

Adsorption Kinetics of Ionic Surfactants with Detailed Account for the Electrostatic Interactions

I. No Added Electrolyte

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The problem of diffusion-controlled adsorption from a non-micellar solution of an ionic surfactant in the absence of added electrolyte is solved analytically for the case of small deviations from equilibrium. For that purpose the electro-diffusion equations of the transport of surfactant ions and counterions are combined with the Poisson–Boltzmann equation for the electrical field. The resulting set of equations is linearized and Laplace transform is applied. Analytical expression for the Laplace image of the adsorption is obtained in terms of elementary functions. Simple formulae for the short-time and long-time asymptotics of adsorption and surface tension relaxation are derived. To illustrate the effect of the electrostatic interactions we calculated the theoretical dependence of the characteristic relaxation time on the bulk surfactant concentration and surface potential for aqueous surfactant solutions in contact with various non-aqueous phases (air, heptane, decane, petroleum ether) and two surfactants: SDS and DTAB. The general trend is that the electrostatic effects decelerate the process of adsorption, as it could be expected. The derived exact analytical expressions quantifying these effects can be directly applied for the interpretation of experimental data for the kinetics of ionic surfactant adsorption. The reliability of our approach is verified through a comparison with other available theories. © 1997 Academic Press

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1. INTRODUCTION

In dynamic processes like formation of foams and emulsions the interfaces are subjected to disturbances, most frequently to expansion. Consequently, in such a non-equilibrium system diffusion of surfactant toward the interfaces occurs. The surfactant transport is driven by the interfacial

perturbation: the larger the deviation from equilibrium adsorption, the larger the diffusion flux tending to eliminate the perturbation.

While the adsorption kinetics from non-ionic surfactant solutions is comprehensively studied (1–10), the respective theory of adsorption from ionic surfactant solutions is somewhat behind. Indeed, there are theoretical studies describing the equilibrium state, i.e., the equation of state of the ionic surfactant adsorption monolayer (11–14). However, the theoretical interpretation of data for adsorption kinetics of ionic surfactants (15–22) meets some difficulties. The latter originate from the non-linearity of the set of equations describing the electro-diffusion process. Three types of approaches to this problem can be found in the literature: (i) numerical methods (23, 24), (ii) approximate analytical expression derived by using an assumption for *quasi-equilibrium regime* of surfactant adsorption (23, 25–28), and (iii) exact asymptotic expressions for the case of *small deviations* from equilibrium. The third is the approach we follow in the present study.

The characteristic extent of the electrical double layer is determined by the Debye length, κ^{-1} (see Eq. 9 below). Dukhin *et al.* (25–28) presented a quasi-equilibrium model of the ionic surfactant adsorption. They assumed that the characteristic diffusion time, t_r , is much greater than the time of formation of the electrical double layer, $t_{dl} = 1/(\kappa^2 D)$, as defined by Wagner (29), with D being the diffusivity of the surfactant ion. Further, they simplified their task by separating the diffusion from the electrical problem depending on the distance x from the interface: for $x > \kappa^{-1}$, common diffusion in electroneutral solution; for $x < \kappa^{-1}$, kinetic barrier against surfactant adsorption due to the surface charge. In other words, these authors reduce the electro-diffusion problem to a mixed barrier-diffusion controlled problem. Such a simplification is correct when the ionic

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strength of solution is high enough in order to have small κ^{-1} , i.e., the electrical double layer is thin enough to be modeled as a kinetic barrier. The concept for quasi-equilibrium electrical double layer (EDL) is also used by Borwankar and Wasan (14, 23).

The requirement for quasi-equilibrium EDL restricts the applicability of these models to the long times and to the cases when a large amount of indifferent electrolyte is present. When the diffusion time has comparable magnitude with the time of formation of the electrical double layer, the quasi-equilibrium model is not applicable. Lucassen *et al.* (30) and Joos *et al.* (31) established that mixtures of anionic and cationic surfactants diffuse as electroneutral combination in the case of small periodic fluctuations of the surface area; consequently, this process is governed by the simple diffusion equation. The electro-diffusion problem was solved by Bonfillon *et al.* (32) for the case of small periodic surface corrugations related to the longitudinal wave method for measuring of viscoelasticity of surfactant monolayers.

The assumption for quasi-equilibrium EDL has been avoided by McLeod and Radke (24), who consider the complete electro-diffusion problem thus for a first time elaborating a rigorous theoretical model for diffusive transport of ionic surfactants to an adsorbing interface. The problem is solved numerically, thus their approach is time consuming. Consequently, it does not allow quickly and simply to draw physical conclusions about the role of the various factors involved in the adsorption process. They also assume no specific adsorption of co- and counterions, i.e. absence of Stern layer that is not much probable especially in the case of presence of background electrolyte.

Our aim in the present study is to obtain an exact analytical solution of the problem for the adsorption kinetics of ionic surfactants, valid for any ratio between the characteristic diffusion relaxation time, t_r , and the time of formation of the electrical double layer t_{dl} . In this aspect our approach is more general than the quasi-equilibrium model (14, 23, 25–28). To be able to solve analytically this more complicated problem, *small deviation* from equilibrium is assumed. Similar assumption for small deviations from equilibrium is used by Sutherland (33) to describe adsorption of *nonionic* surfactants. Another aim of our theory is to account for the contribution of the Stern layer. This effect is expected to be important in the case of higher ionic strength of the solution.

As a first step, the case of absence of background electrolyte is considered. The theory provides explicit analytical expressions for the relaxation of surface tension, adsorption, etc., with time, which are applicable to the interpretation of experimental data. The study is further extended to surfactant solutions containing added electrolyte (34).

2. PHYSICAL BACKGROUND

The process of adsorption of an ionic surfactant is accompanied with a continuous growing of the surface charge den-

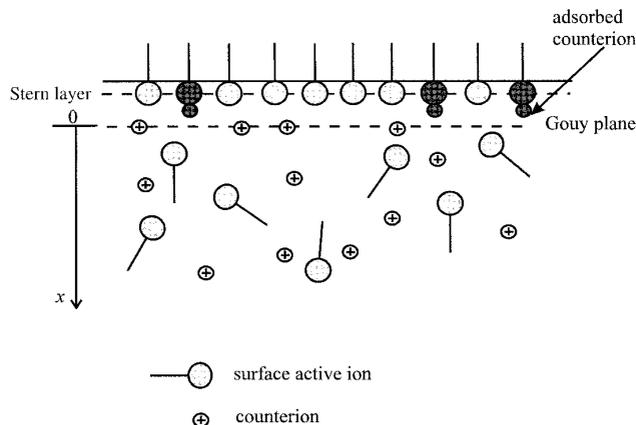


FIG. 1. Sketch of an anionic surfactant adsorption monolayer.

sity and the surface potential with time. In its own turn, the presence of surface electrical potential leads to the formation of electrical double layer inside the solution. The charged surface repels the new-coming surfactant molecules (see Fig. 1), which results in a deceleration of the adsorption process.

