a short stage, where the surface coverage and surface tension change linearly with time because of interfacial kinetics (Figure 5). As discussed in section 4.3, this stage is practically too short to be observed experimentally (usually less than microseconds). During this early stage, the subsurface layer becomes nearly empty, which in turn drives a second, diffusion-limited stage, where molecules of both species diffuse from the bulk with a $t^{1/2}$ time dependence (Figure 4). During this second stage (discussed above in section 4.3), the coverage is dominated by the more mobile species having a faster diffusion. In cases where the less mobile species is more surface-active, a third stage is predicted. Here, one species undergoes desorption, while the coverage gradually becomes dominated by the second, energetically

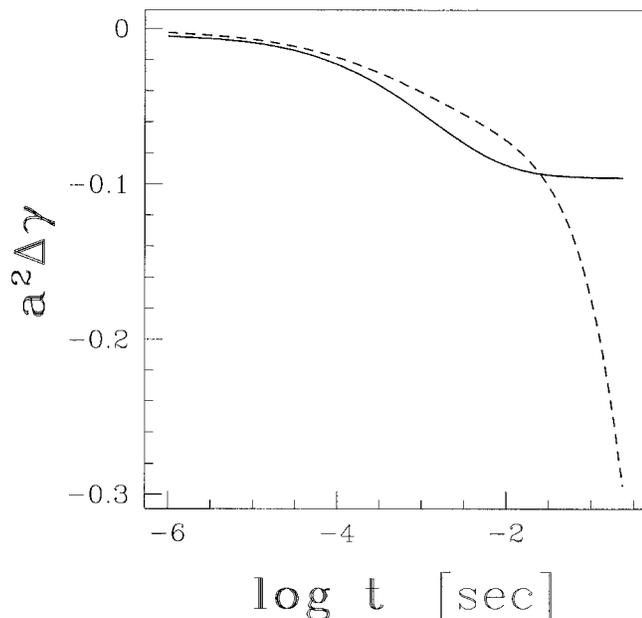


Figure 6. Comparison between the numerical solution of the complete set of equations (solid line) and the analytic solution assuming a linear adsorption isotherm (dashed line). The parameters used in the calculations are $\phi_b = 2 \times 10^{-5}$, $\psi_b = 10^{-4}$, $\alpha_A = 6$, $\alpha_B = 5$, $\beta_A = \beta_B = \epsilon = 0$, $\sqrt{D_A}/a = 2 \times 10^4 \text{ s}^{-1/2}$, and $\sqrt{D_B}/a = 10^4 \text{ s}^{-1/2}$. The linear approximation is valid only in the beginning of the process and fails when the coverage becomes large.

favorable surfactant. This competition can be seen in Figure 1. The final relaxation toward equilibrium is usually diffusion-limited, exhibiting an asymptotic $t^{-1/2}$ behavior (Figure 3), which was explained in section 4.1.

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, our model predicts a significant increase in the limiting time scale due to coupling between the two surfactants.

We have managed to relate the kinetic behavior of the two-surfactant mixture with the properties of its individual constituents, (eq 4.8). The kinetic behavior of the mixture can be predicted on the basis of equilibrium isotherms and single-surfactant data. Our results are in good agreement with experiments. However, since previous experiments were restricted to surfactants of very different adsorption time scales, our theory could be checked only in those experimental conditions. Further experiments on surfactant mixtures, especially with comparable adsorption time scales and equilibrium surface coverages, are needed in order to get a better verification of our model.

The problem we have dealt with in this work is another example of the ease at which the free-energy approach to adsorption kinetics can be generalized. Examples for further extensions are, for instance, the addition of adsorption barriers and treatment of surfactant adsorption from micellar solutions.

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Nomenclature

Below is a summary of the symbols used in this work. To make the formulation as concise as possible, we have extensively used dimensionless forms. Whenever necessary, a translation to the more practical, dimensional quantities is provided, using the symbols of e.g. ref 4.

