

# Influence of electrolytes on the dynamic surface tension of ionic surfactant solutions: Expanding and immobile interfaces

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## Abstract

Here, we derive analytical asymptotic expressions for the dynamic surface tension of ionic surfactant solutions in the general case of nonstationary interfacial expansion. Because the diffusion layer is much wider than the electric double layer, the equations contain a small parameter. The resulting perturbation problem is singular and it is solved by means of the method of matched asymptotic expansions. The derived general expression for the dynamic surface tension is simplified for the special case of immobile interface and for the maximum bubble pressure method (MBPM). The case of stationary interfacial expansion is also considered. The effective diffusivity of the ionic surfactant essentially depends on the concentrations of surfactant and nonamphiphilic salt. To test the theory, the derived equations are applied to calculate the surfactant adsorption from MBPM experimental data. The results excellently agree with the adsorption determined independently from equilibrium surface-tension isotherms. The derived theoretical expressions could find application for interpreting data obtained by MBPM and other experimental methods for investigating interfacial dynamics.

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## 1. Introduction

In the case of ionic surfactants, the existence of a diffuse electric double layer essentially influences the thermodynamics and kinetics of adsorption. The process of adsorption is accompanied with a progressive increase of the surface charge density and electric potential. The charged surface repels the new-coming surfactant molecules, which results in a deceleration of the adsorption process [1,2]. The theoretical studies on dynamics of adsorption encounter difficulties with the nonlinear set of partial differential equations, which describes the electro-diffusion process. The quasi-equilibrium model developed by Dukhin et al. [3–6] employs the simplifying assumption that the characteristic diffusion time is much greater than the time of formation of the electric double layer, and then the electro-diffusion process is modeled as a process of mixed barrier-diffusion control. Similar ap-

proach is followed by Borwankar and Wasan [7]. The solution of the problem for the case of small periodic surface perturbations, like those observed with the oscillating bubble technique [8,9], was obtained by Bonfillon and Langevin [10]; the results were applied to interpret data obtained by means of the longitudinal-wave method for adsorption monolayers of ionic surfactant. McLeod and Radke [11] obtained numerical solutions of the electro-diffusion problem, thus avoiding the simplifying assumptions of the quasi-equilibrium model. Such numerical solutions are mathematically rigorous, but they are time-consuming when applied to process experimental data. The analysis in Ref. [11] was extended by Datwani and Stebe [12] in the electrostatic limit. Their model considers the cases of diffusion control and adsorption–desorption kinetic barriers [12].

Analytical theories of the relaxation of surface tension of a quiescent interface have been proposed for the cases of no added electrolyte [13], small [14], and large [15] deviations from equilibrium. Ferri et al. [16] analyzed the effect of interfacial curvature on the adsorption at the surface of pendant

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bubbles and compared numerical solutions, asymptotic expressions and experimental data. The adsorption dynamics in the case of stationary expansion of a fluid interface has been also investigated [17]. In some of these studies [13,14,17], the adsorption (binding) of counterions at the conversely charged surfactant headgroups in the adsorption layer was taken into account. The bound counterions affect strongly the adsorption kinetics insofar as up to 70–90% of the surface electric charge could be neutralized by them [18–20]. Thus, it turns out that in the case of ionic surfactants (with or without added salt) there are two adsorbing species: the surfactant ions and the counterions.

In the simpler case of *nonionic* surfactants, and for a surface, which had been initially disturbed and after that it was immobile during the whole process of surfactant adsorption, Hansen [21] derived the following expression for the time dependence of the subsurface surfactant concentration,  $c_{1s}(t)$ :

$$c_{1s} = c_{1\infty} - \frac{\Gamma_{1,\text{eq}} - \Gamma_1^0}{(\pi D_1 t)^{1/2}}, \quad (1.1)$$

where  $t$  is time;  $c_{1\infty}$  is the bulk surfactant concentration;  $\Gamma_1^0$  and  $\Gamma_{1,\text{eq}}$  are, respectively, the initial and equilibrium surfactant adsorptions;  $D_1$  is the diffusion coefficient of the surfactant molecules. Equation (1.1) is applicable for surfactant concentrations lower than the critical micelle concentration (CMC). The validity of the Hansen asymptotic formula, Eq. (1.1), was confirmed in [22,23]. For small deviations from equilibrium, one could use the Gibbs adsorption equation:

$$\gamma - \gamma_{\text{eq}} = -kT \Gamma_{1,\text{eq}} \frac{c_{1s} - c_{1\infty}}{c_{1\infty}}, \quad (1.2)$$

where  $\gamma_{\text{eq}}$  is the equilibrium surface tension;  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature. Combining Eqs. (1.1) and (1.2), we obtain

$$\gamma = \gamma_{\text{eq}} + \frac{s_{\gamma,0}}{t^{1/2}}, \quad (1.3)$$

$$s_{\gamma,0} \equiv \frac{kT \Gamma_{1,\text{eq}}^2}{(\pi D_1)^{1/2} c_{1\infty}}. \quad (1.4)$$

$s_{\gamma,0}$  is the slope parameter for an immobile interface; at the last step we have used the assumption  $\Gamma_0 \ll \Gamma_{\text{eq}}$ .

