



ELSEVIER

Colloids and Surfaces

A: Physicochemical and Engineering Aspects 156 (1999) 389–411

COLLOIDS  
AND  
SURFACES

A

www.elsevier.nl/locate/colsurfa

# Adsorption kinetics of ionic surfactants with detailed account for the electrostatic interactions: effect of the added electrolyte

K.D. Danov <sup>a,\*</sup>, P.M. Vlahovska <sup>a</sup>, P.A. Kralchevsky <sup>a</sup>, G. Broze <sup>b</sup>,  
A. Mehreteab <sup>c</sup>

<sup>a</sup> *Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria*

<sup>b</sup> *Colgate–Palmolive R&D, Avenue du Parc Industriel, B-4041 Milmort (Herstal), Belgium*

<sup>c</sup> *Colgate–Palmolive Technology Center, Piscataway, NJ 08854-5596, USA*

Received 20 September 1998; received in revised form 27 November 1998; accepted 22 December 1998

---

## Abstract

We address the problem about the electro-diffusion-controlled adsorption from a submicellar solution of an ionic surfactant in the presence of a non-amphiphilic electrolyte (salt). We consider a disturbance of the surfactant adsorption layer, which is damped by the electro-diffusive transport of surfactant ions, counterions and coions. The evolution of the electric double layer with time is theoretically examined. The counterion adsorption (binding) is taken into account. Our purpose is to find the long-time asymptotic solution of the full electro-diffusion boundary problem. Assuming small perturbations the problem is linearized and a set of three differential operator equations is obtained. In the asymptotic case of long times these differential equations reduce to hypergeometric equations, whose solutions, fortunately, can be expressed in terms of elementary functions. As a result, explicit expressions for the characteristic relaxation times of the adsorptions of surfactant ions and counterions are obtained. Next we determine the characteristic relaxation time of surface tension, which is different from the adsorption relaxation time because of a specific contribution from the dynamic diffuse electric double layer. The thermodynamic parameters, entering the formula for the relaxation time, are expressed for various surfactant adsorption isotherms, those of Henry, Langmuir, Freundlich, Frumkin and van der Waals. The theory gives a quantitative interpretation of the experimental finding that the addition of salt accelerates the relaxation of the surface tension for the higher surfactant concentrations, but decelerates it for the lower surfactant concentrations. The results could be also useful for a theoretical interpretation of the processes in foams and emulsions under dynamic conditions. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Adsorption kinetics; Adsorption relaxation time; Dynamic surface tension; Ionic surfactants; Kinetics of surfactant adsorption

---

\* Corresponding author.

## 1. Introduction

This article is an extension and generalization of our previous theoretical study on the adsorption kinetics of ionic surfactants [1], to the case when a non-amphiphilic electrolyte (salt) is present in the solution. In practical applications, surfactants are often used under non-equilibrium conditions. In such a case the interfacial disturbances give rise to surfactant adsorption and diffusion, which tend to eliminate the interfacial disturbance and eventually to restore the equilibrium. Most frequently the interfacial relaxation is experimentally studied by measuring the time dependence of the (dynamic) surface tension [2–10]. Many of the works in this field deal with solutions of *nonionic* surfactants, for which the kinetic theory of adsorption has been more or less completed. On the other hand, as pointed out by Dukhin et al. [2], ‘systematic investigations of the adsorption kinetics of *ionic* surfactants do not exist’. Instead, the data for kinetics of adsorption of ionic surfactants are sometimes processed by theoretical models, which are rigorously applicable to nonionics only.

The existence of an electric double layer essentially influences the equilibrium [11–20] and dynamic [21–29] interfacial properties of the ionic surfactant solutions. The theoretical studies of dynamic problems encounter difficulties in solving the non-linear set of equations describing the electro-diffusion process. The quasi-equilibrium model developed by Dukhin et al. [30–33] assumes that the characteristic diffusion time is much greater than the time of formation of the electrical double layer, and consequently, the electro-diffusion problem is reduced to a mixed barrier-diffusion controlled problem. Similar approach is followed by Borwankar and Wasan [18]. Bonfillon and Langevin [34] have obtained a solution for the case of small periodic surface corrugations with application to the longitudinal wave method for measuring of viscoelasticity of surfactant monolayers. Joos et al. [35] reduced the kinetic problem for a solution of *mixed* anionic and cationic surfactants to the problem for the adsorption of an electroneutral combination governed by the simple diffusion equation.

MacLeod and Radke [36] obtained numerical solutions of the electro-diffusion problem without making simplifying assumptions. Although the advantage of their rigorous approach is indisputable, the numerical solution is much time-consuming when applied to process experimental data, and it does not entirely elucidate the course of the underlying physical processes. Besides, the model in Ref. [36] does not take into account the effect of counterion binding, i.e. the formation of a Stern layer.

The first part of this study, Ref. [1], is devoted to the problem for the adsorption kinetics of ionic surfactants in the case when background electrolyte is *absent*. There we followed a more general theoretical description avoiding simplifying assumptions about the presence of quasi-equilibrium double layer [30–33] or absence of Stern layer [36]. For the case of small deviations from equilibrium an analytical expression was derived, which relates the characteristic relaxation time to the physico-chemical parameters of the system (surfactant concentration, surface potential, diffusion coefficients).

In the present article we investigate the adsorption kinetics of ionic surfactants in the *presence* of background electrolyte; this system is more interesting from a practical viewpoint than the system in Ref. [1]. On the other hand, the mathematical solution of the problem turns out to be more complicated than that in the case without electrolyte. Indeed, the transport of one more species, the coions due to the additional electrolyte, is to be theoretically described in the present article.

It is known from the experiment that the addition of a non-amphiphilic salt considerably affects (accelerates) the dynamics of adsorption of an ionic surfactant. Our aim in the present study is to quantify the latter effect by obtaining an analytical solution of the problem for the adsorption kinetics of ionic surfactants, valid for any ratio between the characteristic diffusion relaxation time and the time of formation of the electrical double layer. In this aspect our approach is more general than the quasi-equilibrium model [18,30–40]. To be able to get an analytical solution of this complicated problem, we assume *small deviation* from equilibrium. Similar assumption has been

used by Sutherland [37] to describe adsorption of *nonionic* surfactants.

Another aim of our study is to examine theoretically the contribution of the Stern layer to the adsorption kinetics. That effect should be very important because up to 70–90% of the surface electric charge is expected to be neutralized by the counterions in the Stern layer [15,39,40].

The results of this study appear as explicit analytical expressions for the relaxation of surface tension and adsorption, which can be relatively easily applied to the interpretation of experimental data. Our intentions are to further extend this theoretical analysis to dynamic processes in surfactant solutions subjected to an arbitrarily large initial deviation from equilibrium.

## 2. Physical background and basic equations

The process of adsorption of an ionic surfactant at a liquid–fluid interface is accompanied with increase of the surface electric potential and charge density with time. In its own turn, the presence of surface electrical potential is related to the formation of an electric double layer (EDL) inside the solution. The charged surface repels the new-coming surfactant molecules (Fig. 1), which results in a deceleration of the adsorption process.

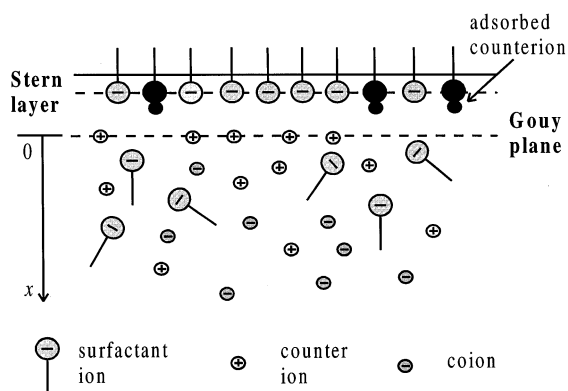


Fig. 1. Sketch of the interfacial zone of an ionic surfactant solution containing dissolved non-amphiphilic electrolyte (salt). The distance between the Stern Layer and the Gouy plane is exaggerated.

Let us consider an aqueous solution of symmetric ( $z:z$ ) ionic surfactant in the presence of additional indifferent symmetric ( $z:z$ ) electrolyte. When the interface is renewed (or disturbed) the equilibrium between the bulk and the interface is destroyed. This gives rise to diffusion transport of the surface active ions, counterions and coions, which is strongly affected by the electric field in the EDL. Following the approach of Borwankar and Wasan [18] we choose the dividing surface to be the Gouy plane (see Fig. 1), which marks the boundary between the diffuse and Stern layers.

With index  $i = 1, 2$  and  $3$  we will denote the surfactant ion, the counterion and the coion, respectively. The transport of the  $i$ -th ionic species, with valency  $z_i$  and diffusion coefficient  $D_i$ , under the influence of electrical potential  $\psi$ , is described by the equation [2,36]:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial x} \left( \frac{\partial c_i}{\partial x} + \frac{z_i e}{kT} c_i \frac{\partial \psi}{\partial x} \right) \quad i = 1, 2, 3 \quad (1)$$

Here  $c_i$  is the bulk concentrations of the  $i$ -th ion which depends on time  $t$  and the distance  $x$  to the interface;  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. The second term in the parentheses in Eq. (1), the so called electromigration term, accounts for the effect of the electric field on diffusion. The electric potential  $\psi$  is related to the bulk charge density through the known Poisson equation,

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi e}{\varepsilon} [z_1 c_1 + z_2 c_2 + z_3 c_3], \quad (2)$$

where  $\varepsilon$  is the dielectric permittivity.

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

$$\begin{aligned} c_i(x, 0) &= c_i^{(0)} \quad \text{at } x = 0, \quad i = 1, 2, 3 \\ c_i(x, 0) &= c_i^{(e)} \quad \text{at } x \neq 0, \quad i = 1, 2, 3 \end{aligned} \quad (3a)$$

where  $c_i^{(0)}$  is the initial concentrations of the ionic species in the subsurface layer of the solution;  $c_i^{(0)}$  is different from its equilibrium value,  $c_i^{(e)}$ , because of an initial interfacial disturbance;  $c_i^{(e)} = c_i^{(e)}(x)$  depends on  $x$  due to the formation of EDL in a vicinity of the interface. Similar initial condition holds for the electric potential:

$$\psi(x, 0) = \psi^{(0)} \quad \text{at } x = 0$$

$$\psi(x,0) = \psi^{(e)} \quad \text{at } x \neq 0 \quad (3b)$$

Here  $\psi^{(0)}$  is the initial value of the surface potential corresponding to the initial adsorption;  $\psi^{(e)} = \psi^{(e)}(x)$  is the equilibrium potential distribution throughout the EDL. In Eqs. (3a) and (3b) and thereafter the superscript e refers to the equilibrium state.

The *boundary conditions* are the following.

1. Far from the interface the electric potential is zero and the bulk concentrations of all solutes are uniform:

$$\psi(\infty, t) = 0, \quad c_i(\infty, t) = c_{i\infty}, \quad i = 1, 2, 3$$

2. The interfacial mass balance, relating the time derivatives of the surfactant or counterion adsorptions,  $\Gamma_i$ , to the respective electro-diffusion influx from the bulk, is

$$\frac{d\Gamma_i}{dt} = D_i \left( \frac{\partial c_i}{\partial x} + \frac{z_i e}{kT} c_i \frac{\partial \psi}{\partial x} \right) \quad \text{at } x = 0 \quad (i = 1, 2) \quad (4)$$

Note that  $\Gamma_2$  denotes the adsorption of counterions belonging to the Stern layer. It is assumed that the coions due to the salt do not adsorb in the Stern layer.

$$\Gamma_3 \equiv 0 \quad (5)$$

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

$$\int_0^\infty [z c_1^{(e)} + (-z) c_2^{(e)} + z c_3^{(e)}] dx + z \Gamma_1^{(e)} + (-z) \Gamma_2^{(e)} = 0 \quad (z_1 = -z_2 = z_3 \equiv z) \quad (6)$$

since both the surfactant and the salt are symmetric  $z:z$ -electrolytes; for the sake of simplicity we have assumed that the counterions of the surfactant and of the non-amphiphilic salt are the same, or can be treated as the same species.

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

$$\Gamma_2^{(e)} = \theta \Gamma_1^{(e)} \quad (7)$$

where  $\theta$  is the equilibrium occupancy of the adsorption sites in the Stern layer by counterions ( $0 \leq \theta \leq 1$ ). Correspondingly,  $(1 - \theta)$  is the apparent degree of dissociation (ionization, charging) of

the adsorbed surfactant molecules [19,38]. In other words,  $\theta$  accounts for the fact that the counterions adsorb at the interface and partially neutralize the surface charge.