Let us consider an aqueous solution of symmetrical ($z:z$) ionic surfactant in the absence of any additional indifferent electrolyte. When the interface is renewed (or disturbed) the equilibrium between the bulk and the interface is destroyed. The transport of the surface active ions, and their counterions, is strongly affected by the electrical field due to the non-uniform ionic distribution in the EDL.

For the description of the interfacial zone we follow the approach of Borwankar and Wasan (14). The dividing surface is chosen to be the Gouy plane (see Fig. 1) which marks the beginning of the diffuse double layer.

The transport of the surface active ions with charge z and diffusion coefficient D under the influence of an electrical potential ψ is described by

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial x} \left(\frac{\partial c}{\partial x} + \frac{zc}{k_B T} \frac{\partial \psi}{\partial x} \right). \quad [1a]$$

Likewise, the transport of the *counterions* with charge z_c and diffusion coefficient D_c under the influence of the electrical potential ψ is described by

$$\frac{\partial c_c}{\partial t} = D_c \frac{\partial}{\partial x} \left(\frac{\partial c_c}{\partial x} + \frac{z_c c_c}{k_B T} \frac{\partial \psi}{\partial x} \right). \quad [1b]$$

Here c and c_c are the bulk concentrations of ions and counterions that depend on the time t and the distance from the interface, x , k_B is the Boltzmann constant, and T is absolute temperature. The last terms in Eqs. [1a, b], the so called “electromigration” terms, account for the effect of the elec-

trical field. The electrical potential is related to the ionic distribution through the Poisson equation,

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi}{\epsilon} [zc + z_c c_c], \quad [2]$$

where ϵ is dielectric permittivity.

The *initial conditions* (for $t = 0$) are the following:

$$c(x, 0) = \begin{cases} c^0 & \text{at } x = 0 \\ c^e & \text{at } x \neq 0 \end{cases}, \quad [3a]$$

$$c_c(x, 0) = \begin{cases} c_c^0 & \text{at } x = 0 \\ c_c^e & \text{at } x \neq 0 \end{cases},$$

where c^0 and c_c^0 are the initial concentrations of ions and counterions in the subsurface layer of the solution; they are deviated from their equilibrium values because of an initial interfacial disturbance. c^e and c_c^e are equilibrium concentration distributions of ions and counterions (see next section). Similar initial condition holds for the electrical potential:

$$\psi(x, 0) = \begin{cases} \psi^0 & \text{at } x = 0 \\ \psi^e & \text{at } x \neq 0 \end{cases}. \quad [3b]$$

Here ψ^0 is the initial value of the potential at the disturbed interface corresponding to the initial adsorption; ψ^e is the equilibrium potential distribution.

The *boundary conditions* are the following.

1. The electrical potential is zero and bulk concentrations of the solutes are uniform far from the interface:

$$\psi(\infty, t) = 0, \quad c(\infty, t) = c_c(\infty, t) = c_\infty.$$

2. The interfacial mass balances, relating the surfactant and counterion adsorptions to their fluxes from the bulk, read

$$\frac{d\Gamma}{dt} = D \left(\frac{\partial c}{\partial x} + \frac{zc}{k_B T} \frac{\partial \psi}{\partial x} \right) \text{ at } x = 0, \quad [4a]$$

$$\frac{d\Gamma_c}{dt} = D_c \left(\frac{\partial c_c}{\partial x} + \frac{z_c c_c}{k_B T} \frac{\partial \psi}{\partial x} \right) \text{ at } x = 0. \quad [4b]$$

3. The electroneutrality condition for the solution as a whole yields

$$\int_0^\infty [zc + z_c c_c] dx + z\Gamma + z_c \Gamma_c = 0. \quad [5]$$

Since the surfactant is supposed to be a symmetrical electrolyte, one has that $z_c = -z$.

In addition, the adsorptions of surfactant ions and counterions are related as follows:

$$\Gamma_c = (1 - \alpha)\Gamma. \quad [6]$$

Here α is the apparent degree of dissociation (ionization) of the adsorbed surfactant molecules that represents the portion of the adsorbed surfactant molecules, whose counterions belong to the diffuse part of the electrical double layer (35, 36). In this way, by means of α , we take into account the formation of the Stern layer, i.e. the fact that the counterions adsorb at the interface and ‘‘neutralize’’ the surfactant ions thus reducing the total surface charge. On the other hand, $(1 - \alpha)$ represents the portion of the adsorbed counterions.

3. EQUILIBRIUM STATE

Before investigating the kinetic problem, let us first briefly discuss the description of the equilibrium state. It should be noted that even at equilibrium the distributions of the different ions are non-uniform and depend on the distance to the surface in accordance with the Boltzmann equation:

$$c^e = c_\infty \exp(-\phi^e), \quad c_c^e = c_\infty \exp(+\phi^e), \quad [7]$$

where $\phi^e \equiv (z/k_B T)\psi^e$. The dimensionless potential, ϕ^e , thus defined is always positive. In fact, Eqs. [7] are solutions of Eqs. [1a, b] for the equilibrium state (when the time derivatives of the concentration at the left hand side of Eqs. [1a, b] disappear).

The non-uniformity of the concentration distributions of the ionic species become even more stronger when the system is disturbed. That is why the assumption that one can apply a *local* electroneutrality condition (31), $zc + z_c c_c = 0$ for all distances $0 < x < \infty$, instead of Eq. [5], is an assumption of restricted applicability. Correspondingly, the idea following from this assumption, that by summing up Eqs. [1a] and [1b] the non-linear ‘‘electromigration’’ terms cancel each other, thus yielding the common diffusion equation, should not be generally used. The latter approach is applicable only in the case, when the characteristic length of the EDL, κ^{-1} , is small compared to the characteristic diffusion length, Γ/c_∞ . The latter represents the characteristic length over which changes in the surfactant concentration occur due to the diffusion–adsorption process. Such a situation is realized when large amount of salt is added, but this is not the system of consideration here.

After substitution of Eq. [7] in Eq. [2] one obtains the Poisson–Boltzmann equation for the equilibrium potential

$$\frac{d^2 \phi^e}{dx^2} = \kappa^2 \sinh(\phi^e). \quad [8]$$

where κ denotes the inverse Debye screening length

$$\kappa^2 \equiv \frac{8\pi z^2}{\epsilon k_B T} c_\infty. \quad [9]$$

Let the surface potential be ϕ_s^e . The solution of Eq. [8], for the equilibrium potential distribution is (37, 38)

$$\tanh\left(\frac{\phi^e}{4}\right) = \tanh\left(\frac{\phi_s^e}{4}\right) \exp(-\kappa x). \quad [10]$$

A useful relation between the surface potential and the equilibrium ionic adsorption Γ can be derived using the electroneutrality condition, Eq. [5]. Substituting Eqs. [7] and [8] into Eq. [5] and applying Eq. [6] one obtains the Graham formula,

$$\Gamma^e = \frac{4c_\infty}{\alpha\kappa} \sinh\left(\frac{\phi_s^e}{2}\right). \quad [11]$$

Thus, if the adsorption isotherm $\Gamma(\phi_s^e, c_\infty)$ is combined with Eq. [11], it allows the calculation of the values of the adsorption, Γ^e , and the surface potential, ϕ_s^e , at a given surfactant bulk concentration, c_∞ .