Here, our aim is to generalize Eqs. (1.3) and (1.4) in two respects: (i) for ionic surfactants in the presence or absence of added electrolyte, and (ii) for an expanding fluid interface, like that realized with the maximum bubble pressure method (MBPM) [24–26], expanding drop method [27–29], the strip method [30,31], and the overflowing cylinder method [17,32–35]. (The  $\gamma(t)$  dependence for immobile interfaces can be deduced as a special case.) In particular, we will show that in the case of MBPM, the generalization of Eqs. (1.3) and (1.4) reads:

$$\gamma = \gamma_{\text{eq}} + \frac{s_{\gamma}}{(t_{\text{age}})^{1/2}}, \quad (1.5)$$

$$s_{\gamma} \equiv \frac{kT \Gamma_{1,\text{eq}}^2 \lambda}{(\pi D_{\text{eff}})^{1/2} \gamma_{\pm}} \left( \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \right), \quad (1.6)$$

where  $t_{\text{age}}$  is the bubble surface age, i.e., the period of time between the minimum pressure (at bubble formation) and the maximum pressure (before bubble detachment);  $\lambda$  is a dimensionless constant of the MBPM apparatus that can be determined in calibration experiments [36];  $c_{2\infty}$  is the bulk concentration of counterions;  $\gamma_{\pm}$  is the activity coefficient;  $D_{\text{eff}}$  is an effective diffusivity that depends on the concentrations of surfactant and salt, and is defined by Eqs. (6.16)–(6.23) below. It is established that Eqs. (1.5) and (1.6) provide exact quantitative interpretation of MBPM experimental data; see Section 8 for details.

The paper is structured as follows. In Sections 2 and 3 we formulate the basic equations, introduce appropriate dimensionless variables. In Sections 4 and 5 we consider the two asymptotic regions: the relatively narrow electric double layer near the interface and the much wider diffusion layer. In Sections 6 and 7 we derive and discuss the expressions for the dynamic surface tension in the cases of nonstationary and stationary interfacial expansion. Finally, in Section 8 we test the derived theoretical expressions by comparison with experimental data obtained by means of the maximum bubble pressure method.

## 2. Formulation of the diffusion problem

We consider adsorption from the solution of an ionic surfactant in the presence of added nonamphiphilic electrolyte (salt). For simplicity, we assume that the counterions due to the surfactant and salt are the same. Thus, the solution contains three components, which will be denoted as follows: 1—surfactant ions; 2—counterions, and 3—coions. For example, in Section 8 we consider solutions of sodium dodecyl sulfate (SDS) + added NaCl, for which component 1 is  $\text{DS}^-$ , component 2 is  $\text{Na}^+$ , and component 3 is  $\text{Cl}^-$ . Because of the electroneutrality of the solution, the bulk concentrations of the three ionic species,  $c_{1\infty}$ ,  $c_{2\infty}$ , and  $c_{3\infty}$ , are related:

$$c_{2\infty} = c_{1\infty} + c_{3\infty}. \quad (2.1)$$

Furthermore, we assume that the valence of the surfactant ions and coions is  $Z$ , while the valence of the counterions is  $-Z$ . Because of the adsorption of charged surfactant molecules, an electric double layer appears near the surface of the solution [37]. The electric potential of the double layer will be denoted by  $\psi$ . It is convenient to introduce the dimensionless electric potential,  $\Phi = Ze\psi/(kT)$ , where  $e$  is the electronic charge; because  $Z$  and  $\psi$  have the same sign, we have  $\Phi \geq 0$ .

Let us consider a flat interface that is subjected to dilatation with expansion rate:

$$\dot{\alpha}(t) \equiv \frac{1}{A} \frac{dA}{dt}. \quad (2.2)$$

Here,  $t$  is time and  $A(t)$  is the interfacial area. Let  $x$  be coordinate normal to the interface and  $x = 0$  at the interface, see Fig. 1. Because of the adsorption process, the concentrations of the ionic species and the electric potential are functions of the spatial coordinate and time:  $c_1(x, t)$ ,  $c_2(x, t)$ ,  $c_3(x, t)$ , and  $\Phi(x, t)$ . The latter four functions can be determined from the

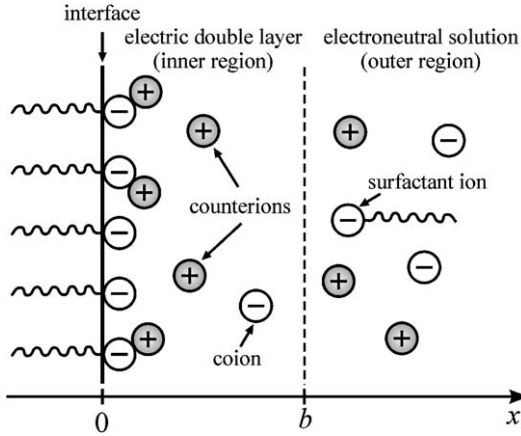


Fig. 1. Sketch of the interfacial zone of an ionic surfactant solution. Both surfactant ions and counterions adsorb, while the coions do not adsorb at the interface. In the “inner” region, an electric double layer of non-zero bulk charge density is developed. In the “outer” region, the bulk charge density is zero, but in spite of that the ionic concentrations vary during the adsorption process. The plane  $x = b$  is located in the transitional zone between the inner and outer regions.

three equations of convective diffusion and the Poisson equation [13–15]:

$$\frac{\partial c_1}{\partial t} - \dot{\alpha}x \frac{\partial c_1}{\partial x} = D_1 \frac{\partial}{\partial x} \left( \frac{\partial c_1}{\partial x} + c_1 \frac{\partial \Phi}{\partial x} \right), \quad (2.3)$$

$$\frac{\partial c_2}{\partial t} - \dot{\alpha}x \frac{\partial c_2}{\partial x} = D_2 \frac{\partial}{\partial x} \left( \frac{\partial c_2}{\partial x} - c_2 \frac{\partial \Phi}{\partial x} \right), \quad (2.4)$$

$$\frac{\partial c_3}{\partial t} - \dot{\alpha}x \frac{\partial c_3}{\partial x} = D_3 \frac{\partial}{\partial x} \left( \frac{\partial c_3}{\partial x} + c_3 \frac{\partial \Phi}{\partial x} \right), \quad (2.5)$$

$$\frac{\partial^2 \Phi}{\partial x^2} = \frac{\kappa^2}{2c_{2\infty}} (c_2 - c_1 - c_3) \quad (2.6)$$

( $x > 0$  and  $t > 0$ ). Here,  $D_1$ ,  $D_2$ , and  $D_3$  are the bulk diffusion coefficient of the respective ions;  $\kappa$  is the Debye screening parameter:

$$\kappa^2 = \frac{8\pi Z^2 e^2 c_{2\infty}}{\epsilon k T}. \quad (2.7)$$

The convective terms in Eqs. (2.3)–(2.5) are written in the framework of the approximation by van Voorst Vader et al. [38], viz.  $\mathbf{v} \cdot \nabla c_i = -\dot{\alpha}x (\partial c_i / \partial x)$ , where  $\mathbf{v}$  is the velocity.

