

Adsorption Relaxation for Nonionic Surfactants under Mixed Barrier-Diffusion and Micellization-Diffusion Control

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Relaxation processes of surfactant adsorption and surface tension, which are characterized by two specific relaxation times, are theoretically investigated. We are dealing with fluid interfaces and small initial deviations from equilibrium. For surfactant concentrations below the critical micellization concentration (CMC), we consider adsorption under mixed barrier-diffusion control. General analytical expressions are derived, which are convenient for both numerical computations and asymptotic analysis. Series expansions for the short- and long-time limit are derived. The results imply that the short-time asymptotics is controlled by the adsorption barrier, whereas the long-time asymptotics is always dominated by diffusion. Furthermore, for surfactant concentrations above the CMC, adsorption under mixed micellization-diffusion control is considered. Again, a general analytical expression is derived for the relaxation of surfactant adsorption and surface tension, whose long- and short-time asymptotics are deduced. The derived equations show that at the short times the relaxation is completely controlled by the diffusion, whereas the long-time asymptotics is affected by both demicellization and diffusion. The micellar effect is manifested as an exponential (rather than square-root) decay of the perturbation. The derived expressions are applied to process available experimental data for the nonionic surfactant Triton X-100 and to determine the respective demicellization rate constant. © 2002 Elsevier Science (USA)

Key Words: adsorption kinetics; mixed barrier-diffusion control; adsorption; from micellar surfactant solutions; demicellization; rate constant; dynamic surface tension; theoretical analysis; kinetics of adsorption; short- and long-time asymptotics; micelles; role in surface tension relaxation; nonionic surfactants; kinetics of adsorption.

1. INTRODUCTION

The rate of surfactant adsorption at fluid interfaces has crucial importance for the processes of foam generation and emulsification. Dynamic surface coverage with adsorbed surfactant monolayers determines whether the gas bubbles or oil drops will coalesce upon collision (1, 2). The physical parameter, which characterizes the surfactant solutions with their ability to quickly

generate adsorption layers, is the relaxation time of the dynamic surface tension, which is liable to direct measurements with various experimental methods (3–7). In the case of adsorption of a nonionic surfactant under diffusion control, the theoretical problem for the relaxation of a small initial perturbation was solved by Sutherland (8), who derived $[\sigma(t) - \sigma_e]/[\sigma(0) - \sigma_e] = F(t, t_d^{-1/2})$; here, t is time, $\sigma(t)$ and σ_e are, respectively, the dynamic and equilibrium surface (interfacial) tension, and t_d is the characteristic diffusion time:

$$F(t, \alpha) \equiv \exp(\alpha^2 t) \operatorname{erfc}(\alpha t^{1/2}); \quad [1]$$

$\operatorname{erfc}(x)$ is the complementary error function (9, 10). Note that in the Sutherland formula we have $\alpha = t_d^{-1/2}$, where $t_d = (\partial\Gamma/\partial c)^2/D$, c is the bulk surfactant concentration, and Γ and D are, respectively, the surfactant adsorption and diffusion coefficient.

The experiment shows that sometimes the dynamics of surface tension can be affected by kinetic barriers to adsorption (3–5, 11, 12). In such cases, the interfacial dynamics depends on two characteristic relaxation times: the diffusion and adsorption times. The respective relaxation problem leads to an expression for the dynamic surface tension in terms of the function $F(t, \alpha)$; see Eq. [10]. However, this time α is, in general, a complex number. The latter fact makes the numerical computations and the derivations of asymptotic expressions for the short and long times much more difficult.

For fast numerical calculation of the function $F(t, \alpha)$, Cody (13) provided precise rational polynomials, based on the Chebyshev approximations. Unfortunately, these approximations are valid only for real values of α . In the present paper we report that the mathematical difficulties can be overcome by using the relationship $F(t, \alpha) = w(i\alpha t^{1/2})$, where w is the so-called “plasma function” (9). The latter has a convenient integral presentation, which can be utilized to compute numerically the relaxation curves of adsorption, subsurface concentration, and surface tension. Moreover, this integral presentation can be used to derive simple analytical expressions describing the relaxation behavior in the long- and short-time limit. This is the subject of section 2 of the present article.

The same theoretical approach can be applied to the case of adsorption from surfactant solutions above the critical micellization concentration (CMC). Insofar as small deviations

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from equilibrium are concerned, the kinetics of demicellization can be formally described in the framework of the pseudo-first-order-reaction (PFOR) approximation (14). In such case, again *two* relaxation times enter the theoretical description: the characteristic diffusion and micellar times. In section 3 below, the integral presentation of the plasma function is applied to derive the respective short- and long-time asymptotics of the dynamic surface tension. To illustrate the applicability of the obtained equations, they are applied to process available dynamic data for micellar solutions of the nonionic surfactant Triton X-100, and the demicellization rate constant of Kresheck *et al.* (15) is determined.

In spite of the fact that the adsorption relaxation time is defined for *small* perturbations, there are indications that it characterizes also the dynamics of adsorption in the case of *large* initial deviations from equilibrium (16).

In the present article we consider only nonionic surfactants. In the case of ionic surfactants the theoretical analysis is more complicated: the existence of dynamic electric double layer and counterionic binding has to be taken into account (3, 11, 16–19). We hope that in the future the results of the present study can be extended to the case of ionic surfactants.