### 3. The equilibrium state

Before considering the kinetic problem, let us first briefly discuss the description of the equilibrium state. Even at equilibrium the distributions of the various ionic species are non-uniform and obey the Boltzmann equation:

$$c_i^{(e)} = c_{i\infty} \exp[(-1)^i \phi^{(e)}], \quad i = 1, 2, 3$$

$$\phi^{(e)} \equiv \frac{ze}{kT} \psi^{(e)} \quad (8)$$

see also Eq. (6). The dimensionless potential,  $\phi^{(e)}$ , thus defined is always positive. In fact, Eq. (8) is a solution of Eq. (1) for the equilibrium state (zero time derivative of the concentration in the left-hand side of Eq. (1)). After substitution of Eq. (8) into Eq. (2) one obtains the Poisson–Boltzmann equation for the potential  $\phi^{(e)}$  within the equilibrium EDL:

$$\frac{d^2 \phi^{(e)}}{dx^2} = \kappa^2 \sinh(\phi^{(e)}), \quad \kappa^2 \equiv \frac{8\pi z^2 e^2}{\epsilon kT} c_{2\infty} \quad (9)$$

here  $\kappa^{-1}$  denotes the inverse Debye screening length. Note that  $c_{2\infty} = c_{1\infty} + c_{3\infty}$  because of the electroneutrality of the bulk solution.

As noted above, both the equilibrium and the disturbed distributions of the ionic species are non-uniform. Therefore, the assumption that one can apply a *local* electroneutrality condition,  $z_1 c_1 + z_2 c_2 + z_3 c_3 = 0$ , for all distances  $0 < x < \infty$  (see Ref. [35]), has a restricted applicability as compared with the general condition for *integral* electroneutrality, Eq. (6). The assumption for *local* electroneutrality is relevant only when the characteristic length of the EDL,  $\kappa^{-1}$ , is small compared to the characteristic diffusion length,  $\Gamma_1^{(e)}/c_{2\infty}$ . The latter represents the width of the zone in which the surfactant concentration changes with time due to the diffusion and adsorption. Such a situation ( $\kappa^{-1} \ll \Gamma_1^{(e)}/c_{2\infty}$ ) is realized when large amount of salt is added to the

solution; hence this is a special case of the general problem investigated here.

The solution of Eq. (9), for the equilibrium potential distribution is [41,42]

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

where the equilibrium value of the surface potential is denoted with  $\phi_s^{(e)}$ .

Integrating Eq. (9) and combining the result with Eqs. (6)–(8) one obtains the formula of Gouy [43,44]

$$\Gamma_1^{(e)} - \Gamma_2^{(e)} = \frac{4c_{2\infty}}{\kappa} \sinh\left(\frac{\phi_s^{(e)}}{2}\right) \quad (11)$$

which relates the surface charge density with the surface potential at equilibrium conditions.

#### 4. Relaxation of adsorption after a small initial perturbation

##### 4.1. Linearization of the problem

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

$$\phi = \phi^{(e)} + \phi^{(p)}, \quad c_i = c_i^{(e)} + c_i^{(p)}, \quad \Gamma_i = \Gamma_i^{(e)} + \Gamma_i^{(p)}, \quad (i = 1, 2, 3) \quad (12)$$

the superscripts e and p denote equilibrium and perturbation, respectively. We make use of the following dimensionless variables:

$$\phi = \frac{ze\psi}{kT}, \quad y = \kappa x, \quad \tau = D\kappa^2 t \quad (13a)$$

$$d_i = \frac{D_i}{D}, \quad C_i = \frac{c_i^{(p)}}{c_{2\infty}^{(p)}}, \quad \eta = \frac{c_{1\infty}}{c_{2\infty}} \quad (i = 1, 2, 3) \quad (13b)$$

$D$  is a scaling parameter with dimension of diffusion coefficient; we have chosen the total counterion concentration  $c_{2\infty}$  to scale all concentrations.

To scale the distance  $x$  the Debye length  $\kappa^{-1}$  is used in Eq. (13a).

By means of Eqs. (12), (13a) and (13b) we linearize the Eqs. (1) and (2), and then we apply Laplace transform with respect to time to derive

$$s\tilde{C}_1 = d_1 \frac{d}{dy} \left( \frac{d\tilde{C}_1}{dy} + \tilde{C}_1 \frac{d\phi^{(e)}}{dy} + \eta \exp(-\phi^{(e)}) \frac{d\tilde{\phi}}{dy} \right) \quad (14a)$$

$$s\tilde{C}_2 = d_2 \frac{d}{dy} \left( \frac{d\tilde{C}_2}{dy} - \tilde{C}_2 \frac{d\phi^{(e)}}{dy} - \exp(\phi^{(e)}) \frac{d\tilde{\phi}}{dy} \right) \quad (14b)$$

$$s\tilde{C}_3 = d_3 \frac{d}{dy} \left( \frac{d\tilde{C}_3}{dy} + \tilde{C}_3 \frac{d\phi^{(e)}}{dy} + (1 - \eta) \exp(-\phi^{(e)}) \frac{d\tilde{\phi}}{dy} \right) \quad (14c)$$

$$\frac{d^2\tilde{\phi}}{dy^2} = \frac{1}{2} (\tilde{C}_2 - \tilde{C}_1 - \tilde{C}_3) \quad (14d)$$

where  $\tilde{C}_i(y, s)$  and  $\tilde{\phi}(y, s)$  are the Laplace transforms of the functions  $C_i(y, \tau)$  and  $\phi^{(p)}(y, \tau)$ . The set of Eqs. (14a), (14b), (14c) and (14d) is not easy to solve analytically because  $\phi^{(e)}$  depends on the dimensionless distance  $y$ , i.e. we deal with differential equations of *variable* coefficients. Nevertheless, as demonstrated below, it is possible to overcome the difficulties following a mathematical procedure, which is similar to that developed in our previous paper [1].

##### 4.2. Fluxes of surfactant ions, counterions and coions

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

$$J_1 \equiv d_1 \left( \frac{d\tilde{C}_1}{dy} + \tilde{C}_1 \frac{d\phi^{(e)}}{dy} + \eta \exp(-\phi^{(e)}) \frac{d\tilde{\phi}}{dy} \right) \quad (15a)$$

$$J_2 \equiv d_2 \left( \frac{d\tilde{C}_2}{dy} - \tilde{C}_2 \frac{d\phi^{(e)}}{dy} - \exp(\phi^{(e)}) \frac{d\tilde{\phi}}{dy} \right) \quad (15b)$$

$$J_3 \equiv d_3 \left( \frac{d\tilde{C}_3}{dy} + \tilde{C}_3 \frac{d\phi^{(e)}}{dy} + (1 - \eta) \exp(-\phi^{(e)}) \frac{d\tilde{\phi}}{dy} \right) \quad (15c)$$

These fluxes are present in the right-hand sides of Eqs. (14a), (14b) and (14c), which thus can be transformed to read

$$s\tilde{C}_1 = \frac{dJ_1}{dy}, \quad s\tilde{C}_2 = \frac{dJ_2}{dy}, \quad s\tilde{C}_3 = \frac{dJ_3}{dy} \quad (16a,b,c)$$

Next, we substitute Eqs. (16a), (16b) and (16c) in the right-hand side of Eq. (14d) and integrate to derive

$$\frac{d\tilde{\phi}}{dy} = -\frac{1}{2s}(J_1 - J_2 + J_3) \quad (16d)$$

Further, we substitute Eqs. (16a), (16b), (16c) and (16d) into Eqs. (15a), (15b) and (15c), which can be transformed as follows:

$$s \exp(\phi^{(e)}) \frac{J_1}{d_1} = \frac{d}{dy} \left[ \exp(\phi^{(e)}) \frac{dJ_1}{dy} \right] + \frac{\eta}{2}(J_2 - J_1 - J_3) \quad (17a)$$

$$s \exp(-\phi^{(e)}) \frac{J_2}{d_2} = \frac{d}{dy} \left[ \exp(-\phi^{(e)}) \frac{dJ_2}{dy} \right] - \frac{1}{2}(J_2 - J_1 - J_3) \quad (17b)$$

$$s \exp(\phi^{(e)}) \frac{J_3}{d_3} = \frac{d}{dy} \left[ \exp(\phi^{(e)}) \frac{dJ_3}{dy} \right] + \frac{(1-\eta)}{2}(J_2 - J_1 - J_3) \quad (17c)$$

Note that Eqs. (17a), (17b) and (17c) form a set of three equations for determining the three unknown functions  $J_1$ ,  $J_2$  and  $J_3$ .

#### 4.3. Obtaining a set of operator equations

The problem we investigate now is more complicated than that in the first part of this study [1]. It requires some additional mathematical tricks in order to accomplish an analytical solution. One of them is the introduction of three auxiliary functions, defined as follows:

$$f_1 = J_1 + J_3, \quad f_2 = \exp(-\phi^{(e)})J_2, \\ f_3 = (1-\eta)J_1 - \eta J_3 \quad (18)$$

Further, two differential operators,  $M$  and  $N$ , are defined:

$$M \equiv \frac{d^2}{dy^2} + \frac{d\phi^{(e)}}{dy} \frac{d}{dy} - \frac{1}{2} \exp(-\phi^{(e)}) \quad (19a)$$

$$N \equiv \frac{d^2}{dy^2} + \frac{d\phi^{(e)}}{dy} \frac{d}{dy} \quad (19b)$$

The summation of Eqs. (17a) and (17c), along with the definitions Eq. (18) and Eq. (19a), yields the following operator equation:

$$M[f_1] - s \left( \frac{\eta}{d_1} + \frac{1-\eta}{d_3} \right) f_1 + \frac{f_2}{2} - s \left( \frac{1}{d_1} - \frac{1}{d_3} \right) f_3 = 0 \quad (20a)$$

In view of Eqs. (18) and (19a), we represent Eq. (17b) in the form

$$M[f_2] - \frac{s}{d_2} f_2 + \frac{1}{2} f_1 = 0 \quad (20b)$$

Next we sum Eq. (17a) multiplied by  $(1-\eta)$  and Eq. (17c) multiplied by  $-\eta$ ; thus in view of Eqs. (18) and (19b) we obtain

$$s\eta(1-\eta) \left( \frac{1}{d_1} - \frac{1}{d_3} \right) f_1 + s \left( \frac{1-\eta}{d_1} + \frac{\eta}{d_3} \right) f_3 = N[f_3] \quad (20c)$$

Finally, from Eqs. (20a), (20b) and (20c) we obtain the following set of three differential operator equations (for explanations see below):

$$M_{22}[f_2] = -\frac{s}{2} \left( \frac{1}{d_1} - \frac{1}{d_3} \right) f_3 \quad (21a)$$

$$M_{12}[f_2] + \frac{1}{2} f_1 = 0 \quad (21b)$$

$$M_{33}[f_3] = s\eta(1-\eta) \left( \frac{1}{d_1} - \frac{1}{d_3} \right) f_1 \quad (21c)$$

where the differential operators are defined as follows:

$$M_{22}[f_2] \equiv M^2[f_2] - s \left( \frac{\eta}{d_1} + \frac{1}{d_2} + \frac{1-\eta}{d_3} \right) M[f_2] \\ - \left[ \frac{1}{4} - \frac{s^2}{d_2} \left( \frac{\eta}{d_1} + \frac{1-\eta}{d_3} \right) \right] f_2 \quad (22a)$$

$$M_{12}[f_2] \equiv M[f_2] - \frac{s}{d_2} f_2 \quad (22b)$$

$$M_{33}[f_3] \equiv N[f_3] - s \left( \frac{1-\eta}{d_1} + \frac{\eta}{d_3} \right) f_3 \quad (22c)$$

Eqs. (21b) and (21c) are equivalent to Eqs. (20b) and (20c), respectively. To derive Eq. (21a) we have expressed  $f_1$  from Eq. (20b) and have

substituted the result into Eq. (20a). Eqs. (20a), (20b) and (20c) represent the sought for set of differential operator equations, whose form is convenient for derivation of the long-time asymptotics of the solution (see below).

#### 4.4. Analytical asymptotic solution for long times

The most ionic surfactants exhibit a very fast relaxation and only the long time asymptotics of the surface tension time dependence is accessible to the widely used *Wilhelmy plate* and *de Nouy ring* methods. This experimental situation motivates us to derive an asymptotic solution of Eqs. (21a), (21b) and (21c) for  $t \rightarrow \infty$ , that is for  $s \rightarrow 0$ . Our aim is to obtain the leading terms,  $f_1^{(0)}$ ,  $f_2^{(0)}$  and  $f_3^{(0)}$  in the asymptotics of  $f_1$ ,  $f_2$  and  $f_3$ , for small  $s$ .