At large distances from the surface, the electric potential is zero and the concentrations of the three ionic components are equal to  $c_{1\infty}$ ,  $c_{2\infty}$ , and  $c_{3\infty}$ . The adsorptions of these components at the interface will be denoted by  $\Gamma_1$ ,  $\Gamma_2$ , and  $\Gamma_3$ , respectively. As a rule, the coions do not adsorb [20], and then  $\Gamma_3 = 0$ . The mass balance equations at the interface ( $x = 0$ ) read [13–15]:

$$\frac{d\Gamma_1}{dt} + \dot{\alpha}\Gamma_1 = D_1 \left( \frac{\partial c_1}{\partial x} + c_1 \frac{\partial \Phi}{\partial x} \right)_{x=0}, \quad (2.8)$$

$$\frac{d\Gamma_2}{dt} + \dot{\alpha}\Gamma_2 = D_2 \left( \frac{\partial c_2}{\partial x} - c_2 \frac{\partial \Phi}{\partial x} \right)_{x=0}, \quad (2.9)$$

$$0 = \left( \frac{\partial c_3}{\partial x} + c_3 \frac{\partial \Phi}{\partial x} \right)_{x=0} \quad (2.10)$$

( $\Gamma_3 = 0$ ). The boundary condition for the normal component of the electric field intensity at the interface [39] can be presented in the form:

$$\frac{\partial \Phi}{\partial x} \Big|_{x=0} = -\frac{\kappa^2}{2c_{2\infty}} (\Gamma_1 - \Gamma_2). \quad (2.11)$$

The considered equations satisfy the electroneutrality condition, which states that the sum of the net surface charge and the bulk excess charge must be equal to zero. Indeed, by integration of the Poisson equation, Eq. (2.6), along with Eqs. (2.1) and (2.11), we obtain

$$\Gamma_1 - \Gamma_2 = \Lambda_2 - \Lambda_1 - \Lambda_3, \quad (2.12)$$

$$\Lambda_i \equiv \int_0^\infty (c_i - c_{i\infty}) dx, \quad i = 1, 2, 3. \quad (2.13)$$

Equation (2.12) can be presented in the alternative form [20,40,41]:

$$\tilde{\Gamma}_2 = \tilde{\Gamma}_1 + \tilde{\Gamma}_3, \quad (2.14)$$

where

$$\tilde{\Gamma}_i \equiv \Gamma_i + \Lambda_i, \quad i = 1, 2, 3, \quad (2.15)$$

is the ‘total’ adsorption, which includes both the ions adsorbed at the interface ( $\Gamma_i$ ) and the excess ions in the diffuse electric double layer ( $\Lambda_i$ ). (In our case  $\Gamma_3 = 0$ .) The computations [20] show that for not too low ionic strengths,  $Z^2 c_{2\infty} \geq 1$  mM, the diffuse electric double layer is relatively narrow, and then  $\Lambda_1$  is negligible, so that  $\tilde{\Gamma}_1 \approx \Gamma_1$ .

### 3. Two length scales and small parameter

Two different length scales characterize the considered system. The first one is determined by the Debye length,  $\kappa^{-1}$ , characterizing the thickness of the electric double layer. The second length scale,  $L_d$ , characterizes the thickness of the layer in which diffusion takes place:  $L_d = (D_1 t_{\text{age}})^{1/2}$ , where  $t_{\text{age}}$  is the characteristic surface age. As mentioned above, for the maximum bubble pressure method,  $t_{\text{age}}$  is the period of time between the moments of minimum pressure (bubble formation) and maximum pressure (before the bubble detachment). For typical parameter values,  $t_{\text{age}} = 1$  ms and  $D_1 = 5.5 \times 10^{-10}$  m<sup>2</sup>/s, we estimate  $L_d = 742$  nm. On the other hand, at ionic strength  $c_{2\infty} = 1$  mM, we calculate  $\kappa^{-1} = 9.6$  nm. Thus, it turns out that the ratio of the two length scales represents a small parameter:

$$\delta = \frac{\kappa^{-1}}{L_d} \ll 1. \quad (3.1)$$

Let us introduce dimensionless coordinate,  $\tilde{x}$ , and time,  $\tilde{t}$ , as follows:

$$\tilde{x} = x/L_d, \quad \tilde{t} = t/t_{\text{age}}. \quad (3.2)$$

In terms of these dimensionless variables, Eqs. (2.3)–(2.6) acquire the form:

$$\frac{\partial c_1}{\partial \tilde{t}} - \tilde{x} \frac{\partial c_1}{\partial \tilde{x}} \frac{d\alpha}{d\tilde{t}} = \frac{\partial}{\partial \tilde{x}} \left( \frac{\partial c_1}{\partial \tilde{x}} + c_1 \frac{\partial \Phi}{\partial \tilde{x}} \right), \quad (3.3)$$