2. BARRIER-DIFFUSION CONTROL BELOW THE CMC

2.1. Physical Background and Basic Equations

Here, we consider the relaxation of surfactant adsorption, Γ , and surface tension, σ , after a small perturbation. Our system is an aqueous solution of nonionic surfactant at concentrations below the CMC. A semi-infinite solution with a flat air–water (or oil–water) interface is considered. At the initial moment, $t = 0$, the interface is perturbed. Next, the equilibrium is restored by exchange of surfactant molecules between the surface and the subsurface layer (adsorption/desorption), accompanied by diffusion transport between the subsurface and the bulk (3, 4). If the adsorbing surfactant molecules have to overcome a barrier to adsorption, then the exchange of surfactant between the surface and subsurface is described by the kinetic equation

$$\frac{d\Gamma}{dt} = \Phi(\Gamma)[c_s - f(\Gamma)/K_1]; \quad [2]$$

see Refs. (3, 4, 19, 20). Here, c_s is the subsurface concentration of surfactant, K_1 is the equilibrium constant of adsorption; the explicit form of the functions $\Phi(\Gamma)$ and $f(\Gamma)$ depends on the type of adsorption isotherm used: that of Henry, Langmuir, Frumkin, Volmer, or van der Waals. Using Table 1.4 in Ref. (19), we find explicit expressions for $\Phi(\Gamma)$ and $f(\Gamma)$, which are given in Table 1. The following notation is used in Table 1: Γ_∞ is the maximum possible adsorption; K_{ads} is the rate constant of adsorption. Note that the equilibrium constant is $K_1 = K_{\text{ads}}/(K_{\text{des}}\Gamma_\infty)$, where K_{des} is the rate constant of desorption, k is the Boltzmann constant, T is the temperature, and β is a parameter which accounts for the interaction between neighboring adsorbed molecules (19, 21).

TABLE 1
Expressions for $\Phi(\Gamma)$ and $f(\Gamma)$ for Various Kinetic Models

Adsorption isotherm	Function $\Phi(\Gamma)$	Function $f(\Gamma)$
Henry	$\Phi(\Gamma) = K_{\text{ads}} = \text{const.}$	$f(\Gamma) = \frac{\Gamma}{\Gamma_\infty}$
Langmuir	$\Phi(\Gamma) = \left(1 - \frac{\Gamma}{\Gamma_\infty}\right) K_{\text{ads}}$	$f(\Gamma) = \frac{\Gamma}{\Gamma_\infty - \Gamma}$
Frumkin	$\Phi(\Gamma) = \left(1 - \frac{\Gamma}{\Gamma_\infty}\right) K_{\text{ads}}$	$f(\Gamma) = \frac{\Gamma}{\Gamma_\infty - \Gamma} \exp\left(-\frac{2\beta\Gamma}{kT}\right)$
Volmer	$\Phi(\Gamma) = K_{\text{ads}} = \text{const.}$	$f(\Gamma) = \frac{\Gamma}{\Gamma_\infty - \Gamma} \exp\left(\frac{\Gamma}{\Gamma_\infty - \Gamma}\right)$
van der Waals	$\Phi(\Gamma) = K_{\text{ads}} = \text{const.}$	$f(\Gamma) = \frac{\Gamma}{\Gamma_\infty - \Gamma} \exp\left(\frac{\Gamma}{\Gamma_\infty - \Gamma} - \frac{2\beta\Gamma}{kT}\right)$

Note that the right-hand side of Eq. [2] represents the difference between the adsorption and desorption fluxes. At equilibrium, these two fluxes counterbalance each other and Eq. [2] reduces to the equilibrium adsorption isotherm,

$$K_1 c_e = f(\Gamma_e), \quad [3]$$

which can be any of the aforementioned types of isotherms; here and hereafter the subscript “e” denotes the equilibrium value of the respective variable.

For small perturbations, denoted with subscript “p”, the bulk and subsurface concentrations as well as the adsorption and surface tension can be presented in the following form: $c(x, t) = c_e + c_p(x, t)$, $c_s(t) = c_e + c_{\text{sp}}(t)$, $\Gamma(t) = \Gamma_e + \Gamma_p(t)$, and $\sigma(t) = \sigma_e + \sigma_p(t)$. The x -axis is oriented normal to the fluid interface, which is situated at $x = 0$. Then, having in mind Eq. [3], one can bring Eq. [2] to the following linearized form, which is valid for small perturbations,

$$\frac{d\Gamma_p}{dt} = k_a \left(c_{\text{sp}} - \frac{\Gamma_p}{G} \right) \quad (t > 0), \quad [4]$$

where

$$k_a \equiv \Phi(\Gamma_e), \quad G \equiv \left(\frac{\partial \Gamma}{\partial c} \right)_e = \left[\frac{1}{K_1} \frac{df}{d\Gamma} \right]_e^{-1}. \quad [5]$$

For the Henry, Volmer, and van der Waals isotherms $k_a = K_{\text{ads}}$, whereas for the Langmuir and Frumkin isotherms we have $k_a = (1 - \Gamma_e/\Gamma_\infty)K_{\text{ads}}$; see Table 1. $df/d\Gamma$ can be calculated by differentiation of $f(\Gamma)$ given in Table 1. The linearized forms of the diffusion equation and its boundary condition are

$$\frac{\partial c_p}{\partial t} = D \frac{\partial^2 c_p}{\partial x^2} \quad (x > 0, t > 0), \quad [6]$$

$$\frac{d\Gamma_p}{dt} = D \frac{\partial c_p}{\partial x} \quad (x = 0, t > 0), \quad [7]$$

where D is the diffusion coefficient of the surfactant molecules. The initial conditions are

$$\Gamma_p(0) = \Gamma_{p0}, \quad \sigma_p(0) = \sigma_{p0}, \quad c_{sp}(0) = 0, \quad [8]$$

where Γ_{p0} and σ_{p0} denote the small initial perturbations in the surfactant adsorption and surface tension, respectively. In other words, the system is initially in equilibrium and then the interface is quickly deformed so that Γ and σ change, while the concentration profile remains unchanged (equilibrium). Then, Γ and σ relax to equilibrium values. In particular, we have $c_{sp}(0) = 0$ because of the presence of kinetic barrier to adsorption, which does not allow the subsurface to respond instantaneously to the surface perturbation. On the other hand, such instantaneous response (equilibration of surface and subsurface) would take place if the surfactant transfer occurs under pure diffusion control; then, the respective initial condition would be $c_{sp}(0) = \Gamma_{p0}/G \equiv c_{sp0}$. The latter quantity is used to scale the subsurface concentration in Eq. [14] below.