Let us first consider Eq. (21a), it can be proven that the right-hand side of this equation gives a higher order contribution and therefore  $f_1^{(0)}$  can be sought as a solution of the equation

$$M_{22}[f_2^{(0)}] = 0 \quad (23)$$

In view of Eq. (22a), Eq. (23) is a fourth order differential equation, whose solution can be expressed as a linear combination of four characteristic functions,  $F_i$ ,  $i = 1, \dots, 4$ . Without entering into mathematical details, we will mention that two of these characteristic functions are singular for  $x \rightarrow \infty$  (in the bulk of solution), and consequently, they must be excluded from the linear combination. The other two characteristic functions are regular for  $x \rightarrow \infty$  and they can be found as solutions of the characteristic equation

$$M[F_i] = \lambda_i F_i \quad (i = 1, 2) \quad (24)$$

Then  $f_2^{(0)}$  can be expressed in the form

$$f_2^{(0)} = A_1 F_1 + A_2 F_2 \quad (25)$$

where  $A_1$  and  $A_2$  are coefficients, which are to be determined from the boundary conditions. A substitution of Eq. (24) into Eq. (23), in view of Eq. (22a), leads to a quadratic equation for the  $\lambda$ , whose solution is

$$\lambda_{1,2} = \frac{1}{2} \left[ s \left( \frac{\eta}{d_1} + \frac{1}{d_2} + \frac{1-\eta}{d_3} \right) \right.$$

$$\left. \pm \sqrt{1 + s^2 \left( \frac{\eta}{d_1} - \frac{1}{d_2} + \frac{1-\eta}{d_3} \right)^2} \right] \quad (26)$$

Let us introduce the notation

$$\beta_i = \sqrt{\lambda_i + \frac{1}{2}} \quad (27)$$

$$\xi \equiv 1 - \exp[-\phi^{(e)}(x)],$$

$$\xi_s \equiv 1 - \exp[-\phi^{(e)}(0)] \quad (28)$$

Note that  $\xi \in [0, \xi_s] \subset [0, 1]$ . We will seek  $F_1$  and  $F_2$  in the form

$$F_i = \left( \frac{\xi}{\xi_s} \right)^{\beta_i} g_i \quad (i = 1, 2) \quad (29)$$

where  $g_i$  are new, unknown functions. By means of Eqs. (19a) and (27)–(29) we transform Eq. (24):

$$\xi(1-\xi) \frac{d^2 g_i}{d\xi^2} + \left[ 2\beta_i + 1 - \left( 2\beta_i + \frac{1}{2} \right) \xi \right] \frac{d g_i}{d\xi} - (\beta_i - 1) \left( \beta_i + \frac{1}{2} \right) g_i = 0 \quad (30)$$

The solution of Eq. (30), which satisfies the boundary condition  $g_i(\xi = 0) = 1$ , is a hypergeometric function [45]:

$$g_i = \frac{{}_2F_1(\beta_i - 1, \beta_i + 1/2, 2\beta_i + 1; \xi)}{{}_2F_1(\beta_i - 1, \beta_i + 1/2, 2\beta_i + 1; \xi_s)} \quad (i = 1, 2) \quad (31)$$

Fortunately, the latter hypergeometric function can be expressed in terms of elementary functions (Eq. (45)); having in mind Eq. (29) we obtain the following relatively simple expression for the characteristic functions:

$$F_i = \frac{2 - \xi + 2\beta_i \sqrt{1 - \xi}}{2 - \xi_s + 2\beta_i \sqrt{1 - \xi_s}} \left( \frac{1 + \sqrt{1 - \xi_s}}{1 + \sqrt{1 - \xi}} \right)^{2\beta_i} \left( \frac{\xi}{\xi_s} \right)^{\beta_i} \quad (32)$$

Next, Eq. (21b), combined with Eqs. (22b), (24) and (25) directly yields an expression for  $f_1^{(0)}$  in terms of  $F_1$  and  $F_2$ :

$$f_1^{(0)} = 2 \left( \frac{s}{d_2} - \lambda_1 \right) A_1 F_1 + 2 \left( \frac{s}{d_2} - \lambda_2 \right) A_2 F_2 \quad (33)$$

Our last task is to find analytical expression for  $f_3^{(0)}$ . With that end in view we consider Eq. (21c),

which can be treated analogously to Eq. (21a). In particular, it can be proven that the right-hand side of Eq. (21c) gives a higher order contribution for  $s \rightarrow 0$ . Therefore,  $f_3^{(0)}$  can be searched as a solution of the equation

$$M_{33}[f_3^{(0)}] \equiv \xi^2(1-\xi) \frac{d^2 f_3^{(0)}}{d\xi^2} + \xi \left(1 - \frac{\xi}{2}\right) \frac{d f_3^{(0)}}{d\xi} - s \left(\frac{1-\eta}{d_1} + \frac{\eta}{d_3}\right) f_3^{(0)} = 0 \quad (34)$$

This equation has a solution for  $f_3^{(0)}$  in terms of elementary functions. As  $f_3^{(0)}$  must be regular for  $\xi \rightarrow 0$  (that is for  $x \rightarrow \infty$ ), from Eq. (34) one obtains

$$f_3^{(0)} = A_3 F_3 \quad (35)$$

where

$$F_3 = \frac{1 + 2\beta_3 \sqrt{1-\xi}}{1 + 2\beta_3 \sqrt{1-\xi_s}} \frac{G(\xi)}{G(\xi_s)} \quad (36)$$

$$G(\xi) \equiv \left(\frac{1 - \sqrt{1-\xi}}{1 + \sqrt{1-\xi}}\right)^{\beta_3}, \quad \beta_3 = h\sqrt{s},$$

$$h^2 \equiv \left(\frac{1-\eta}{d_1} + \frac{\eta}{d_3}\right) \quad (37)$$

We recall that our goal is to find the *leading* terms in the asymptotics of  $f_1$ ,  $f_2$  and  $f_3$  for  $s \rightarrow 0$ . Thus for small  $s$  from Eqs. (26) and (27) one obtains

$$\lambda_1 \rightarrow \frac{1}{2}, \quad \lambda_2 \rightarrow -\frac{1}{2}, \quad \beta_1 \rightarrow 1,$$

$$\beta_2 \rightarrow q\sqrt{s} \quad (s \ll 1) \quad (38)$$

$$q^2 \equiv \frac{1}{2} \left(\frac{\eta}{d_1} + \frac{1}{d_2} + \frac{1-\eta}{d_3}\right) \quad (39)$$

Then from Eq. (32) one derives the leading terms of the asymptotics of  $F_1$  and  $F_2$ :

$$F_1 \rightarrow F_1^{(0)} \equiv \frac{\xi}{\xi_s} \quad (40)$$

$$F_2 \rightarrow F_2^{(0)} \equiv \frac{2-\xi + 2\beta_2^{(0)} \sqrt{1-\xi}}{2-\xi_s + 2\beta_2^{(0)} \sqrt{1-\xi_s}} \left(\frac{1 + \sqrt{1-\xi_s}}{1 + \sqrt{1-\xi}}\right)^{2\beta_2^{(0)}} \left(\frac{\xi}{\xi_s}\right)^{\beta_2^{(0)}} \quad (41)$$

What concerns  $\beta_3$  and  $F_3$ , they coincide with the leading terms of their asymptotics for  $s \rightarrow 0$ :

$$\beta_3^{(0)} \equiv \beta_3 = h\sqrt{s}, \quad F_3^{(0)} \equiv F_3 \quad (42)$$

see Eqs. (36) and (37). Next, combining Eqs. (18), (25), (33), (35) and (38) one obtains asymptotic expressions for the fluxes  $J_i$  ( $i = 1, 2, 3$ ) for  $s \rightarrow 0$ :

$$J_1 \rightarrow J_1^{(0)} \equiv -\eta A_1 F_1^{(0)} + \eta A_2 F_2^{(0)} + A_3 F_3^{(0)} \quad (43a)$$

$$J_2 \rightarrow J_2^{(0)} \equiv \frac{1}{1-\xi} [A_1 F_1^{(0)} + A_2 F_2^{(0)}] \quad (43b)$$

$$J_3 \rightarrow J_3^{(0)} \equiv -(1-\eta) A_1 F_1^{(0)} + (1-\eta) A_2 F_2^{(0)} - A_3 F_3^{(0)} \quad (43c)$$

The integration constants  $A_1$ ,  $A_2$  and  $A_3$  (which are independent of  $\xi$ ) are determined from the boundary conditions in Appendix A.

#### 4.5. Expression for the adsorption relaxation

In the case of small deviations from equilibrium the perturbations in the adsorption of surfactant and counterions can be presented in the form:

$$\Gamma_j^{(p)} = \left(\frac{\partial \Gamma_j}{\partial c_{1s}}\right)^{(e)} c_{1s}^{(p)} + \left(\frac{\partial \Gamma_j}{\partial c_{2s}}\right)^{(e)} c_{2s}^{(p)} \quad (j = 1, 2) \quad (44)$$

where, as before, the superscripts e and p denote equilibrium and perturbation, respectively, and  $c_{is}$  ( $i = 1, 2$ ) denote the subsurface concentrations of the respective species. Next, we apply a Laplace transformation to Eq. (44) and use Eqs. (16a) and (16b); thus Eq. (44) acquires the form

$$\tilde{\Gamma}_j^{(p)} = \frac{c_{2\infty}}{\kappa s} \left[ g_{j1} \left(\frac{dJ_1}{dy}\right)_{y=0} + g_{j2} \left(\frac{dJ_2}{dy}\right)_{y=0} \right] \quad (j = 1, 2) \quad (45)$$

where  $\tilde{\Gamma}_j^{(p)}$  is the Laplace transform of  $\Gamma_j^{(p)}$ , and we have introduced the notation:

$$g_{ji} \equiv \kappa \left(\frac{\partial \Gamma_j}{\partial c_{is}}\right)^{(e)} \quad (i, j = 1, 2) \quad (46)$$

The derivatives of  $J_1$  and  $J_2$ , entering Eq. (45), are determined in Appendix A; the results read:

$$\left(\frac{dJ_1}{dy}\right)_{y=0} = \frac{b}{p} \zeta \sqrt{s} \{2q\eta\zeta + (1-\eta)h\zeta + (1+\zeta^2) + [2q\eta + (1-\eta)h](g_{22} - g_{12})\} \quad (47)$$



$$\left(\frac{dJ_2}{dy}\right)_{y=0} = \frac{b}{p} \sqrt{s} \{2q + [2q\eta + (1-\eta)h] (g_{11} - g_{21})\zeta\} \quad (48)$$

where

$$p \equiv 1 + \zeta^2 + (g_{11} - g_{21})\eta\zeta^3 + (g_{22} - g_{12})/\zeta \quad (49)$$

$$\zeta \equiv \exp(-\phi_s^{(e)}/2) = \sqrt{1 - \zeta_s}, \quad b \equiv \frac{\kappa}{c_{2\infty}} \Delta\Gamma(0) \quad (50)$$

See Eq. (28). Here,  $\Delta\Gamma(0)$  is the deviation of the adsorption from its equilibrium value at the initial moment  $t = 0$ . It is presumed (see Appendix A for details) that the electroneutrality equation holds for the initial perturbation, which implies that the initial perturbations in the adsorptions of surfactant and counterions are equal:

$$\Delta\Gamma_1(0) = \Delta\Gamma_2(0) \equiv \Delta\Gamma(0) \quad (51)$$

Eq. (51) implies that at the initial moment equal amounts of cations and anions are removed from the interface, and thus the overall surface charge density is not perturbed. In other words, the strong electrostatic interaction requires a given ion to be removed from the interface together with its counterion; otherwise the initial perturbation would not be small. As discussed in Appendix A, the relationship  $\Delta\Gamma_1(0) \neq \Delta\Gamma_2(0)$  is incompatible with the present theoretical description based on electrostatic (rather than electrodynamic) treatment of the electric field for the case of small deviations from equilibrium.

The substitution of Eqs. (47) and (48) into Eq. (45), after some transformations, yields

$$\frac{\tilde{\Gamma}_i^{(p)}}{\Delta\Gamma(0)} = \sqrt{\frac{D}{s}} \left( g_{i1}G_1 + \frac{2}{p} \frac{q}{\sqrt{D}} g_{i2} + gG_2 \right) \quad (i = 1, 2) \quad (52)$$

where  $p$  is given by Eq. (49) and we have introduced the notation:

$$g \equiv g_{11}g_{22} - g_{12}g_{21} \quad (53)$$

$$G_1 \equiv \left[ 2\eta \frac{q}{\sqrt{D}} + (1-\eta) (1 + \zeta^2) \frac{h}{\sqrt{D}} \right] \frac{\zeta^2}{p} \quad (54)$$

$$G_2 \equiv \left[ 2\eta \frac{q}{\sqrt{D}} + (1-\eta) \frac{h}{\sqrt{D}} \right] \frac{\zeta}{p} \quad (55)$$

Note that in view of Eqs. (37) and (39) one obtains

$$\frac{h}{\sqrt{D}} \equiv \left( \frac{1-\eta}{D_1} + \frac{\eta}{D_3} \right)^{1/2}, \quad \frac{q}{\sqrt{D}} \equiv \frac{1}{\sqrt{2}} \left( \frac{\eta}{D_1} + \frac{1}{D_2} + \frac{1-\eta}{D_3} \right)^{1/2} \quad (56)$$

Next we apply inverse Laplace transformation to Eq. (52) to obtain

$$\frac{\Gamma_i^{(p)}}{\Delta\Gamma(0)} \equiv \frac{\Gamma_i(t) - \Gamma_i^{(e)}}{\Gamma_i(0) - \Gamma_i^{(e)}} = \sqrt{\frac{\tau_i}{\pi t}} \quad (i = 1, 2) \quad (57)$$

where the adsorption relaxation time  $\tau_i$  is defined as follows

$$\tau_i = \frac{1}{\kappa^2} \left( g_{i1}G_1 + \frac{2}{p} \frac{q}{\sqrt{D}} g_{i2} + gG_2 \right)^2 \quad (i = 1, 2) \quad (58)$$

To obtain the values of  $\tau_1$  and  $\tau_2$  from Eq. (58) one has to first calculate  $g_{ij}$  from the adsorption isotherms of surfactant and counterions, and to calculate  $\zeta = \exp(-\phi_s^{(e)}/2)$  from the equilibrium double layer theory; the necessary equations and the procedure of calculation are described in Section 6.1 below.