4. ADSORPTION RELAXATION FOR SMALL PERTURBATIONS

4.1. Linearization of the Problem

The general problem described in Section 2 is difficult to be solved analytically because of the non-linearity of the set of the electro-diffusion equations. To obtain analytical solution we linearize the problem for the case of small deviations from equilibrium. That is, we assume small deviations of all quantities from their equilibrium values:

$$\begin{aligned} c &= c^e + c^1, & c_c &= c_c^e + c_c^1, \\ \psi &= \psi^e + \psi^1, & \Gamma &= \Gamma^e + \Gamma^1 \end{aligned} \quad [12]$$

Further we introduce the following dimensionless variables:

$$\begin{aligned} C &= c/c_\infty, & C_c &= c_c/c_\infty, \\ \gamma &= \frac{\alpha\kappa}{2c_\infty} \Gamma, & \phi &= \frac{z}{k_B T} \psi, \\ \tau &= D\kappa^2 t, & y &= \kappa x, & k &= D_c/D. \end{aligned} \quad [13]$$

It is natural to choose c_∞ to scale both ion and counterion concentrations. To scale the distance x the Debye length κ^{-1} is used. As already mentioned, two characteristic length

scales can be distinguished: the Debye length, which gauges the EDL, and the diffusion thickness Γ/c_∞ , characterizing the width of diffusion layer in a vicinity of the interface. Since we are interested to examine the electrostatic effects on the diffusion, we choose κ^{-1} to scale the distance, and consequently, it appears in the factor scaling the time.

By means of Eqs. [12] and [13] we linearize the system of Eqs. [1a, b] and [2], and then we apply Laplace transform to derive

$$s\tilde{C} = \frac{d}{dy} \left(\frac{d\tilde{C}}{dy} + \tilde{C} \frac{d\phi^e}{dy} + C^e \frac{d\tilde{\phi}}{dy} \right), \quad [14a]$$

$$s\tilde{C}_c = k \frac{d}{dy} \left(\frac{d\tilde{C}_c}{dy} - \tilde{C}_c \frac{d\phi^e}{dy} - C_c^e \frac{d\tilde{\phi}}{dy} \right), \quad [14b]$$

$$\frac{d^2\tilde{\phi}}{dy^2} = \frac{1}{2} (\tilde{C}_c - \tilde{C}), \quad [14c]$$

where the symbol “ \sim ” denotes the Laplace image of the respective function. The system of equations thus obtained is difficult to solve analytically because C^e , C_c^e , and ϕ^e depend on the distance to the surface, y , i.e., we deal with differential equations of *variable* coefficients. Nevertheless, it is possible to overcome the difficulties as demonstrated below.

4.2. Fluxes of Surfactant Ions and Counterions

Let us introduce Laplace images of the dimensionless fluxes of surfactant ions and counterions,

$$\begin{aligned} J &= \frac{d\tilde{C}}{dy} + \tilde{C} \frac{d\phi^e}{dy} + C^e \frac{d\tilde{\phi}}{dy}, \\ J_c &= \frac{d\tilde{C}_c}{dy} - \tilde{C}_c \frac{d\phi^e}{dy} - C_c^e \frac{d\tilde{\phi}}{dy}, \end{aligned} \quad [15]$$

which appear in the right-hand sides of Eqs. [14a] and [14b]. Next, we combine the integrated Eq. [8] with Eqs. [7] and [15] to derive

$$\exp(\phi^e) J = \frac{d}{dy} [\exp(\phi^e) \tilde{C} + \tilde{\phi}], \quad [16a]$$

$$\exp(-\phi^e) J_c = \frac{d}{dy} [\exp(-\phi^e) \tilde{C}_c - \tilde{\phi}]. \quad [16b]$$

Substituting Eq. [15] into Eq. [14a, b], we get

$$s\tilde{C} = \frac{dJ}{dy}, \quad s\tilde{C}_c = k \frac{dJ_c}{dy}, \quad [17a, b]$$

and Eq. [14c] after integration takes the form

$$s \frac{d\tilde{\phi}}{dy} = \frac{1}{2} (kJ_c - J). \quad [17c]$$

Let us multiply Eq. [17a] by $\exp(\phi^e)$ and Eq. [17b] by $\exp(-\phi^e)$, and let us differentiate the obtained expressions. With the help of Eqs. [16a, b] and Eq. [17c] we obtain

$$\begin{aligned} \frac{d}{dy} \left[\exp(\phi^e) \frac{dJ}{dy} \right] &= s \exp(\phi^e) J \\ &\quad - \frac{1}{2} (kJ_c - J), \quad [18a] \end{aligned}$$

$$\begin{aligned} \frac{d}{dy} \left[\exp(-\phi^e) \frac{dJ_c}{dy} \right] &= s \exp(-\phi^e) J_c \\ &\quad + \frac{1}{2} (kJ_c - J). \quad [18b] \end{aligned}$$

4.3. Reduction of the Problem to a Fourth-Order Differential Equation

In order to solve Eqs. [18a, b] let us introduce a new variable ξ

$$\xi = 1 - \exp(-\phi^e), \quad [19]$$

so that $\xi \in [0, \xi_s] \subset [0, 1]$, ξ_s denotes the value of ξ at the surface of solution. In this manner, Eqs. [18a, b] are transformed to read

$$M[J] - sJ + \frac{k}{2} (1 - \xi)J_c = 0, \quad [20a]$$

$$M[(1 - \xi)J_c] + \frac{1}{2k} J - \frac{s}{k} (1 - \xi)J_c = 0, \quad [20b]$$

where M is a second-order differential operator defined as follows:

$$M \equiv \xi^2 (1 - \xi) \frac{d^2}{d\xi^2} + \xi \left(1 - \frac{\xi}{2} \right) \frac{d}{d\xi} - \frac{1}{2} (1 - \xi). \quad [21]$$

Next we express $(1 - \xi)J_c$ from Eq. [20a] and substitute it into Eq. [20b]; as a result we get an operator equation with *constant* coefficients:

$$M^2[J] - s \left(1 + \frac{1}{k} \right) M[J] - \left(\frac{1}{4} - \frac{s^2}{k} \right) J = 0. \quad [22]$$

Equation [22] is a fourth-order linear differential equation

whose solution can be expressed as a linear combination of four characteristic functions, f_i ($i = 1, \dots, 4$), which satisfy the characteristic equation

$$M[f_i] = \lambda f_i. \quad [23]$$

The values of the characteristic parameter λ can be determined by substituting Eq. [23] into Eq. [22]:

$$\lambda_{1,2} = \frac{1}{2} \left[s \left(1 + \frac{1}{k} \right) \pm \sqrt{1 + s^2 \left(1 - \frac{1}{k} \right)^2} \right]. \quad [24]$$

We note in advance that two of the characteristic functions, f_i , exhibit singularity at the boundary point $\xi = 0$, and must be excluded from the linear combination in order to get a physically meaningful solution. Therefore, the solution of Eq. [22] can be expressed as a combination of the other two characteristic functions, f_1 and f_2 :

$$J = A_1 f_1 + A_2 f_2, \quad (M[f_i] = \lambda_i f_i, \quad i = 1, 2), \quad [25a]$$

where A_1 and A_2 are coefficients independent of ξ . Then from Eq. [20a] we derive

$$(1 - \xi)J_c = -\frac{2}{k} [(\lambda_1 - s)f_1 A_1 + (\lambda_2 - s)f_2 A_2]. \quad [25b]$$

Thus the problem reduces to the determination of the fundamental set of functions, f_1 and f_2 .