$$\frac{\partial c_2}{\partial \tilde{t}} - \tilde{x} \frac{\partial c_2}{\partial \tilde{x}} \frac{d\alpha}{d\tilde{t}} = \frac{D_2}{D_1} \frac{\partial}{\partial \tilde{x}} \left( \frac{\partial c_2}{\partial \tilde{x}} - c_2 \frac{\partial \Phi}{\partial \tilde{x}} \right), \quad (3.4)$$

$$\frac{\partial c_3}{\partial \tilde{t}} - \tilde{x} \frac{\partial c_3}{\partial \tilde{x}} \frac{d\alpha}{d\tilde{t}} = \frac{D_3}{D_1} \frac{\partial}{\partial \tilde{x}} \left( \frac{\partial c_3}{\partial \tilde{x}} + c_3 \frac{\partial \Phi}{\partial \tilde{x}} \right), \quad (3.5)$$

$$\delta^2 \frac{\partial^2 \Phi}{\partial \tilde{x}^2} = \frac{c_2 - c_1 - c_3}{2c_{2\infty}} \quad (3.6)$$

( $\tilde{x} > 0$  and  $\tilde{t} > 0$ ). Here, in view of Eq. (2.2), we have used the notation  $\alpha = \ln A$ . Because a small parameter,  $\delta^2$ , appears before the second derivative in Eq. (3.6), we are dealing with a singular perturbation problem [42–44].

Introducing the dimensionless variables, Eq. (3.2), into the boundary conditions, Eqs. (2.8)–(2.10), we obtain:

$$\frac{d\Gamma_1}{d\tilde{t}} + \Gamma_1 \frac{d\alpha}{d\tilde{t}} = L_d \left( \frac{\partial c_1}{\partial \tilde{x}} + c_1 \frac{\partial \Phi}{\partial \tilde{x}} \right)_{\tilde{x}=0}, \quad (3.7)$$

$$\frac{d\Gamma_2}{d\tilde{t}} + \Gamma_2 \frac{d\alpha}{d\tilde{t}} = L_d \frac{D_2}{D_1} \left( \frac{\partial c_2}{\partial \tilde{x}} - c_2 \frac{\partial \Phi}{\partial \tilde{x}} \right)_{\tilde{x}=0}, \quad (3.8)$$

$$\left( \frac{\partial c_3}{\partial \tilde{x}} + c_3 \frac{\partial \Phi}{\partial \tilde{x}} \right)_{\tilde{x}=0} = 0. \quad (3.9)$$

The small parameter,  $\delta$ , does not appear in the boundary conditions (3.7)–(3.9).

Because we are dealing with a singular perturbation method, we could find a solution of the problem by means of the method of matched asymptotic expansions [42–44]. For this goal, we will consider an *inner* region of characteristic thickness  $\kappa^{-1}$  representing the electric double layer, and an *outer* region of characteristic thickness  $L_d$  where diffusion transport takes place (Fig. 1). We will find the leading terms of the asymptotic solutions in the two regions and will match them by using the approach of Prandtl for matching of the leading terms in the outer and inner asymptotic expansions [44]. The approach used in the present paper is similar to that applied in Ref. [17]. The difference is that here we consider mostly nonstationary processes and that the object of our theoretical survey is not only the adsorption, but also the interfacial tension,  $\gamma$ , and the effective diffusivity,  $D_{\text{eff}}$ ; see below.

The equations in the present paper are formulated for a planar interface. They can be applied also to curved interfaces when the characteristic thickness of the diffusion layer is much smaller than the interfacial curvature radius,  $L_d \ll R$ . In the typical MBPM experiments,  $R \geq 100\text{--}150 \mu\text{m}$  [36], so that the latter relation is satisfied. As established by Ferri et al. [16], the curvature effects could become important at early times for dilute solutions. The analysis of the curvature effects at an expanding interface could be a subject of a subsequent study.

#### 4. The diffusion problem in the inner region

Following the method of matched asymptotic expansions [42–44], we have to “expand” the spatial coordinate in the inner region by introducing a new coordinate:

$$\tilde{x}_{\text{in}} = \tilde{x}/\delta. \quad (4.1)$$

In terms of the new variable, Eqs. (3.3)–(3.5) acquire the form:

$$\delta^2 \left( \frac{\partial c_1}{\partial \tilde{t}} - \tilde{x}_{\text{in}} \frac{\partial c_1}{\partial \tilde{x}_{\text{in}}} \frac{d\alpha}{d\tilde{t}} \right) = \frac{\partial}{\partial \tilde{x}_{\text{in}}} \left( \frac{\partial c_1}{\partial \tilde{x}_{\text{in}}} + c_1 \frac{\partial \Phi}{\partial \tilde{x}_{\text{in}}} \right), \quad (4.2)$$

$$\delta^2 \left( \frac{\partial c_2}{\partial \tilde{t}} - \tilde{x}_{\text{in}} \frac{\partial c_2}{\partial \tilde{x}_{\text{in}}} \frac{d\alpha}{d\tilde{t}} \right) = \frac{D_2}{D_1} \frac{\partial}{\partial \tilde{x}_{\text{in}}} \left( \frac{\partial c_2}{\partial \tilde{x}_{\text{in}}} - c_2 \frac{\partial \Phi}{\partial \tilde{x}_{\text{in}}} \right), \quad (4.3)$$

$$\delta^2 \left( \frac{\partial c_3}{\partial \tilde{t}} - \tilde{x}_{\text{in}} \frac{\partial c_3}{\partial \tilde{x}_{\text{in}}} \frac{d\alpha}{d\tilde{t}} \right) = \frac{D_3}{D_1} \frac{\partial}{\partial \tilde{x}_{\text{in}}} \left( \frac{\partial c_3}{\partial \tilde{x}_{\text{in}}} + c_3 \frac{\partial \Phi}{\partial \tilde{x}_{\text{in}}} \right) \quad (4.4)$$