Let us consider some special cases of Eq. (58). In the limiting case of *high salt concentration* one has  $\eta \rightarrow 0$  and  $\zeta \rightarrow 1$ . In this limit Eq. (58) reduces to

$$\tau_i = \frac{1}{\kappa^2} \left[ \frac{2g_{i1} + g}{p\sqrt{D_1}} + \frac{g_{i2}}{p} \sqrt{\frac{2}{D_2} + \frac{2}{D_3}} \right]^2 \quad (i = 1, 2) \quad (59)$$

where  $p = 2 + (g_{22} - g_{12})$ .

In the limiting case of *nonionic* surfactant there is no counterions and counterion adsorption. Then  $\Gamma_2 \equiv 0$  and consequently  $g_{22} = g_{12} = g_{21} = g = 0$ . Then  $p = 2$  and from Eqs. (46) and (59) one obtains the known expression for nonionic surfactants:

$$\tau_1 = \frac{1}{D_1} \left( \frac{\partial \Gamma_1}{\partial c_1} \right)^2 \quad (60)$$

The comparison between Eqs. (59) and (60) shows that even at high salt concentrations the expressions for the relaxation of adsorption of ionic and nonionic surfactants are different. This

is due to the fact that in the case of ionic surfactant the counterions and coions also take part in the diffusion process.

In the case of solution of an ionic surfactant *without* added non-amphiphilic salt one is to set  $\eta = 1$  in Eq. (58), as well as in Eqs. (54)–(56). The resulting expression is more general than that obtained in our previous paper [1]. Indeed, in Ref. [1] instead of Eq. (44) we have used a simplified expression:  $\Gamma_1^{(p)} \approx (\partial \Gamma_1 / \partial c_{1s})^{(e)} c_{1s}^{(p)}$ . Therefore, the expression for  $\tau_1$ , derived in Ref. [1], can be deduced from Eq. (58) by formally setting  $i = 1$ ,  $\eta = 1$ , and  $g_{22} = g_{12} = g_{21} = g = 0$ .

## 5. Relaxation of surface tension after a small initial perturbation

### 5.1. Thermodynamic background

In Refs. [17,46] it has been established that the surface tension,  $\sigma$ , of an ionic surfactant solution can be expressed in the form

$$\sigma = \sigma_a + \sigma_d \quad (61)$$

where

$$\sigma_d = -\frac{\varepsilon}{4\pi} \int_0^\infty \left( \frac{\partial \psi}{\partial x} \right)^2 dx \quad (62)$$

is a contribution from the *diffuse* part of the electric double layer, and [46]

$$\sigma_a = \sigma_0 - kTJ \quad (63)$$

is a contribution from the *adsorption* layer (surfactant monolayer + bound counterions). Here  $\sigma_0$  is the surface tension of the pure solvent (water) and  $J$  denotes the integral

$$J \equiv \int_0^{c_{1s}} \Gamma_1(\hat{c}_{1s}, c_{2s}) \frac{d\hat{c}_{1s}}{\hat{c}_{1s}} \quad (64)$$

As before, the subscript *s* denotes subsurface concentration. Expressions for  $\Gamma_1(c_{1s}, c_{2s})$  and  $J$ , corresponding to various adsorption isotherms, are listed in Table 1. Note that  $\sigma_d$  represents a *non-local*, integral contribution of the whole electric double layer (see Eq. (62)), whereas  $\theta_a$  is related to the two-dimensional state of the adsorbed surfactant molecules: see Eq. (63) and the

expressions for  $J$  in Table 1. In fact, the integrand in Eq. (62) represents the anisotropy of the Maxwell electric stress tensor, which contributes to the surface tension in accordance with the known Bakker formula. To describe the adsorption (binding) of counterions an adsorption isotherm of Stern type can be used [46,47]:

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_2 c_{2s}}{K_1 + K_2 c_{2s}} \quad (65)$$

where  $K_1$  and  $K_2$  are constants independent of the concentrations of the species. It is proven in Ref. [46] that the necessary and sufficient condition for thermodynamic compatibility of Eq. (65) with either of the adsorption isotherms in Table 1 is:

$$K = K_1 + K_2 c_{2s} \quad (66)$$

Eq. (66) gives the explicit dependence of the parameter  $K$  in Table 1 on the subsurface concentration of counterions  $C_{2s}$ .

For an *equilibrium* electric double layer the Poisson–Boltzmann equation can be applied to carry out the integration in Eq. (62); the result reads [17,46,48]

$$\sigma_d = -\frac{8}{\kappa} kT c_{2\infty} \left[ \cosh\left(\frac{\phi_s^{(e)}}{2}\right) - 1 \right] \quad (67)$$

It is very important to note that the Boltzmann equation (Eq. (8)), and its corollary (Eq. (67)), cannot be used for systems under *dynamic* conditions, like the system investigated in the present article. For dynamic problems one is to apply the general expression for  $\sigma_d$ , Eq. (62), in which the respective dynamic expression for  $\partial\psi/\partial x$  should be substituted. This is done in Section 5.2.

### 5.2. Relaxation of the diffuse-layer-contribution to the surface tension

First, with the help of Eqs. (9) and (13a), let us introduce dimensionless variables in Eq. (62):

$$\sigma_d = -\frac{2}{\kappa} kT c_{2\infty} \int_0^\infty \left( \frac{\partial \phi}{\partial y} \right)^2 dy \quad (68)$$

Next, we consider small deviations from equilibrium:

$$\phi = \phi^{(e)} + \phi^{(p)}, \quad \sigma_d = \sigma_d^{(e)} + \sigma_d^{(p)} \quad (69)$$

Table 1

The most frequently used adsorption isotherms and the respective surface tension isotherms for ionic surfactants

| Surfactant adsorption isotherm       |  |
|--------------------------------------|--|
| Henry                                | $Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty}$   |
| Langmuir                             | $Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}$  |
| Freundlich                           | $\frac{\Gamma_1}{\Gamma_F} = (Kc_{1s})^m$  |
| Volmer                               | $Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}\right)$                             |
| Frumkin                              | $Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT}\right)$  |
| van der Waals                        | $Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}\right)$ |
| Surface tension isotherm Eq. (61)    |  |
| $\sigma = \sigma_0 - kTJ + \sigma_d$ |  |
| Henry                                | $J = \Gamma_1$   |
| Langmuir                             | $J = -\Gamma_\infty \ln(1 - \Gamma_1/\Gamma_\infty)$   |
| Freundlich                           | $J = \Gamma_1/m$   |
| Volmer                               | $J = \Gamma_\infty \Gamma_1 / (\Gamma_\infty - \Gamma_1)$  |
| Frumkin                              | $J = -\Gamma_\infty \ln(1 - \Gamma_1/\Gamma_\infty) - \beta\Gamma_1^2/(kT)$  |
| van der Waals                        | $J = \Gamma_\infty \Gamma_1 / (\Gamma_\infty - \Gamma_1) - \beta\Gamma_1^2/(kT)$   |

where, as usual, the superscripts e and p denote equilibrium and perturbation, respectively. From Eqs. (68) and (69) one derives

$$\sigma_d^{(p)} = -\frac{4}{\kappa} kT c_{2\infty} \int_0^\infty \frac{d\phi^{(e)}}{dy} \frac{\partial \phi^{(p)}}{\partial y} dy \quad (70)$$

Further, we apply Laplace transformation to Eq. (70):

$$L[\sigma_d^{(p)}] = -\frac{4}{\kappa} kT c_{2\infty} \int_0^\infty \frac{d\phi^{(e)}}{dy} \frac{\partial \tilde{\phi}}{\partial y} dy \quad (71)$$

Here  $L$  symbolizes Laplace transformation and, as before,  $\tilde{\phi}(y, s)$  is the Laplace transform of  $\phi^{(p)}(y, \tau)$ . The integral term in Eq. (71) can be

rearranged by means of Eq. (16d):

$$Q \equiv \int_0^\infty \frac{d\phi^{(e)}}{dy} \frac{\partial \tilde{\phi}}{\partial y} dy = \frac{1}{2s} \int_0^\infty (J_2 - J_1 - J_3) \frac{d\phi^{(e)}}{dy} dy \quad (72)$$

Next, we carry out the integration in Eq. (72) by parts, taking into account Eq. (A3) and the fact that  $\phi^{(e)} \rightarrow 0$  for  $y \rightarrow \infty$ . With the help of Eqs. (16a), (16b) and (16c) the result can be presented in the form

$$Q = -\frac{1}{2s} \left[ \phi_s^{(e)} (J_2^{(0)} - J_1^{(0)})_{y=0} + s \int_0^\infty (\tilde{C}_2 - \tilde{C}_1 - \tilde{C}_3) \phi^{(e)} dy \right]$$

$$Q = -\frac{\phi_s^{(e)}}{2s} (J_2^{(0)} - J_1^{(0)})_{y=0} + O(1) \quad (i = 1, 2) \quad (73)$$

Combining Eqs. (71–73) one obtains

$$L[\sigma_d^{(p)}] = \frac{2kT}{\kappa s} c_{2\infty} \phi_s^{(e)} (J_2^{(0)} - J_1^{(0)})_{y=0} + O(1) \quad (74)$$

Taking the Laplace transform of Eq. (4) and using Eqs. (15a), (15b) and (51) one can derive

$$sL[\Gamma_i^{(p)}] - \Delta\Gamma(0) = \frac{c_{2\infty} J_i^{(0)}}{\kappa} \Big|_{y=0} \quad (i = 1, 2) \quad (75)$$

Substituting  $J_1^{(0)}$  and  $J_2^{(0)}$  from Eq. (75) into Eq. (74) one obtains

$$L[\sigma_d^{(p)}] = 2kT \phi_s^{(e)} L[\Gamma_2^{(p)} - \Gamma_1^{(p)}] \quad (76)$$

Finally, the inverse Laplace transformation of Eq. (76) yields

$$\sigma_d^{(p)} = 2kT \phi_s^{(e)} (\Gamma_2^{(p)} - \Gamma_1^{(p)}) \quad (77)$$

### 5.3. Characteristic time of surface tension relaxation

From Eq. (61) one obtains

$$\sigma^{(p)} = \sigma_a^{(p)} + \sigma_d^{(p)} \quad (78)$$

where the meaning of the superscript p is the same as in Eq. (69). The perturbation  $\sigma_a^{(p)}$  can be determined from Eq. (63):

$$\sigma_a^{(p)} = -kT J^{(p)} = -kT \left[ \left( \frac{\partial J}{\partial \Gamma_1} \right)_{\Gamma_2} \Gamma_1^{(p)} \right]$$

$$+ \left( \frac{\partial J}{\partial \Gamma_2} \right)_{\Gamma_1} \Gamma_1^{(p)} \right] \quad (79)$$

Combining Eqs. (77–79) we obtain

$$\sigma^{(p)} = -kT[(J_{\Gamma_1} + 2\phi_s^{(e)})\Gamma_1^{(p)} + (J_{\Gamma_2} - 2\phi_s^{(e)})\Gamma_2^{(p)}] \quad (80)$$

where we have introduced the notation

$$J_{\Gamma_1} \equiv \left( \frac{\partial J}{\partial \Gamma_1} \right)_{\Gamma_2}, \quad J_{\Gamma_2} \equiv \left( \frac{\partial J}{\partial \Gamma_2} \right)_{\Gamma_1} \quad (81)$$

In view of Eq. (51) one can write  $\Gamma_1^{(p)}(0) = \Gamma_2^{(p)}(0) = \Delta\Gamma(0)$  for the initial moment  $t = 0$ . Therefore, setting  $t = 0$  in Eq. (80) one derives

$$\sigma^{(p)}(0) = -kT(J_{\Gamma_1} + J_{\Gamma_2})\Delta\Gamma(0)$$

The combination of Eqs. (80) and (82) yields

$$\frac{\sigma^{(p)}(t)}{\sigma^{(p)}(0)} = \frac{J_{\Gamma_1} + 2\phi_s^{(e)}}{J_{\Gamma_1} + J_{\Gamma_2}} \frac{\Gamma_1^{(p)}}{\Delta\Gamma(0)} + \frac{J_{\Gamma_2} - 2\phi_s^{(e)}}{J_{\Gamma_1} + J_{\Gamma_2}} \frac{\Gamma_2^{(p)}}{\Delta\Gamma(0)} \quad (83)$$

Next, we notice that for all adsorption isotherms in Table 1

$$J_{\Gamma_2} \equiv \left( \frac{\partial J}{\partial \Gamma_2} \right)_{\Gamma_1} \equiv 0 \quad (84)$$

Then Eq. (83) reduces to

$$\frac{\sigma^{(p)}(t)}{\sigma^{(p)}(0)} = \left( 1 + \frac{2\phi_s^{(e)}}{J_{\Gamma_1}} \right) \frac{\Gamma_1^{(p)}}{\Delta\Gamma(0)} - \frac{2\phi_s^{(e)}}{J_{\Gamma_1}} \frac{\Gamma_2^{(p)}}{\Delta\Gamma(0)} \quad (85)$$

Combining Eqs. (57) and (85) we finally obtain

$$\frac{\sigma^{(p)}(t)}{\sigma^{(p)}(0)} \equiv \frac{\sigma(t) - \sigma^{(e)}}{\sigma(0) - \sigma^{(e)}} = \sqrt{\frac{\tau_\sigma}{\pi t}} \quad (86)$$

where the characteristic time of surface tension relaxation,  $\tau_\sigma$ , is defined by the expression

$$\sqrt{\tau_\sigma} \equiv \left( 1 + \frac{2\phi_s^{(e)}}{J_{\Gamma_1}} \right) \sqrt{\tau_1} - \frac{2\phi_s^{(e)}}{J_{\Gamma_1}} \sqrt{\tau_2} \quad (87)$$

The relaxation times of surfactant and counterion adsorption,  $\tau_1$  and  $\tau_2$ , are given by Eq. (58). For reader's convenience the expressions for  $J_{\Gamma_1}$ , corresponding to the various isotherms in Table 1, are listed in Table 2. It is worthwhile noting that the terms with  $\phi_s^{(e)}$  in Eqs. (85) and (87) originate from  $\sigma_d^{(p)}$  (see Eq. (77)), that is from the perturbation of the diffuse electric double layer. If the latter contribution were negligible, one would obtain

$$\tau_\sigma \approx \tau_1 \quad (88)$$

i.e. the characteristic times of the relaxation of surface tension and adsorption coincide, just like it is for the nonionic surfactants. Eq. (88) has been currently used in all previous studies on adsorption of ionic surfactants, including our previous paper [1].