4.4. Determination of the Characteristic Functions

Let us introduce the notation

$$\beta_i = \sqrt{\lambda_i + \frac{1}{2}} \quad [26]$$

and search the characteristic functions, f_1 and f_2 , in the form

$$f_i = \left(\frac{\xi}{\xi_s} \right)^{\beta_i} g_i \quad (i = 1, 2). \quad [27]$$

Here g_i are new, unknown functions. Substituting Eqs. [26] and [27] into Eq. [23] and replacing M with its explicit expression, Eq. [21], we obtain

$$\begin{aligned} \xi(1 - \xi) \frac{d^2 g_i}{d\xi^2} + \left[(2\beta_i + 1) - \left(2\beta_i + \frac{1}{2} \right) \xi \right] \frac{d g_i}{d\xi} \\ - (\beta_i - 1) \left(\beta_i + \frac{1}{2} \right) g_i = 0. \quad [28] \end{aligned}$$

$g_i(\xi_s)$ has a finite value at $\xi = 0$, i.e. in the bulk solution, cf. Eq. [19]. The solutions of Eq. [28] are the hypergeometric functions:

$$g_i = \frac{{}_2F_1\left(\beta_i - 1, \beta_i + \frac{1}{2}, 2\beta_i + 1; \xi\right)}{{}_2F_1\left(\beta_i - 1, \beta_i + \frac{1}{2}, 2\beta_i + 1; \xi_s\right)} \quad (i = 1, 2). \quad [29]$$

Fortunately, these hypergeometric functions can be expressed in terms of elementary functions (39); thus we obtain the following relatively simple expressions for the characteristic functions:

$$f_i = \frac{2 - \xi + 2\beta_i\sqrt{1 - \xi}}{2 - \xi_s + 2\beta_i\sqrt{1 - \xi_s}} \left(\frac{1 + \sqrt{1 - \xi_s}}{1 + \sqrt{1 - \xi}} \right)^{2\beta_i} \left(\frac{\xi}{\xi_s} \right)^{\beta_i}. \quad [30]$$

4.5. Laplace Image of the Adsorption

In order to find the coefficients $A_1(s)$ and $A_2(s)$ in Eqs. [25a, b] we use the boundary conditions, Eqs. [4a, b]. The boundary condition [4a] is first transformed in dimensionless form by means of Eq. [12]. After that, it is linearized, under the assumption for small deviations from equilibrium, i.e. $\gamma = \gamma^e + \gamma^1$, and further Laplace transform is applied. As a result Eq. [4a] is transformed to read

$$\frac{2s}{\alpha} \tilde{\gamma} - \frac{2}{\alpha} \Delta\gamma(0) = J \text{ at } y = 0, \quad [31]$$

where $\tilde{\gamma}$ is the Laplace image of $\gamma^1(t)$, $\Delta\gamma(0)$ is the dimensionless initial deviation of the adsorption from its equilibrium value, i.e. $\Delta\gamma(0) = \gamma^e - \gamma(0)$. A combination of Eqs. [5] and [6], followed by transformation in dimensionless form, yields

$$\int_0^\infty (C - C_c) dy + 2\gamma = 0. \quad [32]$$

Equation [32] along with Eq. [14c] leads to

$$\frac{\partial \phi^1}{\partial y} + \gamma^1 = 0 \text{ at } y = 0. \quad [33]$$

After applying Laplace transform to Eq. [33], having in mind Eq. [17c], we obtain

$$kJ_c - J + 2s\tilde{\gamma} = 0 \text{ at } y = 0. \quad [34]$$

In the case of diffusion-controlled adsorption it is accepted that at every moment the subsurface and the surface are in

local equilibrium so that the subsurface concentration is related to the surfactant adsorption by means of the equilibrium adsorption isotherm. Consequently, the adsorption depends only on the subsurface concentration c_s . For small deviations from equilibrium the adsorption isotherm can be linearized as follows

$$\Gamma^1 = \left(\frac{\partial \Gamma}{\partial c_s} \right)^e c^1 \text{ at } y = 0. \quad [35]$$

A Laplace transform of Eq. [35], followed by a substitution of Eq. [17a] into the resulting equation, yields

$$\tilde{\gamma} = \frac{a}{s} \frac{dJ}{dy}, \quad a = \frac{\alpha\kappa}{2} \left(\frac{\partial \Gamma}{\partial c_s} \right)^e. \quad [36]$$

The boundary conditions [31] and [34] take the form

$$a \frac{dJ}{dy} - \frac{\alpha}{2} J = \Delta\gamma, \quad [37a]$$

$$kJ_c - J + 2a \frac{dJ}{dy} = 0. \quad [37b]$$

Next we multiply Eq. [37a] by 2 and subtract the result from Eq. [37b]. In the obtained equation we substitute Eqs. [25a, b] and obtain expressions for the coefficients $A_1(s)$ and $A_2(s)$:

$$A_1 = - \frac{\Delta\gamma(0)(1 - \xi_s)}{(1 - \alpha)(1 - \xi_s) + 2(\lambda_1 - s)} \times \left(\frac{2B_2 + 1}{B_1 - B_2} \right), \quad [38a]$$

$$A_2 = \frac{\Delta\gamma(0)(1 - \xi_s)}{(1 - \alpha)(1 - \xi_s) + 2(\lambda_2 - s)} \left(\frac{2B_1 + 1}{B_1 - B_2} \right), \quad [38b]$$

where

$$B_i = \frac{1 - \xi_s}{(1 - \alpha)(1 - \xi_s) + 2(\lambda_i - s)} \times \left(\frac{\alpha}{2} + a\sqrt{1 - \xi_s} \frac{2\beta_i^2 - \xi_s + 2\beta_i\sqrt{1 - \xi_s}}{2 - \xi_s + 2\beta_i\sqrt{1 - \xi_s}} \right), \quad i = 1, 2.$$

Finally, combining Eq. [36] and Eq. [37a, b], we derive an exact expression for the Laplace image of the adsorption:

$$\tilde{\gamma} = - \frac{\alpha\kappa}{2} \left(\frac{\partial \Gamma}{\partial c_s} \right)^e \frac{\sqrt{1 - \xi_s}}{s} \left[\frac{2\beta_1^2 - \xi_s + 2\beta_1\sqrt{1 - \xi_s}}{2 - \xi_s + 2\beta_1\sqrt{1 - \xi_s}} A_1 + \frac{2\beta_2^2 - \xi_s + 2\beta_2\sqrt{1 - \xi_s}}{2 - \xi_s + 2\beta_2\sqrt{1 - \xi_s}} A_2 \right]. \quad [39]$$

The Laplace image thus obtained cannot be converted analytically. One possibility to find the original is the numerical approach described in Ref. (40). Another option is to make Laplace transform of the experimental data and then to compare the result with Eq. [39]. However, the latter procedure requires to collect a large amount of experimental data over a long time interval. The necessary amount of experimental data can not be accumulated in the usual experiments, e.g. with the Wilhelmy plate method, because the data at relatively long times are measured. That is the reason why the second way for interpretation of the experimental data is not easy to apply in a real situation.