2.2. Adsorption Time vs Diffusion Time

For adsorption under mixed barrier-diffusion control, two characteristic times can be distinguished, viz. the *diffusion* time, $t_d = G^2/D$, and the *adsorption* time, $t_a = G/k_a$. Dong *et al.* (22) investigated numerically the limiting case $t_a/t_d \gg 1$ (prevailing barrier). Our purpose here is to obtain the exact analytical solution of the relaxation problem for arbitrary values of the ratio t_a/t_d and to derive simpler asymptotic expressions for the limiting cases of short and long times.

To solve the mathematical problem, we apply Laplace transformation with respect to time. The Laplace transforms of the perturbations in adsorption, bulk, and subsurface concentrations are, respectively, $\tilde{\Gamma}_p(s) \equiv L[\Gamma_p(t)]$, $\tilde{c}_p(x, s) \equiv L[c_p(x, t)]$, and $\tilde{c}_{sp}(s) \equiv L[c_{sp}(t)]$. Thus, from the diffusion Eq. [6] and the boundary condition $c_{sp}(t) = c_p(0, t)$, one derives $\tilde{c}_p(x, s) = \tilde{c}_{sp}(s) \exp[-x(s/D)^{1/2}]$. Further, using Eqs. [4], [7], and [8], one can deduce an explicit expression for the Laplace transform of the perturbation in adsorption:

$$\frac{\tilde{\Gamma}_p(s)}{\Gamma_{p0}} = \frac{1}{s^{1/2}} \frac{t_a s^{1/2} + t_d^{1/2}}{t_a s + (s t_d)^{1/2} + 1}. \quad [9]$$

Since we are dealing with small deviations from equilibrium, we have $\sigma_p(t) = (\partial\sigma/\partial\Gamma)_e \Gamma_p(t)$. The latter relationship, written for the moment $t = 0$, yields $\sigma_{p0} = (\partial\sigma/\partial\Gamma)_e \Gamma_{p0}$. In view of the latter two expressions, we can express the inverse Laplace transform of Eq. [9] in the form (20)

$$\frac{\Gamma_p(t)}{\Gamma_{p0}} = \frac{\sigma_p(t)}{\sigma_{p0}} = \frac{1}{\alpha_1 - \alpha_2} [\alpha_1 F(t, \alpha_2) - \alpha_2 F(t, \alpha_1)], \quad [10]$$

where $F(t, \alpha)$ is given by Eq. [1] and the parameters α_1 and α_2

are defined as follows:

$$\alpha_{1,2} = \frac{t_d^{1/2}}{2t_a} [1 \pm (1 - 4t_a/t_d)^{1/2}]. \quad [11]$$

It is important to note that α_1 and α_2 are positive real numbers for $4t_a/t_d < 1$, whereas they are complex numbers with a positive real part for $4t_a/t_d > 1$. As already mentioned, the complex form of Eq. [10] creates mathematical problems for the calculation of the functions $\Gamma_p(t)$ and $\sigma_p(t)$ and for obtaining their asymptotics in the limiting cases $t \rightarrow 0$ and $t \rightarrow \infty$.

To overcome the aforementioned problems, we notice that the function F is related to the so-called plasma function, w ; see Ref. (9):

$$F(t, \alpha) = w(i\alpha t^{1/2}) = \frac{2\alpha t^{1/2}}{\pi} \int_0^\infty \frac{\exp(-\tau^2)}{\tau^2 + \alpha^2 t} d\tau, \quad \text{Re}(\alpha) > 0. \quad [12]$$

With the help of Eqs. [10]–[12], the functions $\Gamma_p(t)$ and $\sigma_p(t)$ can be expressed in a compact and convenient integral form:

$$\frac{\Gamma_p(t)}{\Gamma_{p0}} = \frac{\sigma_p(t)}{\sigma_{p0}} = \frac{2}{\pi} (t_d/t_a)^{1/2} \int_0^\infty \frac{\exp(-t\tau^2/t_a)}{(\tau^2 - 1)^2 + t_d\tau^2/t_a} d\tau. \quad [13]$$

The integrand in Eq. [13] has no singularities and vanishes exponentially at infinity. For this reason, Eq. [13] is suitable for both numerical computations and asymptotic analysis. Similar analytical expression for the subsurface concentration can be deduced from Eqs. [4] and [13]:

$$\frac{c_{sp}(t)}{c_{sp0}} = \frac{2}{\pi} (t_d/t_a)^{1/2} \int_0^\infty \frac{(1 - \tau^2) \exp(-t\tau^2/t_a)}{(\tau^2 - 1)^2 + t_d\tau^2/t_a} d\tau. \quad [14]$$