In the Section 6.2 we consider a typical experimental system as an illustrative example. We calculate  $\tau_1$ ,  $\tau_2$  and  $\tau_\sigma$  as functions of the surfactant and counterion concentrations. In particular, we examine how large is the difference between  $\tau_1$  and  $\tau_\sigma$ .

## 6. Procedure of calculations and numerical results

### 6.1. The equilibrium state

At equilibrium the subsurface concentrations of the ionic species are related to their bulk concentrations by means of the Boltzmann equation:

Table 2

Expressions for the thermodynamic coefficient  $J_{\Gamma_1}$ , corresponding to the isotherms in Table 1

|               | Thermodynamic coefficient   |
|---------------|---|
|               | $J_{\Gamma_1} \equiv \left( \frac{\partial J}{\partial \Gamma_1} \right)_{\Gamma_2}$              |
| Henry         | $J_{\Gamma_1} = 1$  |
| Langmuir      | $J_{\Gamma_1} = \frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1}$                                   |
| Freundlich    | $J_{\Gamma_1} = \frac{1}{m}$  |
| Volmer        | $J_{\Gamma_1} = \frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2}$                             |
| Frumkin       | $J_{\Gamma_1} = \frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}$       |
| van der Waals | $J_{\Gamma_1} = \frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2} - \frac{2\beta\Gamma_1}{kT}$ |

$$c_{is} = c_{1\infty} \exp[(-1)^i \phi_s^{(e)}] \quad (i = 1, 2) \quad (89)$$

Combining Eqs. (61), (63) and (67), one obtains the equilibrium surface tension isotherm [17,46,48]:

$$\sigma = \sigma_0 - kT \left\{ J + \frac{8c_{2\infty}}{\kappa} \left[ \cosh\left(\frac{\phi_s^{(e)}}{2}\right) - 1 \right] \right\} \quad (90)$$

Expressions for  $J$  can be found in Table 1. Let us consider a set of experimental data for the equilibrium surface tension  $\sigma$  as a function of the bulk concentrations of surfactant and salt,  $c_{1\infty}$  and  $c_{2\infty}$ . To determine the theoretical dependence  $\sigma(c_{1\infty}, c_{2\infty})$  we have a full set of equations. These are the following six equations: Eqs. (11), (65), (90), one of the surfactant adsorption isotherms in Table 1, and Eq. (89) for  $i = 1, 2$ , which enable one to determine the following six unknown variables:  $c_{1s}$ ,  $c_{2s}$ ,  $\Gamma_1$ ,  $\Gamma_2$ ,  $\phi_s^{(e)}$  and  $\sigma$ . The theoretical adsorption isotherm depends on four constants,  $K_1$ ,  $K_2$ ,  $\Gamma_\infty$  and  $\beta$  (see Eqs. (65) and (66) and Table 1); these constants are to be determined as adjustable parameters from the best fit of the experimental data. Further, one can calculate the thermodynamic coefficients  $g_{ij}$  ( $i, j = 1, 2$ ), which enter the expressions for the relaxation times (see Eqs. (58) and (87)). As demonstrated in Ref. [46], the Gibbs adsorption equation can be expressed in the form

$$d\sigma_a = -kT(\Gamma_1 d \ln c_{1s} + \Gamma_2 d \ln c_{2s}) \quad (T = \text{constant}) \quad (91)$$

$c_{1s}$  and  $c_{2s}$  are independent variables, and  $d\sigma_a$  is a total differential. Then in accordance with the Euler condition the cross derivatives must be equal; thus from Eqs. (46) and (91) one derives

$$g_{21}c_{1s} = g_{12}c_{2s} \quad (92)$$

Differentiating Eq. (65), along with Eq. (46) we obtain

$$g_{21} = \frac{\Gamma_2}{\Gamma_1} g_{11} \quad (93)$$

From Eqs. (92) and (93) it follows

$$g_{12} = \frac{\Gamma_2 c_{1s}}{\Gamma_1 c_{2s}} g_{11} \quad (94)$$

Finally, differentiating Eq. (65), along with Eqs. (46) and (94) one obtains

$$g_{22} = \frac{\Gamma_2^2 c_{1s}}{\Gamma_1^2 c_{2s}} g_{11} + \frac{\kappa K_1 K_2 \Gamma_1}{(K_1 + K_2 c_{2s})^2} \quad (95)$$

Eqs. (93)–(95) relate  $g_{12}$ ,  $g_{21}$ , and  $g_{22}$  to  $g_{11}$ . To calculate  $g_{11}$  we use Eqs. (46), (81) and (84):

$$J_{\Gamma_1} g_{11} = \kappa \frac{dJ}{d\Gamma_1} \left( \frac{\partial \Gamma_1}{\partial c_{1s}} \right)_{c_{2s}} = \kappa \left( \frac{\partial J}{\partial c_{1s}} \right)_{c_{2s}} = \kappa \frac{\Gamma_1}{c_{1s}} \quad (96)$$

At the last step we have used the definition of  $J$  (Eq. (64)). Thus we obtain

$$g_{11} = \frac{\kappa \Gamma_1}{c_{1s} J_{\Gamma_1}} \quad (97)$$

Expressions for  $J_{\Gamma_1}$ , corresponding to the various isotherms in Table 1, are given in Table 2.

## 6.2. Experimental system and data processing

Below we illustrate the numerical predictions of the theory for an experimental system investigated by Tajima et al. [12,13], who measured the surface tension of solutions of tritiated sodium dodecyl sulfate (TSDS) for two concentrations of NaCl,  $c_{3\infty} = 0$  and  $c_{3\infty} = 0.115$  M. In Ref. [46], their data (Fig. 2), were fitted by using the Frumkin adsorption isotherm (see Table 1)

$$Kc_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT}\right) \quad (98)$$

which is appropriate for air–water interfaces (for oil–water interfaces  $\beta \equiv 0$  and Eq. (98) reduces to the Langmuir isotherm [16,18]). The parameter  $K$  is given by Eq. (66), that is  $K = K_1 + K_2 c_{2s}$ , and the counterion adsorption is determined by the Stern isotherm Eq. (65). Combining Eq. (90) with the Frumkin surface tension isotherm in Table 1 one obtains

$$\frac{\sigma_0 - \sigma}{kT} = -\Gamma_\infty \ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) - \frac{\beta\Gamma_1^2}{kT} + \frac{8c_{2\infty}}{\kappa} \left[ \cosh\left(\frac{\phi_s^{(e)}}{2}\right) - 1 \right] \quad (99)$$

Theoretically, the six unknown variables,  $c_{1s}$ ,  $c_{2s}$ ,  $\Gamma_1$ ,  $\Gamma_2$ ,  $\phi_s^{(e)}$  and  $\sigma$  are determined from the set of the six equations (Eqs. (11), (65), (98), (99) and (89) for  $i = 1, 2$ ). In Ref. [46] the theoretical and

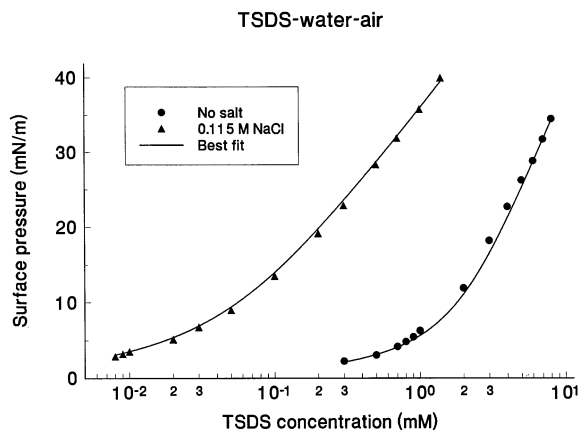


Fig. 2. Surface pressure at air–water interface,  $\sigma_0 - \sigma$  versus the surfactant (TSDS) concentration,  $c_{1\infty}$ , for two fixed NaCl concentrations: 0 and 0.115 M; the symbols are experimental data from Refs. [12,13]; the continuous lines represent the best fit by means of the theory from Ref. [46].

experimental dependencies  $\sigma = \sigma(c_{1\infty}, c_{2\infty})$  have been compared (see Fig. 2) and the following values of the parameters of the model have been obtained:  $\Gamma_\infty = 4.42 \times 10^{-6} \text{ mol m}^{-2}$ ,  $K_1 = 156 \text{ m}^3 \text{ mol}^{-1}$ ,  $K_2 = 0.128 \text{ m}^6 \text{ mol}^{-2}$  and  $\beta\Gamma_\infty/(k_B T) = 0.400$ . These parameters values are obtained by simultaneous processing of all data points in Fig. 2 by means of the least-squares method. Once having determined  $\Gamma_\infty$ ,  $K_1$ ,  $K_2$  and  $\beta$  one can further calculate all necessary thermodynamic parameters ( $c_{1s}$ ,  $c_{2s}$ ,  $\Gamma_1$ ,  $\Gamma_2$ ,  $\phi_s^{(e)}$ ,  $J_{\Gamma_1}$ ,  $g_{11}$ ,  $g_{12}$ ,  $g_{21}$  and  $g_{22}$ ) using equations given above in this paper.

In addition, we use the following values of the diffusion coefficients of the surfactant ions,  $\text{Na}^+$  ions and  $\text{Cl}^-$  ions:  $D_1 = 5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $D_2 = 6.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $D_3 = 6.61 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , respectively. The above value of  $D_1$  is experimentally determined in Ref. [49], whereas the values of  $D_2$  and  $D_3$  are calculated by means of the Stokes–Einstein formula substituting 3.6 and 3.3 Å for the radii of the hydrated  $\text{Na}^+$  and  $\text{Cl}^-$  ions, respectively.

It is worthwhile nothing that the Frumkin-type isotherms used by us (Eqs. (98) and (99)), can be obtained also from the thermodynamic theory by Kalinin and Radke [20], if their parameter  $(\Omega_{\beta d})^{-1}$  is set equal to zero. Our parameter  $\beta$  is

related to the parameters of their model as follows:  $\beta = -(\omega/\Gamma_\infty + e^2/\Omega_{0\beta})/2$ .

### 6.3. Numerical results and discussion

In Fig. 3 the occupancy of the Stern layer,  $\theta = \Gamma_2/\Gamma_1$ , is plotted versus the surfactant concentration for the two experimental curves shown in Fig. 2. One sees that the increase of the occupancy for the solution *without* NaCl is especially strong as a function of the surfactant concentration:  $\Gamma_2/\Gamma_1$  rises from 0.15 to 0.74 and then exhibits a tendency to level off. As it could be expected, the occupancy  $\Gamma_2/\Gamma_1$  is higher for the solution *with* NaCl; even at surfactant concentration  $10^{-5} \text{ M}$  the occupancy is about 0.40; for the higher surfactant concentrations it levels off, again at  $\Gamma_2/\Gamma_1 = 0.74$ . The data in Fig. 3 imply that the counterion adsorption must not be neglected.