On the other hand, the experimental situation motivates us to investigate the asymptotic behavior of Eq. [39] at long times, hoping to derive an analytical expression for the adsorption relaxation in this time scale. Our derivation of the long-time asymptotics is presented in the Section 6 below. In the next section we derive the short-time asymptotics stemming from Eq. [39]; the latter asymptotics can be important for the interpretation of data from fast methods of dynamic surface tension measurements.

5. SHORT-TIME ASYMPTOTICS OF THE ADSORPTION KINETICS

For short times, $t \rightarrow 0$, the Laplace parameter takes large values, $s \rightarrow \infty$. Therefore, as a small parameter we will use $1/\sqrt{s}$. Expanding Eqs. [24] for $s \rightarrow \infty$ we get

$$\lambda_1 = s + O\left(\frac{1}{s}\right), \quad \lambda_2 = \frac{s}{k} + O\left(\frac{1}{s}\right). \quad [40]$$

Combination of Eqs. [26] and [40] leads to

$$\beta_1 = \sqrt{s} + \frac{1}{4\sqrt{s}} + O\left(\frac{1}{s\sqrt{s}}\right),$$

$$\beta_2 = \sqrt{\frac{s}{k}} + \frac{1}{4} \sqrt{\frac{k}{s}} + O\left(\frac{1}{s\sqrt{s}}\right). \quad [41]$$

After the substitution of Eqs. [40] and [41] into Eq. [39] and some transformations, we derive

$$\tilde{\gamma} = \Delta\gamma(0) \left(\frac{1}{s} - \frac{\alpha}{2a} \frac{1}{s\sqrt{s}} \right). \quad [42]$$

The reverse Laplace transform of Eq. [42] yields

$$\frac{\Gamma^e - \Gamma(t)}{\Gamma^e - \Gamma(0)} = 1 - 2\sqrt{\frac{Dt}{\pi}} \left[\left(\frac{\partial\Gamma}{\partial c_s} \right)^e \right]^{-1}$$

$$= 1 - 2\sqrt{\frac{Dt}{\pi}} \left[\left(\frac{\partial\Gamma}{\partial c_\infty} \right)_{\phi_s}^e \right]^{-1} \exp(-\phi_s), \quad [43]$$

where as usual c_s is the subsurface surfactant concentration and the superscript ‘‘e’’ means that the derivative is taken at equilibrium. The Eq. [43] almost identical with the known short-time asymptotics for the adsorption of the nonionic surfactants (33, 41–44):

$$\frac{\sigma^e - \sigma(t)}{\sigma^e - \sigma(0)} = \frac{\Gamma^e - \Gamma(t)}{\Gamma^e - \Gamma(0)} = 1 - 2\sqrt{\frac{Dt}{\pi}} \left(\frac{\partial\Gamma}{\partial c_\infty} \right)^{-1}, \quad [44]$$

where σ denotes surface tension. The only difference between Eqs. [43] and [44] is that in the derivative of Γ the bulk concentration, c_∞ , is replaced by the subsurface concentration, $c_s = c_\infty \exp(-\phi_s)$. If the derivatives $(\partial\Gamma/\partial c_\infty)$ in Eqs. [43] and [44] have comparable magnitudes, one may conclude that the short-time relaxation decelerates with the increase of the surface potential, ϕ_s . It is interesting to note, that the short-time asymptotics, Eq. [43], depends on the diffusivity of the surfactant ions, D , but is independent of the diffusivity of the counterions, D_c .

6. LONG-TIME ASYMPTOTICS OF THE ADSORPTION KINETICS

Now let us expand in series Eq. [39] for long times ($t \rightarrow \infty$), i.e., for small values of the Laplace parameter, $s \rightarrow 0$. First we expand in Eq. [24]:

$$\lambda_1 = \frac{1}{2} + \frac{s}{2} \left(1 + \frac{1}{k} \right) + O(s^2),$$

$$\lambda_2 = -\frac{1}{2} + \frac{s}{2} \left(1 + \frac{1}{k} \right) + O(s^2). \quad [45]$$

Combination of Eqs. [26] and [45] leads to

$$\beta_1 = 1 + \frac{s}{4} \left(1 + \frac{1}{k} \right) + O(s^2),$$

$$\beta_2 = \sqrt{\frac{s}{2} \left(1 + \frac{1}{k} \right)} + O(s\sqrt{s}). \quad [46]$$

After that A_1 and A_2 (see Eqs. [38a, b]) are also expanded in series and together with Eq. [46] are substituted in Eq. [39], which acquires the form

$$\tilde{\gamma} = \frac{4a(1 - \xi_s)\Delta\gamma(0)}{\alpha(2 - \xi_s)\sqrt{\frac{2k}{k+1}} \left[1 + \frac{2a}{2 - \xi_s} (1 - \xi_s)^{3/2} \right]} \frac{1}{\sqrt{s}}. \quad [47]$$

Applying the reverse Laplace transform to Eq. [47] we get equation, which resembles the well known ‘‘long-time asymptotics’’ (33, 44, 45)

$$\frac{\sigma^e - \sigma(t)}{\sigma^e - \sigma(0)} = \frac{\Gamma^e - \Gamma(t)}{\Gamma^e - \Gamma(0)} = \sqrt{\frac{t_r}{\pi t}}, \quad (t/t_r \gg 1), \quad [48]$$

but t_r is the relaxation time defined as follows:

$$t_r = \frac{1}{D_*} \left[\left(\frac{\partial \Gamma}{\partial c_\infty} \right)_{\phi_s^e}^e \right]^2 \left[\frac{1}{2} + \frac{1}{2} \exp(-\phi_s^e) + a \exp\left(-\frac{3\phi_s^e}{2}\right) \right]^{-2} \quad (\text{ionic surfactant}), \quad [49]$$

and

$$\frac{1}{D_*} \equiv \frac{1}{2} \left(\frac{1}{D} + \frac{1}{D_c} \right);$$

$$a \equiv \frac{\alpha \kappa}{2} \left(\frac{\partial \Gamma}{\partial c_s} \right)^e = \frac{\alpha \kappa}{2} \left(\frac{\partial \Gamma}{\partial c_\infty} \right)_{\phi_s^e}^e \frac{1}{\exp(-\phi_s^e)}, \quad [50]$$

cf. Eq. [36]. A formal transition to electroneutral surface, $\phi_s \rightarrow 0$, $\alpha \rightarrow 0$, reduces Eq. [49] to the known expression for the relaxation time of nonionic surfactants,

$$t_r = \frac{1}{D} \left[\left(\frac{\partial \Gamma}{\partial c_\infty} \right)^e \right]^2 \quad (\text{nonionic surfactant}), \quad [51]$$

but with an effective diffusivity, D_* , instead of D , cf. Eqs. [49] and [51]. The difference between D_* and D (cf. Eq. 50) accounts for the electrolytic dissociation of the ionic surfactant.