In the short-time limit ($t \rightarrow 0$), Eq. [13] has the following asymptotic expansion:

$$\begin{aligned} \frac{\Gamma_p(t)}{\Gamma_{p0}} = \frac{\sigma_p(t)}{\sigma_{p0}} = & 1 - \frac{t}{t_a} + \frac{4t_d^{1/2}}{3(\pi t_a)^{1/2}} \left(\frac{t}{t_a}\right)^{3/2} + \frac{t_a - t_d}{2t_a} \left(\frac{t}{t_a}\right)^2 \\ & - \frac{8(2t_a - t_d)t_d^{1/2}}{15\pi^{1/2}t_a^{3/2}} \left(\frac{t}{t_a}\right)^{5/2} + \dots, \end{aligned} \quad [15]$$

which is applicable for $t \ll t_a^2/t_d$. One sees that for $t \rightarrow 0$ the leading term of the time dependence in Eq. [15] is the linear term t/t_a ; this indicates the presence of barrier control of adsorption at the short times. The typical diffusion term $\propto (t/t_d)^{1/2}$ does not appear in Eq. [15]. In other words, the short-time asymptotics is always controlled by the kinetic barrier to adsorption.

In the long-time limit ($t \rightarrow \infty$), Eq. [13] has the following asymptotic expansion,

$$\frac{\Gamma_p(t)}{\Gamma_{p0}} = \frac{\sigma_p(t)}{\sigma_{p0}} = \left(\frac{t_d}{\pi t}\right)^{1/2} - \frac{t_d - 2t_a}{2\pi^{1/2}t_d} \left(\frac{t_d}{t}\right)^{3/2} + \frac{3(t_d - t_a)(t_d - 3t_a)}{4\pi^{1/2}t_d^2} \left(\frac{t_d}{t}\right)^{5/2} + \dots, \quad [16]$$

which is valid for $t \gg |t_d/2 - t_a|$. One sees that the leading term in the long-time asymptotics is the diffusion term $\propto (t_d/t)^{1/2}$. Therefore, we can conclude that the long-time asymptotics is always controlled by the diffusion.

2.3. Numerical Results and Discussion

Numerical results for the relaxation of small perturbations in the surfactant subsurface concentration $c_{sp}(t)$, adsorption $\Gamma_p(t)$, and surface tension $\sigma_p(t)$ are shown in Fig. 1. Using Eqs. [13] and [14], we have calculated the respective time dependencies for various values of t_a/t_d . The upper curve in Fig. 1a corresponds to $t_a/t_d = 0$, that is, to the regime of pure diffusion control. With the increase of the ratio t_a/t_d (i.e., with the rise of the adsorption barrier), the initial perturbation in the subsurface concentration (that for $t = 0$) becomes smaller and smaller. The latter behavior is due to the fact that when the barrier grows higher, the flux of subsurface molecules, which overcome the barrier to compensate the surface perturbation, becomes smaller. At longer times $c_{sp}(t)$ exhibits a maximum, and soon after that the respective curve practically coincides with the curve corresponding to $t_a/t_d = 0$. In other words, at the longer times, the effect of barrier vanishes and the process of relaxation gradually approaches the regime of diffusion control. In addition, Fig. 1a shows that $c_{sp}(t) \approx 0$ for $t_a/t_d = 100$ (high barrier to adsorption, curve G), which means that in this case the subsurface concentration is almost equal to the bulk one, and the process of relaxation is close to the regime of pure barrier control (fast diffusion).

In Fig. 1b, the three curves A, B, and C, corresponding to $t_a/t_d = 0, 0.001$, and 0.01 , merge with each other. Hence, for $t_a/t_d \leq 0.01$ the effect of the barrier on the relaxation of adsorption and surface tension is negligible and the process exhibits diffusion control. Note that the subsurface concentration, $c_{sp}(t)$, is more sensitive to the barrier than the adsorption, $\Gamma_p(t)$, and the surface tension, $\sigma_p(t)$: compare curves A, B, and C in Figs. 1a and 1b. Moreover, Fig. 1b clearly shows that the barrier decelerates the relaxation of surface tension and adsorption: greater values of t_a/t_d (higher barrier) lead to a shift of the relaxation curve to the right (to the longer times) and to an increase in the difference between the respective curve and curve A referring to diffusion control. Nevertheless, however high the barrier might be, at sufficiently long times all curves $\Gamma_p(t)$ and $\sigma_p(t)$ approach asymptotically curve A.

It turns out that the coinciding curves A, B, and C in Fig. 1b, corresponding to $t_a/t_d \leq 0.01$, can be well described by the known expression for relaxation under pure diffusion control,