Fig. 4 shows the relaxation times of surface tension, surfactant adsorption and counterion adsorption,  $\tau_\sigma$ ,  $\tau_1$ , and  $\tau_2$ , respectively. They are calculated by means of Eqs. (58) and (87) as functions of the surfactant concentration,  $c_{1\infty}$ , for one fixed concentration of the added NaCl:  $c_{3\infty} = 0.115 \text{ M}$ . First of all, one notices the wide range of variation of the relaxation times, which is six to eight orders of magnitude. In particular, the relax

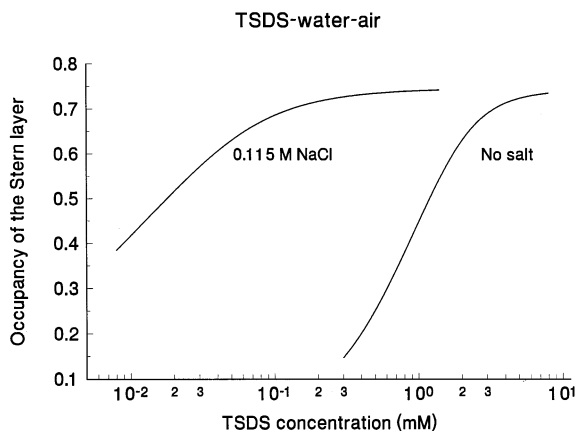


Fig. 3. Calculated occupancy of the Stern layer by adsorbed counterions,  $\Gamma_2/\Gamma_1$ , versus the surfactant (TSDS) concentration,  $c_{1\infty}$ , for two fixed NaCl concentrations: 0 and 0.115 M. The lines correspond to the best fits of the data in Fig. 2.

ation time of surface tension,  $\tau_\sigma$ , drops from almost 100 s down to  $5 \times 10^{-6}$  s. Secondly, one sees that systematically  $\tau_2 < \tau_1 < \tau_\sigma$ ; the difference between these three relaxation times can be greater than one order of magnitude for the lower surfactant concentrations. Thus one can conclude that the terms with  $\phi_s^{(c)}$  in Eq. (87), which lead to a difference between  $\tau_1$  and  $\tau_\sigma$ , play an important role, especially for the lower surfactant concentrations. We recall that the terms of question originate from the relaxation of  $\sigma_{db}$ , which is the contribution of the diffuse electric double layer to the surface tension (see Eq. (62)). If this contribution were not taken into account, the theory would predict much smaller values of  $\tau_\sigma$ , much less than the experimentally observed range for the lower surfactant concentrations:  $10 < \tau_\sigma < 100$  s. Fig. 4 demonstrates that the approximation  $\tau_\sigma \approx \tau_1$ , which is widely used in literature, is applicable only for the higher surfactant concentrations, for which  $\tau_\sigma \rightarrow \tau_1$ . Note also that  $\tau_2$  keeps always smaller than  $\tau_1$  and  $\tau_\sigma$ , that is the adsorption of counterions relaxes always faster than does the adsorption of surfactant ions and the surface tension.

Fig. 5 shows that the difference between the three relaxation times,  $\tau_\sigma$ ,  $\tau_1$ ,  $\tau_2$  and  $\tau_2$  becomes even greater when there is no NaCl in the solution. In this case the difference between  $\tau_\sigma$  and  $\tau_1$  can reach two orders of magnitude. In general,  $\tau_\sigma$  and  $\tau_1$  decrease with the rise of surfactant concentration. In contrast,  $\tau_2$  exhibits non-monotonic behavior (Fig. 5). This interesting finding can be interpreted in the following way. The supply of counterions to the relaxing interface is promoted by the gradient of the electric field,  $\nabla\psi$ , but opposed by the gradient of concentration  $\nabla c_2$ . The two effects compensate each other in such a way that the effect of  $\nabla\psi$  is slightly predominant (otherwise there would not be supply of counterions from the bulk to the surface). The strong increase of the occupancy of the Stern layer,  $\Gamma_2/\Gamma_1$ , with the rise of surfactant concentration (see Fig. 3, the curve without salt) leads to a decrease of the surface charge density and a proportional decrease of the driving force of counterion supply,  $\nabla\psi$ . This can explain the initial increase in  $\tau_2$  with the rise of the TSDS concentration (Fig. 5). Since the ionic surfactant is also an

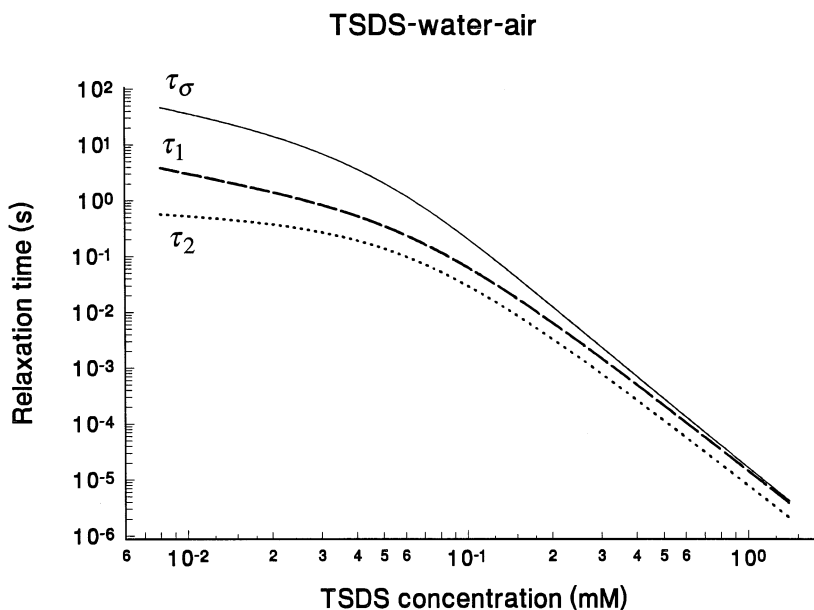


Fig. 4. Surfactant solution with 0.115 M NaCl: relaxation times of surface tension,  $\tau_\sigma$ , of surfactant adsorption,  $\tau_1$ , and of counterion adsorption,  $\tau_2$ , calculated by means of Eqs. (58) and (87) as functions of surfactant (TSDS) concentration,  $c_{100}$ , using parameters values determined from the best fit of the data in Fig. 2.

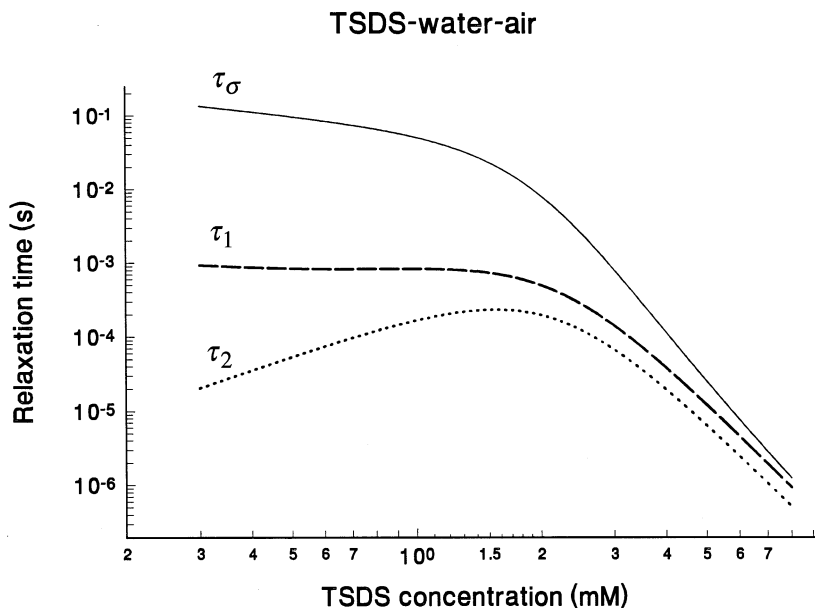


Fig. 5. Surfactant solution without added salt: relaxation times of surface tension,  $\tau_\sigma$ , of surfactant adsorption,  $\tau_1$ , and of counterion adsorption,  $\tau_2$ , calculated by means of Eqs. (58) and (87) as functions of surfactant (TSDS) concentration,  $c_{100}$ , using parameters values determined from the best fit of the data in Fig. 2.

electrolyte, at higher concentrations it suppresses the development of the diffuse electric double layer, and decreases  $Vc_2$  thus accelerating the supply of counterions to the interface; as a result  $\tau_2$  begins to decrease at the higher TSDS concentrations.

Fig. 6 shows plots of  $\tau_\sigma$  versus the surfactant concentration,  $c_{100}$ ; each of the four curves corresponds to a given fixed value of the NaCl concentration,  $c_{3\infty}$ , shown in the figure. It is important to note that the curves in Fig. 6 correspond to relatively high submicellar surfactant concentrations including the region just below the critical micellization concentration (CMC). The curves in Fig. 6 show a pronounced decrease of the surface-tension-relaxation time,  $\tau_\sigma$ , with the increase of the NaCl concentration. This prediction of the theory is consonant with numerous experimental observations that the addition of salt accelerates the kinetics of surface tension relaxation. Note however, that for lower surfactant concentrations this tendency can be inverted, see Fig. 7.

In Fig. 7  $\tau_\sigma$  is plotted versus  $c_{1\infty}$  for a range of surfactant concentrations, which is wider than

that in Fig. 6 and includes lower concentrations. The data in Fig. 6 correspond to the right-hand side of Fig. 7. As seen in Fig. 7, the theory predicts that the addition of salt (NaCl) accelerates the relaxation of the surface tension for the higher surfactant concentrations, but decelerates it for the lower surfactant concentrations. This curious inversion of the tendency can be interpreted in the following way. The accelerating effect of salt at the higher surfactant concentrations can be attributed to the suppression of the electric double layer by the added salt. At the lower surfactant concentrations (in the region of Henry) the latter effect is dominated by another effect of the opposite direction. This is the increase of  $(\partial\Gamma/\partial c_{1\infty})_{c_{2\infty}}$  due to the added salt. Indeed, the asymptotic form of Eq. (87) for the lower surfactant concentrations is

$$\tau_\sigma \equiv \frac{1}{D_1} \left( \frac{\partial\Gamma}{\partial c_{1\infty}} \right)_{c_{2\infty}}^2 (1 + 2\phi_s^{(e)})^2 \quad (100)$$

Physically, the effect of  $(\partial\Gamma/\partial c_{1\infty})_{c_{2\infty}}$  can be explained as follows. At low surfactant concentrations the diffusion supply of surfactant is very



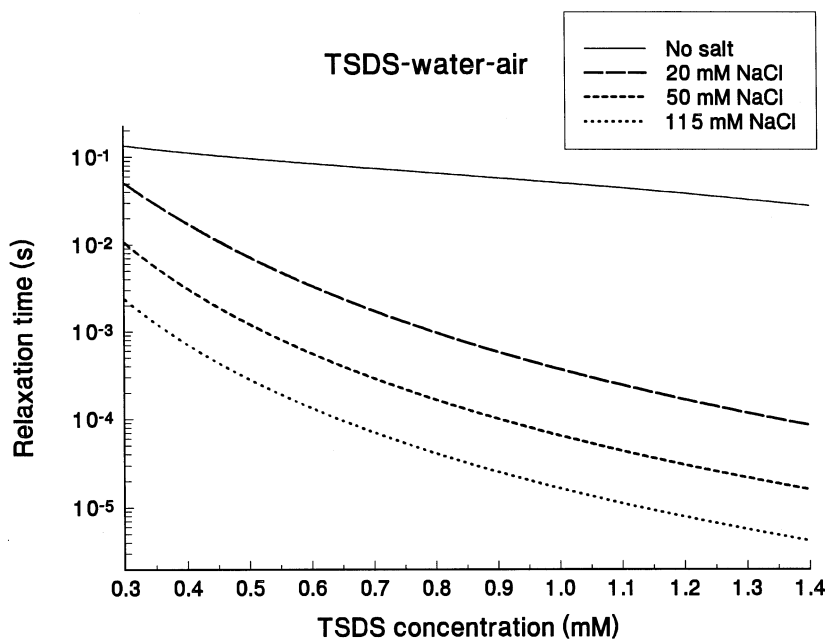


Fig. 6. Relaxation of surface tension at *relatively high* submicellar surfactant concentrations: relaxation time,  $\tau_\sigma$ , versus surfactant (TSDS) concentration,  $c_{1\infty}$ , calculated by means of Eq. (87) for four different NaCl concentrations using parameters values determined from the best fit of the data in Fig. 2.

slow and it controls the kinetics of adsorption. In the absence of salt the equilibrium surfactant adsorption monolayer is comparatively diluted, so the diffusion flux from the bulk is able to quickly equilibrate the adsorption layer. The addition of salt at low surfactant concentrations strongly increases the equilibrium surfactant adsorption; consequently, much longer time is needed for the slow diffusion influx to equilibrate the interface. This corresponds to the left-hand side branches of the curves in Fig. 7.

On the other hand, at higher surfactant concentrations the adsorption monolayer is dense and the adsorption is very weakly dependent on the surfactant and salt concentrations. In such a case the shrinking of the electric double layer because of added salt gets the upper hand and accelerates the adsorption process. This corresponds to the right-hand side branches of the curves in Fig. 7.