If the derivatives $(\partial \Gamma / \partial c_\infty)$ in Eqs. [49] and [51] have comparable magnitudes, one may conclude that the long-time relaxation decelerates with the increase of the surface potential, ϕ_s^e . The numerical calculation for the given system can quantitatively reveal the effect of the electrostatic interaction (see Section 7 below). Anyway, the functional time dependence of the long-time asymptotics is the same ($\propto 1/\sqrt{t}$) for the kinetics of adsorption of ionic and nonionic surfactants under diffusion control, cf. Eq. [48]. The latter equation can be directly applied to interpret experimental data for surface tension relaxation.

7. NUMERICAL RESULTS AND DISCUSSION

In order to obtain numerical results, first of all we need an equilibrium adsorption isotherm to calculate $(\partial \Gamma / \partial c_\infty)$ and other related thermodynamic parameters. For that pur-

pose below we will use the isotherm derived by Borwankar and Wasan (14),

$$\frac{\Gamma}{\Gamma - \Gamma_\infty} \exp\left(-A \frac{\Gamma}{\Gamma_\infty}\right) = K c_\infty \exp(-\phi_s^e), \quad [52]$$

which generalizes the Langmuir adsorption isotherm for the case of ionic surfactants; here Γ_∞ is the adsorption of a saturated monolayer, A accounts for the non-ideality of the adsorption monolayer (the interactions between the adsorbed molecules), K has meaning of equilibrium constant of the process adsorption–desorption.

As demonstrated by Borwankar and Wasan (14), the combination of Eq. [52] with the Gibbs equation yields the following expression for the surface tension σ of the solution:

$$\sigma_w - \sigma = -k_B T \Gamma_\infty \left[\ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) + \frac{A}{2} \left(\frac{\Gamma}{\Gamma_\infty}\right)^2 \right] + \sqrt{\frac{8\epsilon \gamma_a c_\infty (k_B T)^3}{\pi e^2}} \left[\cosh\left(\frac{\phi_s^e}{2}\right) - 1 \right], \quad [53]$$

where σ_w is the surface tension of the pure water, γ_a is the activity coefficient used to account for the ionic interactions in the bulk of the solution.

In the derivation of Eq. [53] it is assumed, that there is no specific counterion adsorption, i.e., the apparent surface degree of ionization, α , is set equal to 1. Although in this way the effect of the *Stern layer* is disregarded, we use Eq. [53] to get numerical results illustrating the effect of the *diffuse* electrical double layer on the kinetics of adsorption. Moreover, the assumption $\alpha = 1$ is probably acceptable in the case of ionic surfactant solution in absence of added salt and especially at the low surfactant concentrations (below CMC) because of the very low counterion concentration.

In Ref. (14) experimental data for the interfacial tension of surfactant solutions have been processed by means of Eqs. [52] and [53] and the parameters Γ_∞ , A , and K of the adsorption isotherm have been determined. In our numerical calculations we used the values of Γ_∞ , A , and K thus determined for sodium dodecyl sulfate (SDS) solutions for the interfaces water/air, water/decane, water/heptane, and water/petroleum ether, as well as for the interface DTAB-solution/petroleum ether, see Table 1. Note that the interaction parameter A turns out to be zero for the water–oil interfaces.

Figures 2 and 3 represent equilibrium isotherms relative adsorption, Γ/Γ_∞ , and the dimensionless surface potential, ϕ_s^e , of SDS and DTAB solutions. The curves are calculated by means of Eqs. [11], [52], and [53] with the parameters values listed in Table 1. The differences between the curves in Figs. 2 and 3 demonstrate a pronounced effect of the

TABLE 1
Parameters of the Borwankar–Wasan Isotherm
for Various Interfaces (15)

| System | K (m ³ /mol) | Γ_{∞} (mol/m ²) | A |
|-------------------------------|----------------------------|--|------|
| DTAB in water–petroleum ether | 2.28×10^3 | 3.25×10^{-6} | 0 |
| SDS in water–petroleum ether | 8.39×10^3 | 4.25×10^{-6} | 0 |
| SDS in water–decane | 1.078×10^4 | 3.67×10^{-6} | 0 |
| SDS in water–heptane | 3.2×10^3 | 4.45×10^{-6} | 0 |
| SDS in water–air | 6.8×10^2 | 1.0×10^{-5} | 0.65 |

nature of the non-aqueous phase. In particular, the relative adsorption and the surface potential decrease with the increase of the polarity (and the dielectric constant) of the non-aqueous phase. The surface potential exhibits a maximum, which can be attributed to the fact that after the formation of a dense adsorption monolayer a further addition of ionic surfactant (which is electrolyte) rather suppresses the electrical double layer, than increases the adsorption (and the surface charge). In Fig. 2 the relative adsorption is defined as Γ/Γ_{∞} . As discussed above, $\Gamma_{\infty} = 10^{-5}$ mol/m². Hence, with $\Gamma/\Gamma_{\infty} = 0.4$ we calculate $\Gamma = 4 \times 10^{-6}$ mol/m² for the SDS adsorption, which is a reasonable value. For some model systems MacLeod and Radke (24) calculated even lower relative adsorptions (0.2), see e.g., Fig. 4 in Ref. (24).

Figure 4 shows the relaxation time, t_r , vs. the bulk surfactant concentration, c_{∞} , for the interfaces of consideration, see Table 1. A well-pronounced correlation between the behavior of the surface potential, ϕ_s^e , Fig. 3, and the relaxation time, t_r , Fig. 4, is observed: namely, the higher the surface

potential the longer the relaxation time at same bulk surfactant concentration. This correlation is visualized in Fig. 5, where t_r is plotted vs. ϕ_s^e for several given values of the bulk surfactant concentration, c_{∞} . The increase of t_r with ϕ_s^e can be attributed to the fact that the charged interface repels the surfactant ions thus decreasing the rate of their supply by diffusion. In this way the electrostatic repulsion decelerates the process of relaxation of the disturbed interface to its equilibrium state.

7.1. Comparison with Exact Numerical Solution

To verify the reliability of our model, we calculated the long-time asymptotics of the surface tension of 1 mol/m³ SDS solution by means of our theory and compared the results with those reported by MacLeod and Radke (24); see Fig. 6. One sees that the two curves completely coincide for $t \gg t_r$, where $t_r = 3.33 \times 10^{-4}$ is the characteristic relaxation time, t_r , calculated from our Eq. [49].

In their paper MacLeod and Radke (24) discuss the comparison between their exact transient adsorption model (24) and the quasi-equilibrium model (23, 25–27) and find out that the differences between them are minor. This is due to the fact that the concentration of SDS (which plays the role of an electrolyte) is rather high in their example; this leads to a very thin electric double layer. In such a case the quasi-equilibrium model is really valid. It is expected, however, that at lower SDS concentrations (this case was not discussed by MacLeod and Radke) the difference between the predictions of the aforementioned two models will be significant.