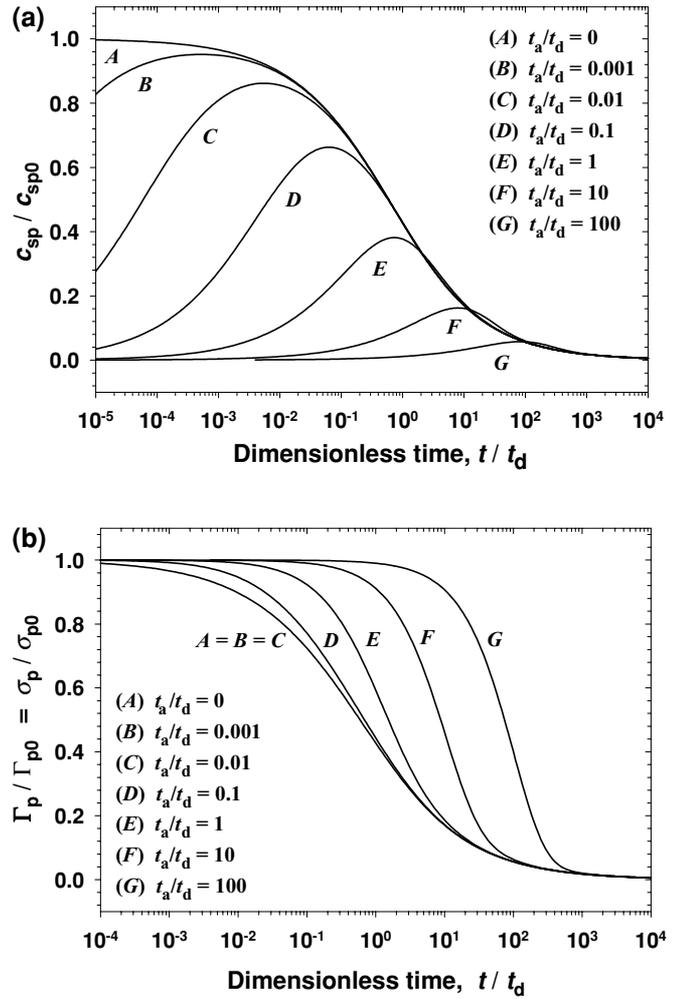


FIG. 1. Barrier-diffusion control: (a) Relaxation of perturbations in the subsurface concentration, $c_{sp}(t)$, computed by means of Eq. [14]. (b) Relaxation of perturbations in the surfactant adsorption, $\Gamma_p(t)$, and surface tension, $\sigma_p(t)$, calculated with the help of Eq. [13]. Each curve corresponds to a fixed value of the ratio t_a/t_d .

$\Gamma_p/\Gamma_{p0} = \sigma_p/\sigma_{p0} = \exp(t/t_d)\text{erfc}(t^{1/2}/t_d^{1/2})$, in the time range presented in Fig. 1. For $t_a/t_d > 0.01$ the effect of the adsorption barrier becomes significant and one has to use the more general expression, Eq. [13], or the asymptotic expansions, Eqs. [15] and [16], in the ranges of their validity.

Equation [13] and its short-time asymptotics, Eq. [15], can be relatively easily applied to process experimental data and to verify whether in a given specific case the surfactant adsorption is influenced by the presence of a kinetic barrier. For example, recently we applied Eq. [13] to fit experimental data for dynamic surface tension of aqueous solutions of the milk proteins β -lactoglobulin and Na-caseinate (23). The data have been obtained by using the fast-formed drop (FFD) technique (24, 25). The fits show that, in the experimental time interval, the β -lactoglobulin adsorbs under diffusion control, whereas the adsorption of Na-caseinate encounters a kinetic barrier with a

characteristic adsorption time $t_a = 2.7 \pm 0.3$ s; see Ref. (23) for details.

3. MICELLIZATION-DIFFUSION CONTROL

3.1. Adsorption Relaxation after a Small Perturbation

Here, we consider again the relaxation of adsorption, Γ , and surface tension, σ , after a small perturbation, but this time for surfactant concentrations above the CMC. At the initial moment, $t = 0$, the air–water (or oil–water) interface is slightly expanded. Next, the equilibrium is restored by a diffusion transport of surfactant monomers from the bulk of solution to the interface, which is accompanied by a supply of monomers by the surfactant micelles (4, 14).

As known, the experiments on the relaxation of small perturbations in the *bulk* of micellar solutions show the existence of a fast and a slow relaxation process, with characteristic times τ_1 and τ_2 , respectively (26–28). According to the detailed theory of micellization kinetics by Aniansson and Wall (26, 27), the fast process corresponds to the release of separate surfactant monomers by the micelles at constant total micelle concentration. In contrast, the slow process is related to the decomposition of a part of the micelles to monomers, which is accompanied by a decrease in the total micelle concentration.

To describe the release of monomers from the micelles, we will use the pseudo-first-order reaction (PFOR) approximation. Indeed, every complicated reaction (or system of reactions) can be approximately described as a pseudo-first-order reaction, if the deviations from equilibrium are small, which allows linearization of the respective kinetic equations. As shown in Ref. (14), in the case of adsorption from surfactant solutions after a small interfacial perturbation, the micelles serve as sources of monomers rather than as surfactant carriers. Correspondingly, to describe the transport of surfactant, in the framework of the PFOR approximation, we will use the Eqs. (3, 4, 14, 29–31)

$$\frac{\partial c_p}{\partial t} = D \frac{\partial^2 c_p}{\partial x^2} - \frac{c_p}{t_m} \quad (x > 0, t > 0), \quad [17]$$

where the last term describes a source of surfactant monomers due to the presence of micelles; t_m is the characteristic time of the micellar supply of monomers. Because of the used PFOR approximation, t_m^{-1} is not a simple rate constant of an elementary first-order reaction, but is a function of the micelle concentration and the rate constants of the real demicellization reactions (4, 14, 15). We will use an expression due to Kresheck *et al.* (15)

$$t_m^{-1} = k_0 \left(\frac{C_s - \text{CMC}}{\text{CMC}} \right), \quad [18]$$

where k_0 is a rate-constant parameter, independent of the total surfactant concentration C_s . In section 3.3 we discuss the relation between t_m and the two micellar relaxation times, τ_1 and τ_2 .