( $\tilde{x}_{\text{in}} > 0$  and  $\tilde{t} > 0$ ). Because  $\delta$  is a small parameter, the leading order solution of Eqs. (4.2)–(4.4) represents a steady-state Boltzmann distribution:

$$c_2 = c_{2b} \exp(\Phi - \Phi_b), \quad c_i = c_{ib} \exp[-(\Phi - \Phi_b)], \quad i = 1, 3. \quad (4.5)$$

Here,  $c_{1b}$ ,  $c_{2b}$ ,  $c_{3b}$ , and  $\Phi_b$ , are the values of the concentrations and the electric potential at the outer boundary of the inner region, i.e. at  $\tilde{x}_{\text{in}} \gg 1$ . The values of the latter four parameters have to be determined by matching with the solution in the outer region. From Eq. (3.6), it follows that in leading-order approximation, in the outer region we have:

$$c_{2b} = c_{1b} + c_{3b}, \quad (4.6)$$

i.e., at its outer boundary the inner region (the electric double layer) is bordered by an electroneutral solution, as it could be expected. Substituting Eqs. (4.1) and (4.5) into the Poisson equation (3.6), we obtain

$$\frac{\partial^2}{\partial \tilde{x}_{\text{in}}^2} (\Phi - \Phi_b) = \frac{c_{2b}}{c_{2\infty}} \sinh(\Phi - \Phi_b). \quad (4.7)$$

The solution of Eq. (4.7) is

$$\tanh\left(\frac{\Phi - \Phi_b}{4}\right) = \tanh\left(\frac{\Phi_s - \Phi_b}{4}\right) \exp(-\kappa_b x). \quad (4.8)$$

Here,  $\Phi_s = \Phi_s(t)$  is the surface electric potential (at  $x = 0$ , Fig. 1), and  $\kappa_b$  is the Debye parameter in terms of  $c_{2b}$ , that is  $\kappa_b^2 = \kappa^2 c_{2b}/c_{2\infty}$ . The form of Eq. (4.8) is analogous to the known expression for the distribution of the electric potential in an equilibrium electric double layer [37].

Equations (4.5)–(4.7) show that the leading term of the asymptotics in the inner region describes a quasistatic electric double layer, which exists in equilibrium with the outer region. Our next task is to determine the parameters  $c_{1b}$ ,  $c_{2b}$ , and  $c_{3b}$ .

#### 5. The diffusion problem in the outer region

In the *outer* region, in leading-order approximation the Poisson equation (3.6) yields:

$$c_2 = c_1 + c_3 \quad (5.1)$$

( $\delta \ll 1$ ). Equation (5.1) means that the solution is electroneutral everywhere in the outer region. In particular, Eq. (4.6) represents a limiting form of Eq. (5.1) for the inner boundary of the outer region. In view of Eq. (5.1), we sum up Eqs. (3.3) and (3.5) and subtract Eq. (3.4). The result reads:

$$\frac{\partial}{\partial \tilde{x}} \left\{ (D_1 - D_2) \frac{\partial c_1}{\partial \tilde{x}} + (D_3 - D_2) \frac{\partial c_3}{\partial \tilde{x}} + [(D_1 + D_2)c_1 + (D_3 + D_2)c_3] \frac{\partial \Phi}{\partial \tilde{x}} \right\} = 0. \quad (5.2)$$

Integrating Eq. (5.2), we obtain

$$\frac{\partial \Phi}{\partial \tilde{x}} = \frac{D_2 - D_1}{D_{21}c_1 + D_{23}c_3} \frac{\partial c_1}{\partial \tilde{x}} + \frac{D_2 - D_3}{D_{21}c_1 + D_{23}c_3} \frac{\partial c_3}{\partial \tilde{x}}, \quad (5.3)$$

$$D_{ij} = D_i + D_j, \quad i, j = 1, 2, 3. \quad (5.4)$$

The integration constant in Eq. (5.3) is zero because all derivatives in this equation tend to zero at  $\tilde{x} \rightarrow \infty$ . Because the concentrations in the outer region are not uniform,  $c_1 = c_1(\tilde{x}, \tilde{t})$ ,  $c_3 = c_3(\tilde{x}, \tilde{t})$ , Eq. (5.3) leads to the nontrivial conclusion that the electric potential,  $\Phi = \Phi(\tilde{x}, \tilde{t})$ , is not zero in the outer region, despite the electroneutrality of the solution; see Eq. (5.1). The substitution of Eq. (5.3) into Eqs. (3.3) and (3.5) gives:

$$\frac{\partial c_1}{\partial \tilde{t}} - \tilde{x} \frac{\partial c_1}{\partial \tilde{x}} \frac{d\alpha}{d\tilde{t}} = \frac{\partial}{\partial \tilde{x}} \left( f_{11} \frac{\partial c_1}{\partial \tilde{x}} + f_{13} \frac{\partial c_3}{\partial \tilde{x}} \right), \quad (5.5)$$

$$\frac{\partial c_3}{\partial \tilde{t}} - \tilde{x} \frac{\partial c_3}{\partial \tilde{x}} \frac{d\alpha}{d\tilde{t}} = \frac{D_3}{D_1} \frac{\partial}{\partial \tilde{x}} \left( f_{31} \frac{\partial c_1}{\partial \tilde{x}} + f_{33} \frac{\partial c_3}{\partial \tilde{x}} \right) \quad (5.6)$$

( $\tilde{x} > 0$  and  $\tilde{t} > 0$ ), where

$$f_{11}(c_1, c_3) = \frac{2D_2c_1 + D_{23}c_3}{D_{21}c_1 + D_{23}c_3}, \quad (5.7)$$

$$f_{13}(c_1, c_3) = \frac{(D_2 - D_3)c_1}{D_{21}c_1 + D_{23}c_3}, \quad (5.8)$$

$$f_{31}(c_1, c_3) = \frac{(D_2 - D_1)c_3}{D_{21}c_1 + D_{23}c_3}, \quad (5.9)$$

$$f_{33}(c_1, c_3) = \frac{D_{21}c_1 + 2D_2c_3}{D_{21}c_1 + D_{23}c_3}. \quad (5.10)$$

Thus, the problem is reduced to determining  $c_1$  and  $c_3$  from Eqs. (5.5) and (5.6). Next,  $c_2$  and  $\Phi$  can be found from Eqs. (5.1) and (5.3).