The comparison of our theoretical results with the experiment can be carried out in the following way. The surface tension,  $\sigma$ , can be measured by

means of the Wilhelmi plate or du Nouy ring method (for various surfactant and salt concentrations). The relaxation of  $\sigma$  with time  $t$  can be recorded until the equilibrium value is reached. Thus one obtains equilibrium and relaxation data in the *same* experiment. Next, the relaxation data for surface tension are to be plotted versus  $1/\sqrt{t}$  and the slopes of the experimental curves (in the long-time region) have to be compared with the theory using Eqs. (86) and (87). Such an experimental study is now under way.

One way to check the correctness of the analytical expressions derived by us (as well as the computer program used to calculate the results in Figs. 4–7) is to compare the output of our analytical expressions with the numerical results of MacLeod and Radke [36]. The latter numerical results have been obtained using the thermodynamic theory by Borwankar and Wasan [18] to calculate the equilibrium parameters. The counterion binding is neglected in Ref. [18], but it is taken into account in our theory, based on Eqs. (65), (66), (98) and (99). Our theory (and com-

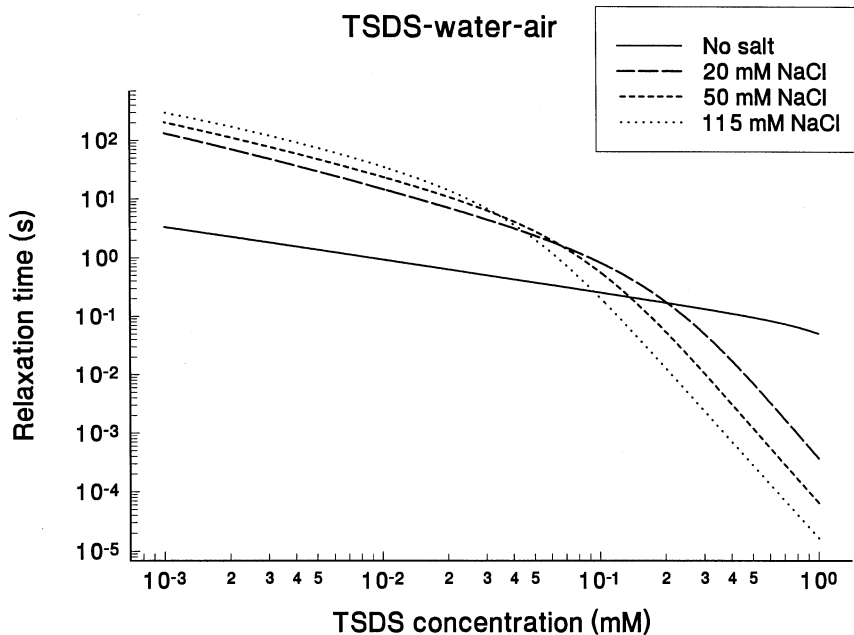


Fig. 7. Relaxation of surface tension at *low* surfactant concentrations: relaxation time,  $\tau_\sigma$ , versus surfactant (TSDS) concentration,  $c_{1\infty}$ , calculated by means of Eq. (87) for four different NaCl concentrations using parameters values determined from the best fit of the data in Fig. 2.

puter program) automatically reduce to the theory by Borwankar and Wasan setting  $K_2 = 0$  in Eqs. (65) and (66), and  $\tau_\sigma \equiv \tau_1$ . In such a case, combining Eqs. (57) and (86) we obtain

$$\begin{aligned} \sigma(t) - \sigma^{(e)} &= \left( \frac{\partial \sigma}{\partial \Gamma_1} \right)^{(e)} [\Gamma_1(t) - \Gamma_1^{(e)}] \\ &= \left( \frac{\partial \sigma}{\partial \Gamma_1} \right)^{(e)} [\Gamma_1(0) - \Gamma_1^{(e)}] \sqrt{\frac{\tau_1}{\pi t}} \end{aligned} \quad (101)$$

The continuous lines in Fig. 8 present our numerical result obtained by means of Eq. (101), which is compared with the numerical results from Fig. 17 in the paper by MacLeod and Radke [36]. The latter are presented by the full and empty symbols for solutions with and without NaCl, respectively (Fig. 8); the dotted line among the symbols is a guide to the eye. The used values of the parameters  $K$  and  $\Gamma_\infty$  have been originally determined in Ref. [36] for 1 mM solution of SDS, with 10 mM NaCl and without NaCl. One

sees in Fig. 8 that our theoretical curve coincides with the numerical results of MacLeod and Radke [36] for the *longer* times. This is an excellent agreement because Eq. (101) is in fact a long-time asymptotics, and it really behaves in this way as seen in Fig. 8.

Moreover, two additional facts deserve a special discussion. First, one sees in Fig. 8 that the numerical predictions of Eq. (101) are close to the exact computer results of Ref. [36] even for the *shorter* times. Second, the initial condition used by MacLeod and Radke [36] is  $\Gamma_1(0) = 0$ , which corresponds to a *large* initial perturbation. In other words, it turns out Eq. (101) gives good numerical predictions out of the expected range of its validity (long times, small perturbations). To explain the later fact in Table 3 we compare the values of the surfactant relaxation time  $\tau_1$  calculated by means of our Eq. (58) (corresponding to the solid lined in Fig. 8) with the respective values of  $\tau_1$  obtained by the theory of large initial perturbation developed in Ref. [50]. The data in Table 3 show that the values of the relaxation time  $\tau_1$

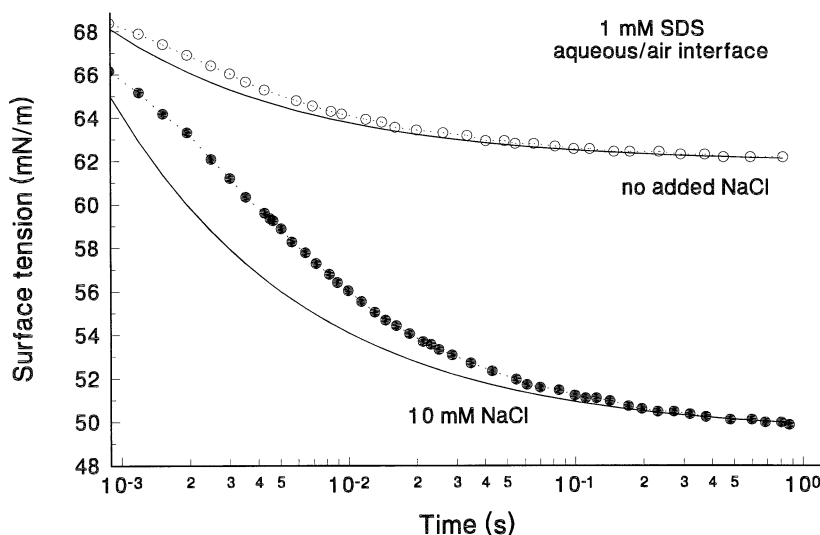


Fig. 8. Comparison with the results of MacLeod and Radke [36]. The continuous lines present our numerical results. The full and empty symbols are the numerical results of MacLeod and Radke [36].

predicted by the theories of *large* and *small* initial perturbations are very close to each other. For the time being we do not know whether this coincidence is fortuitous, or it has some physical reasons; the latter issue could be a subject of a separate study.

Finally, we would like to warn the reader, that the data in Fig. 8 are just a numerical test of our formulas, but they are not expected to agree with *experimental* data for the relaxation of surface tension of SDS solutions. This is because to calculate the curves in Fig. 8 (after Refs. [18,36]) we have neglected the counterion binding and the difference between  $\tau_\sigma$  and  $\tau_1$ ; the latter difference turns out to be a considerable effect (see Figs. 4 and 5). Therefore, to fit experimental data one should use Eq. (87), which takes into account the fact that  $\tau_\sigma \neq \tau_1$  and the effect of counterion binding.

## 7. Concluding remarks

In the present article we examine the relaxation of the surface tension of ionic surfactant solutions in the presence of dissolved non-amphiphilic salt. A disturbance of the surfactant adsorption layer

is damped by electro-diffusive transport of surfactant ions, counterions and coions. We consider the evolution of the electric double layer with time and take into account the counterion adsorption (binding). Our purpose is to find the long-time asymptotic solution of the full electro-diffusion boundary problem, Eqs. (1), (2) and (4). The basic, non-disturbed, state is a double electric layer. Assuming small perturbations the problem is linearized and a set of three differential operator equations, Eqs. (21a), (21b) and (21c), is obtained. In the asymptotic case of long times these differential equations reduce to hypergeometric equations, whose solutions, fortunately, can be expressed in terms of elementary functions, see Eqs. (32) and (36). As a result we obtain explicit expressions for the characteristic relaxation times of the adsorptions of surfactant ions and counterions in terms of the diffusivities of the ionic species and thermodynamic parameters of the adsorption layer (see Eqs. (53)–(58)). Next we determine the characteristic relaxation time of surface tension, which is different from the adsorption relaxation time because of a specific contribution from the dynamic diffuse electric double layer (see Eqs. (86) and (87)). This more general approach helped us to overcome a controversial point: we

Table 3

Comparison of values of  $\tau_1$  calculated for  $K_2 = 0$  (no counterion binding) by means of Eq. (58) and by means of the theory of relaxation after a large initial perturbation [50]<sup>a</sup>

| Concentration of NaCl (M) | $\tau_1$ (ms), from Eq. (58) (small initial perturbation) | $\tau_1$ (ms), from Ref. [50] (large initial perturbation) |
|---------------------------|---|--|
| 0                         | 1.19  | 1.16   |
| 0.01                      | 1.43  | 1.44   |

<sup>a</sup> The values of  $K$  and  $\Gamma_\infty$  are taken from Ref. [18] and correspond to 1 mM SDS concentration.

avoided using the Davies expression (Eq. (67) or Eq. (90)), which is a corollary from the *equilibrium* Boltzmann distribution of the ionic species, to calculate the perturbation of surface tension, which is in fact related to a *non-equilibrium*, diffusion controlled, ionic distribution within the electric double layer. Expressions for the equilibrium thermodynamic coefficients,  $g_{ij}$  and  $J_{\Gamma_1}$ , are derived (see Eqs. (93)–(95) and (97) and Table 2). As an illustrative example we used the best fit from Ref. [46] of the data by Tajima et al. [12,13] (see Fig. 2). The fit gives the parameters of the theoretical model,  $K_1$ ,  $K_2$ ,  $\Gamma_\infty$  and  $\beta$ . Then the corresponding adsorption and surface tension relaxation times are calculated as functions of the surfactant and salt concentrations (see Figs. 4–7). The numerical results show that the relaxation times of surface tension, surfactant adsorption and counterion adsorption,  $\tau_\sigma$ ,  $\tau_1$ , and  $\tau_2$ , respectively, satisfy the relationship  $\tau_2 < \tau_1 < \tau_\sigma$ ; the difference between these three relaxation times can be greater than one order of magnitude. The theory predicts that the addition of salt accelerates the relaxation of the surface tension for the higher surfactant concentrations, but decelerates it for the lower surfactant concentrations. This prediction is consonant with the experimental observations.

The results can be applied to interpret experimental data for surface tension relaxation at surfactant and salt concentrations in the range below the CMC. They could be also useful for a theoretical interpretation of the processes in foams and emulsions under dynamic conditions.

## Acknowledgements

This support of this study by Colgate-Palmolive is acknowledged with gratitude.

## Appendix A. Determination of the unknown coefficients from the boundary conditions

### A.1. Initial and boundary conditions for the adsorptions

The known electrostatic relation between surface charge density and gradient of the surface potential, written in terms of perturbations, reads

$$\frac{\varepsilon}{4\pi z e} \left( \frac{\partial \psi^{(p)}}{\partial x} \right)_{x=0} + \Gamma_1^{(p)} - \Gamma_2^{(p)} = 0 \quad (\text{A1})$$

Next, we substitute Eq. (44) into Eq. (A1), introduce dimensionless variables, apply Laplace transformation and use Eq. (16a), (16b) and (16d). As a result Eq. (A1) acquires the form

$$J_2 - J_1 + (g_{11} - g_{21}) \frac{dJ_1}{dy} + (g_{12} - g_{22}) \frac{dJ_2}{dy} = 0 \quad (\text{A2})$$

for  $y = 0$

When deriving Eq. (A2) we have taken into account that there is no adsorption of coions ( $\Gamma_3 \equiv 0$ ), and consequently

$$J_3 = 0 \quad \text{for } y = 0 \quad (\text{A3})$$

The interfacial mass balance of surfactant and counterions, Eq. (4), provides two additional boundary conditions. We first linearize Eq. (4), then we substitute Eq. (44) and finally we apply

Laplace transformation; in view of Eqs. (15) and (16) the result can be presented in the form

$$g_{i1} \frac{dJ_1}{dy} + g_{i2} \frac{dJ_2}{dy} - J_i = b_i \quad \text{for } y = 0 \quad (i = 1, 2) \quad (\text{A4})$$

$$b_i \equiv \frac{\kappa}{c_{2\infty}} \Delta\Gamma_i(0) \quad (\text{A5})$$

where  $\Delta\Gamma_1(0)$  and  $\Delta\Gamma_2(0)$  are the perturbations of the adsorptions of surfactant ions and counterions, respectively, at the initial moment  $t = 0$ . Summing up the forms of Eq. (A4) for  $i = 1$  and  $i = 2$ , and comparing the result with the electroneutrality condition, Eq. (A2), one obtains

$$b_1 = b_2 = b \equiv \frac{\kappa}{c_{2\infty}} \Delta\Gamma(0) \quad (\text{A6})$$

where  $\Delta\Gamma(0)$  is given by Eq. (51). In other words, we obtain that at the initial moment,  $t = 0$ , the adsorptions of surfactant ions and counterions must be equal. This requirement could seem too restrictive, but it has a deep physical meaning, which is discussed below.