Demicellization accelerates the diffusion supply of monomers, which facilitates the manifestation of the adsorption barrier (if any). However, if the theoretical model includes also a kinetic barrier to adsorption (in addition to the diffusion and demicellization), one arrives at a more complicated relaxation problem, with three characteristic times (t_a , t_d , and t_m), which could be a subject of a subsequent study. To simplify the mathematical problem, here, we assume that there is no kinetic barrier to the surfactant adsorption at the interface. Thus, we arrive at a relaxation problem with two characteristic times: the diffusion time $t_d = G^2/D$ and the micellar time t_m . We have to solve Eq. [17] along with the boundary condition provided by Eq. [7] and the relationships

$$\Gamma_p(0) = \Gamma_{p0}, \quad \sigma_p(0) = \sigma_{p0}, \quad c_{sp}(t) \equiv \Gamma_p(t)/G. \quad [19]$$

The latter relationship, $c_{sp} \equiv \Gamma_p/G$, is a corollary from the absence of barrier to adsorption, which leads to an instantaneous equilibration between subsurface and surface. We apply again the Laplace transformation. Thus, for the Laplace transform of the perturbation in the bulk surfactant concentration, one obtains

$$\tilde{c}_p = \frac{\tilde{\Gamma}_p}{G} \exp\left(-x \sqrt{\frac{st_m + 1}{Dt_m}}\right). \quad [20]$$

By substituting Eq. [20] into the Laplace image of Eq. [7], one derives

$$\frac{\tilde{\Gamma}_p}{\Gamma_{p0}} = \frac{t_m^{1/2} t_d^{1/2}}{t_m^{1/2} t_d^{1/2} s + (t_m s + 1)^{1/2}}. \quad [21]$$

The reverse Laplace transformation of Eq. [21] yields (14)

$$\frac{\Gamma_p}{\Gamma_{p0}} = \frac{\sigma_p}{\sigma_{p0}} = \frac{\exp(-t/t_m)}{\beta_1 + \beta_2} [\beta_1 F(t, \beta_1) - \beta_2 F(t, \beta_2) + 2\beta_2 \exp(\beta_2^2 t)], \quad [22]$$

where the parameters β_1 , β_2 , and β are defined by the expressions

$$\beta_{1,2} = (\beta \pm 1)/(2t_d^{1/2}), \quad \beta = (1 + 4t_d/t_m)^{1/2}. \quad [23]$$

Equation [22] is equivalent to Eq. [5.7] in Ref. (14). The numbers β_1 and β_2 are ≥ 0 ; this gives the possibility to apply again Eq. [12]. Thus, Eq. [22] acquires the form

$$\frac{\Gamma_p}{\Gamma_{p0}} = \frac{\sigma_p}{\sigma_{p0}} = \frac{\beta - 1}{\beta} \exp\left(-\frac{\beta - 1}{2} \frac{t}{t_d}\right) + \frac{2}{\pi} \int_0^\infty \frac{\exp[-(t/t_m + t\tau^2/t_d)]}{(\tau^2 + t_d/t_m)^2 + \tau^2} \tau^2 d\tau. \quad [24]$$

3.2. Asymptotic Expressions

The short-time asymptotic expansion of Eq. [24], for $t \rightarrow 0$, reads

$$\begin{aligned} \frac{\Gamma_p}{\Gamma_{p0}} = \frac{\sigma_p}{\sigma_{p0}} = & 1 - \frac{2}{\pi^{1/2}} \left(\frac{t}{t_d}\right)^{1/2} + \frac{t}{t_d} - \frac{2(2t_m + t_d)}{3\pi^{1/2}t_m} \left(\frac{t}{t_d}\right)^{3/2} \\ & + \frac{t_m + t_d}{2t_m} \left(\frac{t}{t_d}\right)^2 - \frac{8t_m^2 + 12t_mt_d - t_d^2}{15\pi^{1/2}t_m^2} \left(\frac{t}{t_d}\right)^{5/2} \\ & + \dots, \end{aligned} \quad [25]$$

which is valid for $t \ll t_d$. Equation [25] implies that the time-limiting factor at short times is the diffusion of surfactant monomers. The first three terms in the right-hand side of Eq. [25] are the same for surfactant concentrations below the CMC and above the CMC (no adsorption barrier); note that the micellar characteristic time, t_m , appears in the fourth and the higher order terms. In the limit $t_m \rightarrow \infty$, Eq. [25] reduces to the respective expansion for concentrations below the CMC.

The long-time asymptotics of Eq. [24] is

$$\frac{\Gamma_p}{\Gamma_{p0}} = \frac{\sigma_p}{\sigma_{p0}} = \frac{\beta - 1}{\beta} \exp\left(-\frac{\beta - 1}{2} \frac{t}{t_d}\right) + \dots \quad (t \rightarrow \infty), \quad [26]$$

where higher order terms are neglected; β is defined by Eq. [23]. Hence, in contrast with the short-time limit, the long-time asymptotics is strongly affected by the presence of surfactant micelles: Eq. [26] predicts an exponential decay of the perturbation, instead of the slower square root decay [$\Gamma_p/\Gamma_{p0} \propto (t_d/t)^{1/2}$] for concentrations below the CMC. Equation [26] shows that above the CMC the characteristic decay time is $\tau = 2t_d/(\beta - 1)$. One sees that τ depends on both t_m and t_d ; that is, the relaxation is affected by both the micelles and the diffusion of monomers.

For $t_d \gg t_m$, i.e., for diffusion of monomers much slower than their supply by the micelles, Eq. [26] reduces to

$$\frac{\Gamma_p}{\Gamma_{p0}} = \frac{\sigma_p}{\sigma_{p0}} \approx \exp\left(-\frac{t}{t_d^{1/2}t_m^{1/2}}\right) \quad (t \rightarrow \infty, t_d \gg t_m). \quad [27]$$

In Ref. (14) an incorrect form of Eq. [27], viz. $\sigma_p/\sigma_{p0} \approx \exp(-t/t_m)$, was given. The correct form of Eq. [27] can be deduced from the steady-state analysis by Johner and Joanny (30). In addition, Eq. [27] has been obtained by Joos (4) using the concept for the diffusion penetration depth. Note, however, that Eq. [26] is more general than Eq. [27], and as demonstrated below, Eq. [26] should be preferably used when processing experimental data.