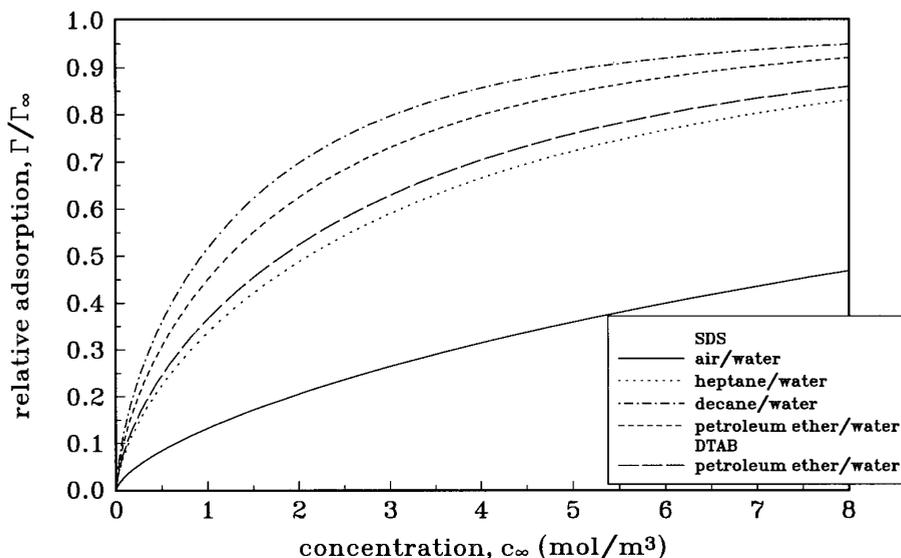


FIG. 2. Relative adsorption, Γ/Γ_{∞} , vs. bulk surfactant concentration, c_{∞} , vs. the bulk surfactant concentration, c_{∞} , for SDS and DTAB solutions at different interfaces calculated by means of Eqs. [52] and [53] and the parameter values in Table 1 (data from Borwankar and Wasan, Ref. 14).

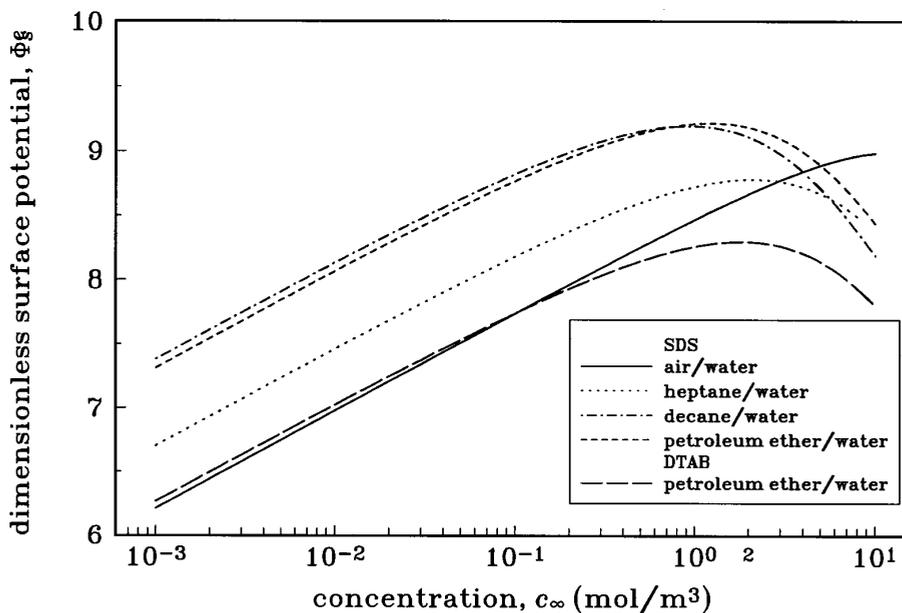


FIG. 3. Surface potential, ϕ_s^e , vs. bulk surfactant concentration, c_∞ , for the same SDS and DTAB solutions as in Fig. 2.

7.2. Comparison with Experimental Data

Obviously the most reliable test for our model would be the experiment. The characteristic relaxation time for SDS solution at air/water interface, predicted by our theory, is of the same order of magnitude as the data reported in the literature (46, 47). However, a precise comparison seems to be impossible for the time being. As discussed by MacLeod and Radke (24), currently no suitable data for dynamic

surface tension of ionic surfactants solutions exist to test their (and our) theory. Moreover, our model is suitable for small deviation from equilibrium. A technique which can be used, the dynamic Wilhelmy plate method, is reliable only for times greater than few seconds. Solutions of common ionic surfactants exhibit very fast relaxation, less than few seconds. Such is the case with SDS at air/water (47) and water/hexane (17) interfaces; myristyl-, dodecyl-, and decyl trimethyl bromides (15, 16); sodium decyl, tetradecyl, and

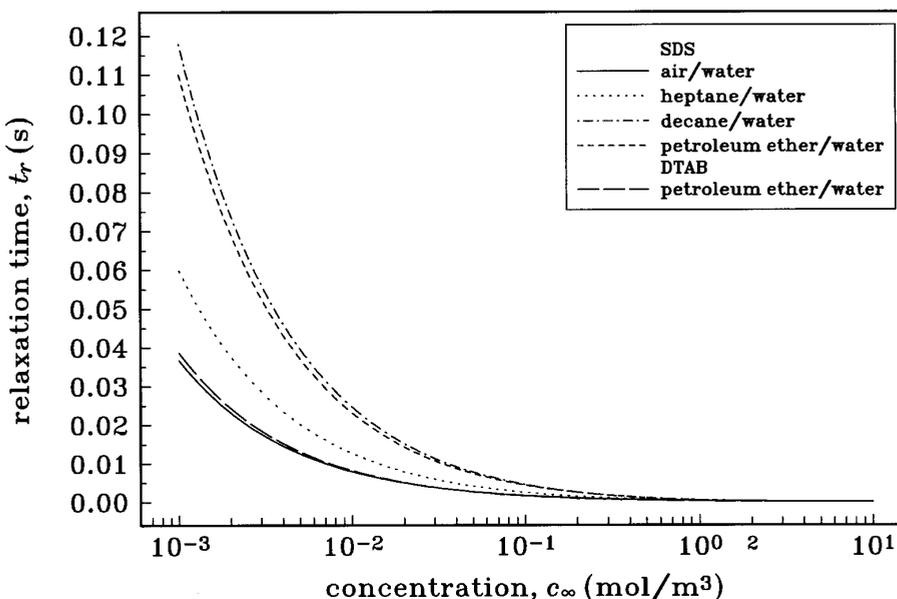


FIG. 4. Plots of the characteristic relaxation time, t_r , vs. the bulk surfactant concentration, c_∞ , for the same SDS and DTAB solutions as in Figs. 2 and 3.