Symbols

a = molecular dimension (equal to the inverse square root of the maximum surface density, $\Gamma_\infty^{-1/2}$)

D = diffusion coefficient

Δf = excess free energy per unit volume of the bulk solution

f_0 = interfacial contribution to the free energy per unit area

t = time

x = distance from the interface

α = energy (in units of $k_B T$) gained by a surfactant molecule by migrating to the interface

β = energy (in units of $k_B T$) of lateral attraction between two surfactant molecules of the same species

$\Delta\gamma$ = change in interfacial tension

ϵ = energy (in units of $k_B T$) of lateral attraction between two surfactant molecules of different species

μ = chemical potential (in units of $k_B T$)

τ = time scale of a kinetic process

ϕ, ψ = volume fractions of the two surfactant species (equal to the corresponding concentrations multiplied by a^3 ; $\phi = a^3 c_A$, $\psi = a^3 c_B$)

ϕ_0, ψ_0 = surface coverages of the two surfactant species (equal to the corresponding surface densities multiplied by a^2 ; $\phi_0 = a^2 \Gamma_A$, $\psi_0 = a^2 \Gamma_B$)

ϕ_0, ψ_0 = surface coverages in the single-surfactant solutions

Subscripts

A, B = corresponding to surfactant A, B

0 = value at the interface

1 = value at the subsurface layer of the solution

b = value at the bulk reservoir

eq = value at equilibrium

Appendix: Numerical Scheme

The objective of the numerical scheme is to solve the set of four equations—the two Ward–Tordai equations (2.8) and the two interfacial ones (2.9). The hardcore of the problem is the evaluation of the integral in eq 2.8:

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

This is done by discretizing the time variable t and transforming the integral into a recursion relation.¹⁹ The singularity in the integrand is removed by substituting $x = \sqrt{t-\tau}$. Evaluating the integral at discrete time steps, $\Delta t = t_{k+1} - t_k$, we obtain

$$\int_0^t \frac{\phi_1(\tau)}{\sqrt{t-\tau}} d\tau \rightarrow \sum_{k=1}^n \left[\phi_1(t_n - t_k) + \phi_1(t_n - t_{k-1}) \right] (\sqrt{t_k} - \sqrt{t_{k-1}})$$

where $t_k \equiv k \Delta t$ and $t_n \equiv t$. The initial conditions are $\phi_0(0) = \phi_1(0) = \phi_b$ and $\psi_0(0) = \psi_1(0) = \psi_b$. Adding the rest of the terms in the Ward–Tordai equations, we obtain linear relations between ϕ_0 and ϕ_1 , and between ψ_0 and ψ_1 . Substituting these relations into the kinetic boundary conditions (2.9) and using a finite difference to evaluate the first time derivative, $\partial\phi_0/\partial t \rightarrow [\phi_0(t_{k+1}) - \phi_0(t_k)]/\Delta t$, we obtain a set of four algebraic equations, relating the values

of ϕ_0 , ψ_0 , ϕ_1 , and ψ_1 at the current time step, $t = t_n$:

$$\phi_0(t_n) = \frac{1}{a} \sqrt{\frac{D_A}{\pi}} \left[2\phi_b \sqrt{t_n} - \sum_{k=1}^{n-1} \phi_1(t_n - t_k) (\sqrt{t_{k+1}} - \sqrt{t_{k-1}}) - \phi_0(\sqrt{t_n} - \sqrt{t_{n-1}}) \right] + 2\phi_b - \left(1 + \frac{1}{a} \sqrt{\frac{D_A}{\pi}} \sqrt{\Delta t} \right) \phi_1(t_n)$$

$$\phi_0(t_n) = \phi_0(t_{n-1}) + \frac{D_A}{a^2} \Delta t \left\{ \phi_1(t_n) \ln \left[\frac{\eta_0(t_n) \phi_1(t_n)}{\phi_0(t_n)} \right] + \alpha_A + \beta_A \phi_0(t_n) + \epsilon \psi_0(t_n) \right\}$$

and similar two equations for surfactant B. This set of equations is solved numerically, using a binary search method.

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