3.3. Numerical Predictions and Comparison with Experiment

Figure 2 shows theoretical curves for the relaxation of the perturbation in the surface tension, $\sigma_p(t)$, and the adsorption, $\Gamma_p(t)$, calculated by means of the general expression, Eq. [24]. The

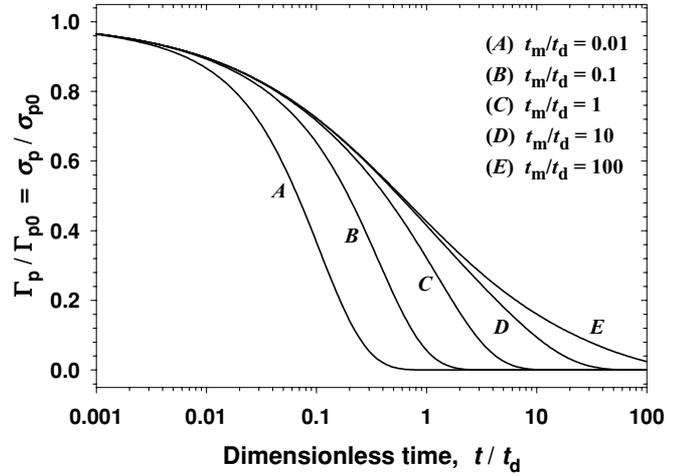


FIG. 2. Micellization-diffusion control: Relaxation of perturbations in the surfactant adsorption, $\Gamma_p(t)$, and surface tension, $\sigma_p(t)$, calculated by means of Eq. [24]; each curve corresponds to a fixed value of the ratio t_m/t_d .

different curves correspond to different values of the ratio t_m/t_d . With the increase of t_m/t_d , the rate of supply of monomers by the surfactant micelles becomes slower and slower, which decelerates the surface tension relaxation. For example, in view of Eq. [18], the decrease of micelle concentration leads to increasing of the ratio t_m/t_d . At small dimensionless times, t/t_d , all curves merge into one, which is described by the short-time asymptotics, Eq. [25].

It turns out that Eq. [26], which has been derived as long-time asymptotics, quite accurately describes the whole relaxation curves A, B, and C in Fig. 2 (for $0.001 \leq t/t_d \leq 100$). In other words, if $t_m/t_d \leq 1$, the relatively simple Eq. [26] can be used to quantify the whole relaxation process. Likewise, Eq. [27], which is a special case of Eq. [26], accurately describes the whole relaxation process if $t_m/t_d \leq 0.1$. On the other hand, for $t_m/t_d > 1$ one has to use the general integral formula, Eq. [24], which is applicable for all values of the ratio t_m/t_d .

The first three columns of Table 2 show data by Joos for micellar solutions of the nonionic surfactant Triton X-100 [octyl-phenol-ether-(EO)₁₀]; see Table 10.2 in Ref. (4). More

TABLE 2
Diffusion and Micellar Relaxation Times for Solutions
of Triton X-100

$(C_s - \text{CMC})/\text{CMC}$	t_d (s), Ref. (4)	t_m (s), Ref. (4)	t_m (s), Eq. [28]
0.5	7.00×10^{-1}	1.00	4.56×10^{-1}
1	3.82×10^{-1}	7.91×10^{-1}	3.24×10^{-1}
4	1.23×10^{-1}	1.13×10^{-1}	5.77×10^{-2}
9	3.52×10^{-2}	3.52×10^{-2}	1.76×10^{-2}
14	1.43×10^{-2}	3.14×10^{-2}	1.27×10^{-2}
19	1.46×10^{-2}	2.87×10^{-2}	1.19×10^{-2}
29	1.42×10^{-2}	1.42×10^{-2}	7.10×10^{-3}
39	1.20×10^{-2}	1.20×10^{-2}	6.00×10^{-3}
49	9.71×10^{-3}	9.71×10^{-3}	4.86×10^{-3}

precisely, the experiment gives t_d and the characteristic decay time τ . In view of Eq. [27], Joos has calculated t_m using the expression $t_m = \tau^2/t_d$ (the third column of Table 2). However, the comparison of the second and third columns in Table 2 show that the condition $t_d \gg t_m$ is not fulfilled, and consequently, Eq. [27] is not applicable in the considered case.

To determine more accurately the values of t_m for Triton X-100, we proceed in the following way. First, we recover the experimental values of the characteristic decay time, $\tau = (t_d t_m)^{1/2}$, using the data in the second and third columns of Table 2. Next, we utilize the more precise asymptotics, Eq. [26], which gives $\tau = 2t_d/(\beta - 1)$, and consequently

$$t_m = \frac{4t_d}{(2t_d/\tau + 1)^2 - 1}. \quad [28]$$

The latter equation was used to recalculate the micellar time t_m (the last column in Table 2); the respective values are about 2 times smaller than those computed in Ref. (4): compare the last two columns in Table 2.

Finally, we plot t_m^{-1} , computed from the last column of Table 2, vs $(C_s - \text{CMC})/\text{CMC}$; see Fig. 3. It is seen that the data points comply well with a straight line (correlation coefficient 0.992) in accordance with the equation of Kresheck *et al.* (15), Eq. [18]. From the slope of the linear regression in Fig. 3 we determine the kinetic parameter for Triton X-100 to be $k_0 = 4.2 \pm 0.1 \text{ s}^{-1}$; see Eq. [18].