To solve the problem, we need also initial and boundary conditions. Because at the initial moment only the interface is disturbed, the initial conditions in the outer region are:

$$c_i(\tilde{x}, 0) = c_{i\infty}, \quad i = 1, 2, 3. \quad (5.11)$$

In comparison with the length scale in the outer region, the inner region (the electric double layer) is very narrow, and in first-order approximation it can be treated as a two-dimensional continuum. This viewpoint is equivalent to the thermodynamic approach of Gibbs [45,46], where the solution is considered as a uniform phase (in our case—electroneutral phase), and the excesses of all components in the subsurface zone are ascribed to the interface as adsorptions,  $\tilde{\Gamma}_i$ ,  $i = 1, 2, 3$ . We recall that the ‘total’ adsorptions  $\tilde{\Gamma}_i$  include contributions from both the adsorption layer and diffuse electric double layer; see Eq. (2.15) and Fig 1. The only difference with the equilibrium case is that in Eq. (2.13)  $c_{i\infty}$  has to be replaced by  $c_{ib}$ ; see Appendix A for details. Thus, the inner boundary conditions for the outer region are analogous to Eqs. (2.8)–(2.10), with the only difference that  $\tilde{\Gamma}_i$  is replaced by  $\tilde{\Gamma}_i$ :

$$\frac{d\tilde{\Gamma}_1}{d\tilde{t}} + \tilde{\Gamma}_1 \frac{d\alpha}{d\tilde{t}} = L_d \left( \frac{\partial c_1}{\partial \tilde{x}} + c_1 \frac{\partial \Phi}{\partial \tilde{x}} \right)_{\tilde{x}=0}, \quad (5.12)$$

$$\frac{d\tilde{\Gamma}_2}{d\tilde{t}} + \tilde{\Gamma}_2 \frac{d\alpha}{d\tilde{t}} = L_d \frac{D_2}{D_1} \left( \frac{\partial c_2}{\partial \tilde{x}} - c_2 \frac{\partial \Phi}{\partial \tilde{x}} \right)_{\tilde{x}=0}, \quad (5.13)$$

$$\frac{d\tilde{\Gamma}_3}{d\tilde{t}} + \tilde{\Gamma}_3 \frac{d\alpha}{d\tilde{t}} = L_d \frac{D_3}{D_1} \left( \frac{\partial c_3}{\partial \tilde{x}} + c_3 \frac{\partial \Phi}{\partial \tilde{x}} \right)_{\tilde{x}=0} \quad (5.14)$$

(in our case,  $\Gamma_3 = 0$  and  $\tilde{\Gamma}_3 = \Lambda_3$ ). The derivation of Eqs. (5.12)–(5.14) from Eqs. (2.3)–(2.5) and (2.8)–(2.10) is given in Appendix A. It should be noted that Eqs. (5.12)–(5.14) are compatible with the condition for electroneutrality of the electric double layer,  $\tilde{\Gamma}_2 = \tilde{\Gamma}_1 + \tilde{\Gamma}_3$ . Indeed, if we sum up Eqs. (5.12) and (5.14), and subtract Eq. (5.13), with the help of Eqs. (2.14) and (5.3) we obtain an identity. Therefore, among the three considered boundary conditions there are only two independent. We choose Eqs. (5.12) and (5.14) as independent boundary conditions. In view of Eqs. (5.3) and (5.7)–(5.10), they can be transformed to read:

$$\frac{d\tilde{\Gamma}_1}{d\tilde{t}} + \tilde{\Gamma}_1 \frac{d\alpha}{d\tilde{t}} = D_1 \left( f_{11} \frac{\partial c_1}{\partial x} + f_{13} \frac{\partial c_3}{\partial x} \right)_{x=0}, \quad (5.15)$$

$$\frac{d\tilde{\Gamma}_3}{d\tilde{t}} + \tilde{\Gamma}_3 \frac{d\alpha}{d\tilde{t}} = D_3 \left( f_{31} \frac{\partial c_1}{\partial x} + f_{33} \frac{\partial c_3}{\partial x} \right)_{x=0}. \quad (5.16)$$

In Eqs. (5.15) and (5.16) we have introduced the dimensional variables ( $x, t$ ), in accordance with Eq. (3.2). The initial values of  $\tilde{\Gamma}_1$  and  $\tilde{\Gamma}_3$  (at  $t = 0$ ), are supposed to be known:

$$\tilde{\Gamma}_1(0) = \tilde{\Gamma}_1^0, \quad \tilde{\Gamma}_3(0) = \tilde{\Gamma}_3^0. \quad (5.17)$$

Our next task is to solve the diffusion equations (5.5) and (5.6), along with initial and boundary conditions given by Eqs. (5.11) and (5.15)–(5.17).