As usual in adsorption relaxation problems, we presume that at the initial moment,  $t = 0$ , only the interface is disturbed, whereas the bulk of solution (including the distributions of the ionic species throughout the diffuse electric double layer) remains at the equilibrium state.

Let us assume that Eq. (51) is violated, i.e. that  $\Delta\Gamma_1(0) \neq \Delta\Gamma_2(0)$ . Then a perturbation surface charge density,  $\Delta\rho_s(0) = z_1 e [\Delta\Gamma_1(0) - \Delta\Gamma_2(0)]$ , appears, which gives rise to an additional electric field linearly increasing with the distance  $x$  from the interface:

$$\Delta\psi(x, 0) = \frac{2\pi}{\epsilon} \Delta\rho_s(0)x \quad (\text{A7})$$

In accordance with the electrostatic superposition principle the full electric field at the initial moment will be the sum:  $\psi(x, 0) = \psi^{(e)}(x) + \Delta\psi(x, 0)$ , where  $\psi^{(e)}(x)$  is the equilibrium potential of the double electric layer. From a *physical* viewpoint the appearance of an electric field linearly increasing in the bulk of an ionic solution is not acceptable; indeed, the appearance of such a field will be immediately damped by exchange

(adsorption–desorption) of ionic species between the surface and the subsurface. Moreover, from a purely formal, *mathematical*, viewpoint the existence of a linearly increasing electric field at the initial moment is also not acceptable: such a field would lead to a drastic deviations of the ionic concentrations from their equilibrium distribution, which contradicts to the underlying assumption for small deviations from equilibrium, used in this paper to linearize the electro-diffusion equations. Therefore, from both physical and mathematical viewpoint, Eq. (51) (or Eq. (A6)) is the only initial condition, which is compatible with the standard quasistatic electro-diffusion theoretical model accepted in the present study.

### A.2. Derivation of Eqs. (47) and (48)

Combining Eq. (43c) with Eq. (A3) one obtains

$$A_3 = (1 - \eta)(A_2 - A_1) + O(s) \quad (\text{A8})$$

Then from Eqs. (43a), (43b) and (A8) one derives

$$J_1^{(0)} = A_2 - A_1, \quad J_2^{(0)} = \frac{1}{\zeta^2}(A_1 + A_2) \quad \text{for } y = 0 \quad (\text{A9})$$

where  $\zeta$  is defined by Eq. (50). Differentiating Eqs. (25), (33) and (35) one can deduce

$$\left(\frac{df_1^{(0)}}{dy}\right)_{y=0} = \zeta A_1 + \zeta \frac{1 - \zeta^2}{1 + \zeta^2} A_2 - \left(\frac{2\zeta}{1 + \zeta^2}\right)^2 q A_2 \sqrt{s} + O(s) \quad (\text{A10})$$

$$\left(\frac{df_2^{(0)}}{dy}\right)_{y=0} = -\zeta A_1 + \zeta \frac{1 - \zeta^2}{1 + \zeta^2} A_2 - \left(\frac{2\zeta}{1 + \zeta^2}\right)^2 q A_2 \sqrt{s} + O(s) \quad (\text{A11})$$

$$\left(\frac{df_3^{(0)}}{dy}\right)_{y=0} = -\zeta^2 h A_3 \sqrt{3} + O(s) \quad (\text{A12})$$

Combining Eqs. (A10), (A11) and (A12) with Eqs. (18) and (A8) one derives

$$\left(\frac{dJ_1}{dy}\right)_{y=0} = \eta \zeta \left( A_1 + \frac{1 - \zeta^2}{1 + \zeta^2} A_2 \right) - \left[ \eta \left( \frac{2\zeta}{1 + \zeta^2} \right)^2 q A_2 + \zeta^2 h (1 - \eta)(A_2 - A_1) \right] \sqrt{s} + O(s) \quad (\text{A13})$$

$$\left(\frac{dJ_2}{dy}\right)_{y=0} = -\frac{1}{\zeta^3} \left( A_1 + \frac{1-\zeta^2}{1+\zeta^2} A_2 \right) - \left( \frac{2\zeta}{1+\zeta^2} \right)^2 qA_2\sqrt{s} + O(s) \quad (\text{A14})$$

The parameters  $A_1$  and  $A_2$  are to be determined by substituting Eqs. (A13) and (A14) into the boundary condition (Eq. (A4)). These equations show that the solution for  $A_1$  and  $A_2$  has the form

$$\begin{aligned} A_1 &= A_1^{(0)} + A_1^{(1)}\sqrt{s} + O(s), \\ A_2 &= A_2^{(0)} + A_2^{(1)}\sqrt{s} + O(s) \end{aligned} \quad (\text{A15})$$

Combining Eqs. (A4), (A13), (A14) and (A15) for the zeroth-order approximation one obtains

$$A_1^{(0)} = (1 - \zeta^2)\frac{b}{2}, \quad A_2^{(0)} = -(1 + \zeta^2)\frac{b}{2} \quad (\text{A16})$$

where Eq. (A6) has been also taken into account. In view of Eq. (A16) the terms of the order of  $s^0$  in Eqs. (A13) and (A14) are zero, and consequently, the leading term in the right-hand side of these equations is  $\propto \sqrt{s}$ . Further, let us introduce the notation

$$B \equiv A_1^{(1)} + \frac{1 - \zeta^2}{1 + \zeta^2} A_2^{(1)}. \quad (\text{A17})$$

Then from Eqs. (A9), (A15), (A16) and (A17) one derives

$$J_2^{(0)} - J_1^{(0)} = \frac{1 + \zeta^2}{\zeta^2} B\sqrt{s} + O(s) \quad (\text{A18})$$

Likewise, from Eqs. (A13), (A14), (A15), (A16) and (A17) one deduces

$$\left(\frac{dJ_1}{dy}\right)_{y=0} = \left[ \eta\zeta B + \frac{2\zeta^2}{1 + \zeta^2} qb + \zeta^2 h(1 - \eta)b \right] \sqrt{s} + O(s) \quad (\text{A19})$$

$$\left(\frac{dJ_2}{dy}\right)_{y=0} = \left( -\frac{B}{\zeta^3} + \frac{2qb}{1 + \zeta^2} \right) \sqrt{s} + O(s) \quad (\text{A20})$$

Next, we substitute Eqs. (A18), (A19) and (A20) into Eq. (A2) and determine the constant  $B$ :

$$\begin{aligned} B &= \frac{b}{p} \left\{ \frac{2\zeta q}{1 + \zeta^2} [(g_{22} - g_{12}) - \eta\zeta^2 (g_{11} - g_{21})] \right. \\ &\quad \left. - (1 - \eta)\zeta^4 (g_{11} - g_{21})h \right\} \end{aligned} \quad (\text{A21})$$

where  $p$  is defined by Eq. (49). Finally, a substitution of Eq. (A21) into Eqs. (A19) and (A20), after some algebra, yields Eqs. (47) and (48).

## References

- [1] P.M. Vlahovska, K.D. Danov, A. Mehreteab, G. Broze, *J. Colloid Interface Sci.* 192 (1997) 194.
- [2] S.S. Dukhin, G. Kretzschmar, R. Miller, *Dynamics of Adsorption at Liquid Interfaces: Theory, Experiment, Application*, Elsevier, Amsterdam, 1995.
- [3] G. Bleys, P. Joos, *J. Phys. Chem.* 89 (1985) 1027.
- [4] J. van Hunsel, P. Joos, *Colloid Polym. Sci.* 267 (1989) 1026.
- [5] R. Miller, *Colloid Polym. Sci.* 259 (1981) 375/1124.
- [6] R. Miller, G. Kretzschmar, *Adv. Colloid Interface Sci.* 37 (1991) 97.
- [7] G. Kretzschmar, R. Miller, *Adv. Colloid Interface Sci.* 36 (1991) 65.
- [8] L.K. Filippov, *J. Colloid Interface Sci.* 163 (1994) 49; 164 (1994) 471.
- [9] P.A. Kralchevsky, Y.S. Radkov, N.D. Denkov, *J. Colloid Interface Sci.* 161 (1993) 361.
- [10] K.D. Danov, P.M. Vlahovska, T.S. Horozov, C.D. Dushkin, P.A. Kralchevsky, A. Mehreteab, G. Broze, *J. Colloid Interface Sci.* 183 (1996) 223.
- [11] E.H. Lucassen-Reynders, *Adsorption at Fluid Interfaces*, Marcel Dekker, New York, 1981.
- [12] K. Tajima, M. Muramatsu, T. Sasaki, *Bull. Chem. Soc. Jpn.* 43 (1970) 1991.
- [13] K. Tajima, *Bull. Chem. Soc. Jpn.* 43 (1970) 3063.
- [14] K. Tajima, *Bull. Chem. Soc. Jpn.* 44 (1971) 1767.
- [15] A.W. Cross, G.G. Jayson, *J. Colloid Interface Sci.* 162 (1994) 45.
- [16] E.H. Lucassen-Reynders, *J. Phys. Chem.* 70 (1966) 1777.
- [17] S. Hachisu, *J. Colloid Interface Sci.* 33 (1970) 445.
- [18] R.P. Borwankar, D.T. Wasan, *Chem. Eng. Sci.* 43 (1988) 1323.
- [19] D.G. Hall, *Colloid Surf. A* 90 (1994) 285.
- [20] V.V. Kalinin, C.J. Radke, *Colloid Surf. A* 114 (1996) 337.
- [21] R. van den Bogaert, P. Joos, *J. Phys. Chem.* 83 (1979) 17.
- [22] V.B. Fainerman, *Koll. Zh.* 40 (1978) 924.
- [23] V.B. Fainerman, V.D. Jamilova, *Zh. Fiz. Khim.* 60 (1986) 1184.
- [24] V.B. Fainerman, *Colloids Surf. A* 57 (1991) 249.
- [25] V.B. Fainerman, A.V. Makievski, R. Miller, *Colloids Surf. A* 87 (1994) 61.
- [26] G. Geeraerts, Ph.D. Thesis, Department of Chemistry, University of Antwerpen, 1994.
- [27] P. Joos, J. Fang, G. Serrien, *J. Colloid Interface Sci.* 151 (1992) 144.
- [28] A. Bonfillon, F. Sicoli, D. Langevin, *J. Colloid Interface Sci.* 168 (1994) 497.
- [29] X.Y. Hua, M.J. Rosen, *J. Colloid Interface Sci.* 141 (1991) 180.

- [30] S. Dukhin, R. Miller, G. Kretzschmar, *Colloid Polym. Sci.* 261 (1983) 335.
- [31] S. Dukhin, R. Miller, G. Kretzschmar, *Colloid Polym. Sci.* 263 (1985) 420.
- [32] S. Dukhin, R. Miller, *Colloid Polym. Sci.* 269 (1991) 923.
- [33] S. Dukhin, R. Miller, *Colloid Polym. Sci.* 272 (1994) 548.
- [34] A. Bonfillon, D. Langevin, *Langmuir* 10 (1994) 2965.
- [35] P. Joos, J. van Hunsel, G. Bleys, *J. Phys. Chem.* 90 (1986) 3386.
- [36] C. MacLeod, C. Radke, *Langmuir* 10 (1994) 3555.
- [37] K. Sutherland, *Austr. J. Sci. Res. Ser. A* 5 (1952) 683.
- [38] P.A. Kralchevsky, T.D. Gurkov, I.B. Ivanov, *Colloids Surf.* 56 (1991) 149.
- [39] S.B. Johnson, S.J. Drummond, P.J. Scales, S. Nishimura, *Langmuir* 11 (1995) 2367.
- [40] R.G. Alargova, K.D. Danov, J.T. Petkov, P.A. Kralchevsky, G. Broze, A. Mehreteab, *Langmuir* 13 (1997) 5544.
- [41] A.W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York, 1986.
- [42] J.N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1992.
- [43] G. Gouy, *J. Phys. Radium* 9 (1910) 457.
- [44] J.T. Davies, E.K. Rideal, *Interfacial Phenomena*, Academic Press, London, 1963.
- [45] M. Abramowitz, I.A. Stegun, *Handbook of Mathematical Functions*, Dover, New York, 1965.
- [46] P.A. Kralchevsky, K.D. Danov, G. Broze, A. Mehreteab, *Langmuir* 15 (1999) 2351.
- [47] O. Stern, *Ztschr. Elektrochem.* 30 (1924) 508.
- [48] J.T. Davies, *Proc. R. Soc. Ser. A* 208 (1951) 224.
- [49] N. Kamenka, B. Lindman, B. Brun, *Colloid Polym. Sci.* 252 (1974) 144.
- [50] V.L. Kolev, K.D. Danov, P.A. Kralchevsky, G. Broze, A. Mehreteab (in preparation).