3.4. Discussion

Aniansson and co-workers (26–28) found the following expressions for the characteristic times of the fast and slow micellar

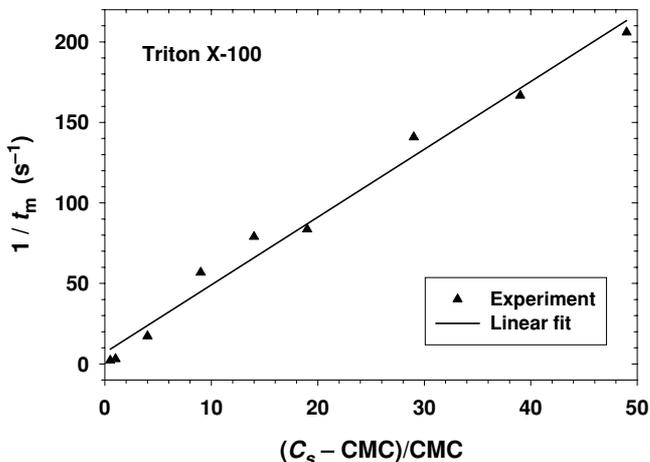


FIG. 3. Plot of the inverse micellar relaxation time, t_m^{-1} (the last column in Table 2), vs the dimensionless concentration of surfactant in micellar form, $(C_s - \text{CMC})/\text{CMC}$. The points represent experimental data for aqueous solutions of Triton X-100; the straight line is drawn in accordance with Eq. [18].

relaxation processes,

$$\tau_1^{-1} = \frac{k^-}{\tilde{\sigma}^2} + \frac{k^-}{n_a} \left(\frac{C_s - \text{CMC}}{\text{CMC}} \right), \quad [29]$$

$$\tau_2^{-1} = \frac{n_a^2 R^{-1}}{\text{CMC}} \left(1 + \frac{(C_s - \text{CMC}) \tilde{\sigma}^2}{\text{CMC} n_a} \right)^{-1}, \quad [30]$$

where k^- is the stepwise micelle dissociation rate constant; n_a is the most probable micelle aggregation number; $\tilde{\sigma}$ is the half-width of the micellar size distribution; R is the resistance to “flow” through the region of the least probable micellar aggregates. Note that τ_1 and τ_2 depend in a rather different way on $C_s - \text{CMC}$.

Dushkin *et al.* (14) found that one can *approximately* identify $t_m \approx \tau_1$ or $t_m \approx \tau_2$ depending on whether the fast or the slow demicellization process dominates the supply of monomers from the micelles. In our case, Fig. 3 shows that t_m^{-1} increases linearly with $C_s - \text{CMC}$, just as τ_1^{-1} increases in accordance with Eq. [29]. Consequently, in our case one could identify t_m with τ_1 , rather than with τ_2 . In other words, the supply of surfactant monomers by the micelles in the considered process of surface tension relaxation seems to be dominated by the fast demicellization process.

The above conclusion is supported also by the experimental values of the slow process relaxation time, $\tau_2 = 3.5\text{--}4 \text{ s}$ for Triton X-100, reported by Patist *et al.* (32, 33). Since the values of t_m in Table 2, determined by means of Eq. [28], are markedly smaller than 4 s, then it is more likely that $t_m \approx \tau_1$. Note that the nonionics, like Triton X-100, exhibit a much longer micelle relaxation in comparison with the ionic surfactants, such as sodium dodecyl sulfate, SDS (32, 33).

If really $t_m \approx \tau_1$, then in view of Eq. [29] from the *slope* of the line in Fig. 3 one determines the demicellization rate constant of Triton X-100 to be $k^- = 584 \pm 14 \text{ s}^{-1}$. For the micelle aggregation number of Triton X-100 we have used the value $n_a = 139$ reported in Ref. (34). The considerable experimental error of the *intercept* of the linear regression in Fig. 3 does not allow one to determine a reliable value of $\tilde{\sigma}$ using Eq. [29].

4. SUMMARY AND CONCLUSIONS

This article is devoted to relaxation processes of surfactant adsorption and surface tension, which are characterized by two specific relaxation times. We are dealing with fluid interfaces and small initial deviations from equilibrium.

For surfactant concentrations below the CMC we consider adsorption under mixed barrier-diffusion control, characterized by the adsorption and diffusion relaxation times. General analytical expressions are derived for the relaxation of surfactant adsorption, surface tension, and subsurface concentration; see Eqs. [13] and [14]. The numerical computations show that the subsurface concentration is more sensitive to the kinetic barrier than the adsorption and the surface tension; cf. Figs. 1a and 1b.

Asymptotic expansions for the short- and long-time limit are derived; see Eqs. [15] and [16]. The results imply that the short-time asymptotics is controlled by the adsorption barrier, whereas the long-time asymptotics is always dominated by the diffusion.

For surfactant concentrations above the CMC we consider adsorption under mixed micellization-diffusion control, characterized by the micellar and diffusion relaxation times. Since we are dealing with small perturbations, we apply the pseudo-first order reaction approximation; see Eq. [17]. Again, a general analytical expression is derived for the relaxation of surfactant adsorption and surface tension; see Eq. [24]. The numerical computations (Fig. 2) visualize the speeding up of the surface tension relaxation, owing to the supply of surfactant monomers by the micelles. The derived short- and long-time asymptotic expressions, Eqs. [25] and [26], show that, at the short times, the relaxation is completely controlled by the diffusion, whereas the long-time asymptotics is affected by both demicellization and diffusion. In particular, the effect of micelles is manifested as an exponential (rather than square-root) decay of the perturbation. The derived asymptotic expression, Eq. [26], is applied to process available experimental data for the nonionic surfactant Triton X-100 and to determine the respective demicellization rate constant; see Table 2 and Fig. 3.

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