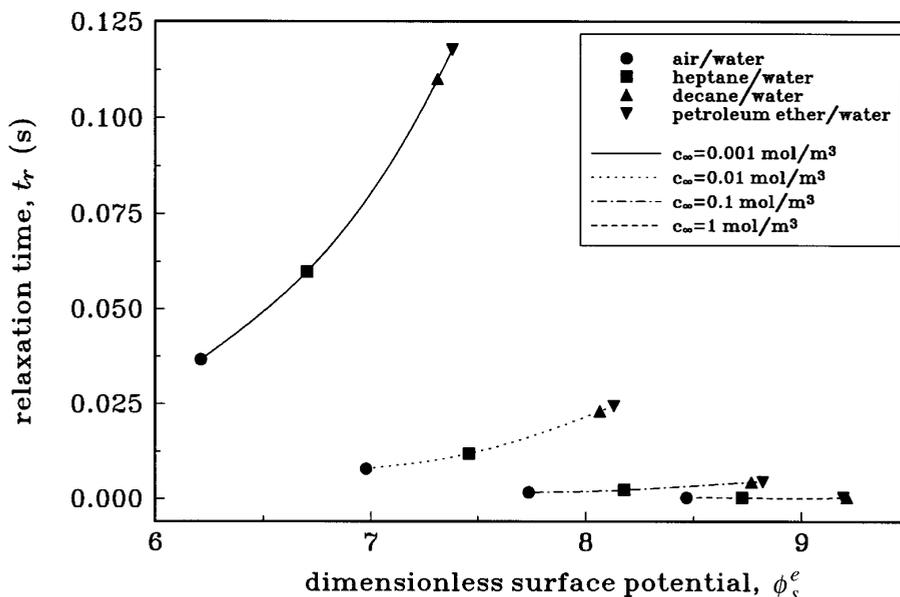


FIG. 5. Plot of the characteristic relaxation time, t_r , vs. the surface potential, ϕ_s^e , for various fixed surfactant concentrations. The symbols correspond to various interfaces denoted on the figure; the interpolating curves mark the trend of the dependencies.

hexadecyl sulfates (22), etc. Measurements with the capillary-wave method (46) also give adsorption relaxation time of order of 10^{-3} s for some ionic surfactants as SDS, octylamine hydrochloride, and dodecylamine hydrochloride. An opportunity to check the theory against the experiment is to perform measurements with more slowly adsorbing surfactants. A second opportunity is to investigate the adsorption kinetics of *ionic* surfactants by means of a “fast” experimental methods, such as the maximum bubble pressure method, and the oscillating jet. However, these methods op-

erate with large deviations from equilibrium, which requires to solve the general problem for the adsorption kinetics of *ionic* surfactants at large deviation. This work is underway.

8. CONCLUSIONS

Exact analytical solution of the electro-diffusion problem for the kinetics of adsorption of an ionic surfactant is obtained in the case of small deviations from equilibrium. For this purpose the electro-diffusion equations of the transport

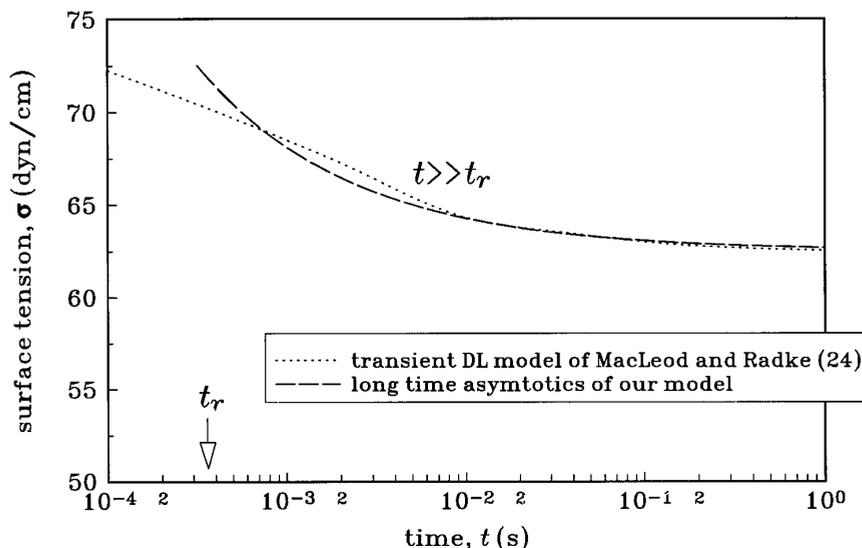


FIG. 6. Comparison between the result for the long-time asymptotics of dynamic surface tension of 1 mol/m^3 SDS solution calculated by our theory with the numerical result reported by MacLeod and Radke (24).

of surfactant ions and counterions, Eqs. [1a, b], are combined with the Poisson–Boltzmann equation for the electrical field, Eq. [2]. The resulting set of equations is linearized for small deviations from equilibrium and Laplace transform is applied. As a result, an analytical expression for the Laplace image of the adsorption is obtained in terms of elementary functions, Eq. [39]. Unfortunately, Eq. [39] cannot be converted analytically to get the explicit *time* dependence of the adsorption and surface tension. By means of series expansions from Eq. [39] we derive the short-time and long-time asymptotics of adsorption and surface tension, see Eqs. [43] and [48–50]. The obtained theoretical expression for the relaxation time, t_r , accounts for the contribution of the electrostatic interaction. On the other hand, t_r is an experimentally measurable quantity, and hence the predictions of the theory can be used for the interpretation of experimental data.

To illustrate the effect of the electrostatic interactions we calculated the dependence of t_r on the bulk surfactant concentration and the surface potential, see Figs. 4 and 5. To do that we employed the equilibrium adsorption isotherm of Borwankar and Wasan (14), which gave us the possibility to calculate the thermodynamic parameters entering the theoretical expressions for the adsorption kinetics, see Figs. 2 and 3. The thermodynamic parameters depend also on the nature of the non-aqueous phase (air, heptane, decane, petroleum ether). Calculations for two typical surfactants, an anionic one, SDS, and a cationic one, DTAB, have been carried out.

The general trend is that the electrostatic effects increase the adsorption time and decelerate the process of adsorption, as it could be expected. The contribution of the present study is the derivation of exact analytical expressions to quantify these effects.

To verify the reliability of our approach, we compared the long-time relaxation of the surface tension of 1 mol/m³ SDS, as predicted by our analytical theory, with the output of the numerical solution of MacLeod and Radke (24). As seen in Fig. 6, the two curves coincide completely at times longer than the characteristic relaxation time calculated from our theory.

Our results for the relaxation time, t_r , for SDS solutions at air–water interface, calculated from Eq. [49], are of the same order of magnitude as the values reported in the literature. However, due to the lack of suitable data on dynamic surface tension, a precise quantitative comparison of the theoretical predictions with the experiment could not be realized for the time being.

Finally, we note that in the present article we theoretically investigated an ionic surfactant solution *without* added electrolyte. In a subsequent study, Ref. (34), we extend the present analysis to the case of surfactant solutions *with* added electrolyte. This is not a trivial generalization of the present

study in so far as the transport of one more species, the electrolyte co-ions, should be theoretically described.

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