To determine the time dependence of the surface tension,  $\gamma$ , we will use the Gibbs adsorption equation in the form [20]:

$$-\frac{d\gamma}{kT} = \tilde{\Gamma}_1 d \ln c_{1b} + \tilde{\Gamma}_2 d \ln c_{2b} + \tilde{\Gamma}_3 d \ln c_{3b}. \quad (5.18)$$

Here, we have taken into account the fact that if the adsorptions are expressed in terms of  $\tilde{\Gamma}_i$  (i.e., if they include the diffuse electric double layer) the subsurface concentrations have to be expressed in terms of  $c_{ib}$ . In Eq. (5.18),  $c_{ib}$ ,  $i = 1, 2, 3$ , represent concentrations at the outer limit of the quasistatic inner region, which must coincide with the concentrations at the inner limit of the outer region, in accordance with the Prandtl matching procedure [42–44]. As indicated by the calculations of the adsorptions of ionic surfactants [20,47], as a rule we have  $\tilde{\Gamma}_3 \ll \tilde{\Gamma}_1, \tilde{\Gamma}_2$ . The neglecting of  $\tilde{\Gamma}_3$  in Eq. (2.14) yields  $\tilde{\Gamma}_2 \approx \tilde{\Gamma}_1$ , and then Eq. (5.18) reduces to

$$-\frac{d\gamma}{kT} = \tilde{\Gamma}_1 \left( \frac{dc_{1b}}{c_{1b}} + \frac{dc_{2b}}{c_{2b}} \right). \quad (5.19)$$

Our next goal is to determine  $c_{1b}(t)$  and  $c_{2b}(t)$ , whose substitution in Eq. (5.19) would give us the dependence  $\gamma(t)$ .

## 6. Solution of the nonstationary diffusion problem

### 6.1. Basic equations

In general, we consider the case, in which the interfacial area is a function of time,  $A(t)$ , see Eq. (2.2). To remove the convective terms in Eqs. (5.5) and (5.6), we replace the coordinates

$(x, t)$  with the new variables  $(y, \tau)$  defined as follows [48]:

$$y = \frac{A}{A_0}x \quad \text{and} \quad \tau = t_{\text{age}}^{-1} \int_0^t \frac{A^2(\hat{t})}{A_0^2} d\hat{t}, \quad (6.1)$$

where  $A_0 = A(0)$  and  $\hat{t}$  is an integration variable. In terms of the new variables  $(y, \tau)$ , Eqs. (5.5) and (5.6) acquire the form:

$$\frac{1}{t_{\text{age}}} \frac{\partial c_1}{\partial \tau} = D_1 \frac{\partial}{\partial y} \left( f_{11} \frac{\partial c_1}{\partial y} + f_{13} \frac{\partial c_3}{\partial y} \right), \quad (6.2)$$

$$\frac{1}{t_{\text{age}}} \frac{\partial c_3}{\partial \tau} = D_3 \frac{\partial}{\partial y} \left( f_{31} \frac{\partial c_1}{\partial y} + f_{33} \frac{\partial c_3}{\partial y} \right) \quad (6.3)$$

( $y > 0$  and  $\tau > 0$ ). We have used also Eq. (3.2) and the definition  $L_d = (D_1 t_{\text{age}})^{1/2}$ . In terms of the new variables  $(y, \tau)$ , the boundary conditions, Eqs. (5.15) and (5.16) reduce to

$$\frac{1}{t_{\text{age}}} \frac{d}{d\tau} \left( \tilde{\Gamma}_1 \frac{A}{A_0} \right) = D_1 \left( f_{11} \frac{\partial c_1}{\partial y} + f_{13} \frac{\partial c_3}{\partial y} \right)_{y=0}, \quad (6.4)$$

$$0 = \left( f_{31} \frac{\partial c_1}{\partial y} + f_{33} \frac{\partial c_3}{\partial y} \right)_{y=0}. \quad (6.5)$$

At the last step we used the approximation  $\tilde{\Gamma}_3 \approx 0$ .

The deviations of the concentrations from their bulk values are:

$$\Delta c_1 = c_1 - c_{1\infty}, \quad \Delta c_3 = c_3 - c_{3\infty}. \quad (6.6)$$

The boundary problem (6.2)–(6.5) is nonlinear and it cannot be solved analytically. However, analytical solution can be found in the special case when  $\Delta c_1$  and  $\Delta c_2$  are small. In this case, the coefficients  $f_{ij}$  in Eqs. (6.2)–(6.5) could be treated as constant, and the problem can be solved by Laplace transformation with respect to  $\tau$ . The Laplace transforms of Eqs. (6.2)–(6.5) are:

$$\frac{s}{t_{\text{age}}} L[\Delta c_1] = a_{11} \frac{d^2 L[\Delta c_1]}{dy^2} + a_{13} \frac{d^2 L[\Delta c_3]}{dy^2}, \quad (6.7)$$

$$\frac{s}{t_{\text{age}}} L[\Delta c_3] = a_{31} \frac{d^2 L[\Delta c_1]}{dy^2} + a_{33} \frac{d^2 L[\Delta c_3]}{dy^2}, \quad (6.8)$$

$$\frac{1}{t_{\text{age}}} L \left[ \frac{d}{d\tau} \left( \tilde{\Gamma}_1 \frac{A}{A_0} \right) \right] = \left\{ a_{11} \frac{dL[\Delta c_1]}{dy} + a_{13} \frac{dL[\Delta c_3]}{dy} \right\}_{y=0}, \quad (6.9)$$

$$0 = \left\{ a_{31} \frac{dL[\Delta c_1]}{dy} + a_{33} \frac{dL[\Delta c_3]}{dy} \right\}_{y=0}, \quad (6.10)$$

where  $L$  denotes Laplace transformation,  $s$  is the Laplace parameter, and the coefficients  $a_{ij}$  are defined as follows:

$$a_{ij} = D_i f_{ij}(c_{1\infty}, c_{3\infty}), \quad i, j = 1, 3, \quad (6.11)$$

see Eqs. (5.7)–(5.10). For small deviations from equilibrium, Eq. (5.19) acquires the form:

$$-\frac{dy}{kT} = \tilde{\Gamma}_{1,\text{eq}} \left( \frac{d\Delta c_{1b}}{c_{1\infty}} + \frac{d\Delta c_{2b}}{c_{2\infty}} \right), \quad (6.12)$$

where  $\tilde{\Gamma}_{1,\text{eq}}$  is the equilibrium value of  $\tilde{\Gamma}_1$ , and

$$\Delta c_{ib} = \Delta c_i|_{y=0}, \quad i = 1, 2, 3. \quad (6.13)$$

Integrating Eq. (6.12), we obtain

$$\gamma = \gamma_{\text{eq}} - \tilde{\Gamma}_{1,\text{eq}} kT \left( \frac{\Delta c_{1b}}{c_{1\infty}} + \frac{\Delta c_{1b} + \Delta c_{3b}}{c_{2\infty}} \right), \quad (6.14)$$

where we have used Eqs. (2.1), (4.6), and (6.6).

## 6.2. Dynamic surface tension and effective diffusivity

In Appendix B, Eqs. (6.7) and (6.8) are solved by using the boundary conditions, Eqs. (6.9) and (6.10), and the functions  $L[\Delta c_i]$ ,  $i = 1, 3$ , are determined. Next, with the help of Eqs. (6.13) and (6.14), we derive the following expression for the time dependence of the surface tension:

$$\gamma = \gamma_{\text{eq}} + \frac{\tilde{\Gamma}_{1,\text{eq}}^2 kT}{(\pi D_{\text{eff}} t_{\text{age}})^{1/2}} \left( \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \right) \times \left( \frac{\tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0}{\tau^{1/2} \tilde{\Gamma}_{1,\text{eq}}} + \int_0^\tau \frac{1}{(\tau - \tilde{\tau})^{1/2}} \frac{d}{d\tilde{\tau}} \left( \frac{A}{A_0} \right) d\tilde{\tau} \right), \quad (6.15)$$

where  $\tau$  is given by Eq. (6.1), and  $D_{\text{eff}}$  is an effective diffusion coefficient of the ionic surfactant defined as follows:

$$D_{\text{eff}} = (a_{11} + a_{33} + 2a^{1/2})q^2, \quad (6.16)$$

where

$$q = \frac{(c_{1\infty} + c_{2\infty})a^{1/2}}{(a_{33} - a_{31} + a^{1/2})c_{1\infty} + (a_{33} + a^{1/2})c_{2\infty}}, \quad (6.17)$$

$$a = a_{11}a_{33} - a_{13}a_{31} = \frac{2c_{2\infty}}{B} D_1 D_2 D_3, \quad (6.18)$$

$$B = D_1 c_{1\infty} + D_2 c_{2\infty} + D_3 c_{3\infty} \quad (6.19)$$

(details in Appendix B). In view of Eqs. (5.4), (5.7)–(5.10), and (6.11), the explicit expressions for the coefficients  $a_{ij}$  are:

$$a_{11} = D_1 + \frac{D_2 - D_1}{B} D_1 c_{1\infty}, \quad (6.20)$$

$$a_{13} = \frac{D_2 - D_3}{B} D_1 c_{1\infty}, \quad (6.21)$$

$$a_{31} = \frac{D_2 - D_1}{B} D_3 c_{3\infty}, \quad (6.22)$$

$$a_{33} = D_3 + \frac{D_2 - D_3}{B} D_3 c_{3\infty}. \quad (6.23)$$

In the special case of *high salt* concentration or *low surfactant* concentration,  $c_{1\infty}/c_{3\infty} \ll 1$ , we have

$$a_{11} \approx D_1, \quad a_{13} \approx 0, \quad a \approx D_1 a_{33}, \quad q^2 \approx \frac{D_1}{(a_{33}^{1/2} + D_1^{1/2})^2}. \quad (6.24)$$

Substituting Eq. (6.24) into Eq. (6.16) we obtain

$$D_{\text{eff}} \approx D_1, \quad c_{1\infty}/c_{3\infty} \ll 1. \quad (6.25)$$

In the *absence* of nonamphiphilic electrolyte ( $c_{3\infty} = 0$ ), we have

$$a_{11} = \frac{2D_1 D_2}{D_1 + D_2}, \quad a_{31} = 0, \quad a = a_{11} a_{33},$$

$$q^2 = \frac{a_{11}}{(a_{11}^{1/2} + a_{33}^{1/2})^2}. \quad (6.26)$$

Substituting Eq. (6.26) into Eq. (6.16), we derive

$$\frac{1}{D_{\text{eff}}} = \frac{1}{2} \left( \frac{1}{D_1} + \frac{1}{D_2} \right), \quad c_{3\infty} = 0. \quad (6.27)$$

Equation (6.27) coincides with the results in Refs. [13,49] for the effective diffusivity of an ionic surfactant in the absence of added nonamphiphilic electrolyte.

In the general case, one has to calculate  $D_{\text{eff}}$  from Eq. (6.16), along with Eqs. (6.17)–(6.23). The latter equations are applicable for concentrations below the CMC. For concentrations above the CMC, one could use expressions for  $D_{\text{eff}}$  derived in Refs. [50,51]. What concerns the expression for the surface tension, Eq. (6.15), it could be simplified for some special dynamic regimes, as demonstrated below.

### 6.3. Special dynamic regimes

#### 6.3.1. Relaxation of the surface tension of an immobile interface

This dynamic regime is realized by the fast-formed-drop method [52,53] and the inclined plate method [31,54,55]. The interface is disturbed only in the initial moment,  $t = 0$ . After that the surfactant adsorbs at an immobile interface, i.e.,  $A = A_0 = \text{const}$  and  $\dot{\alpha} = 0$ . In this case, the last integral term in Eq. (6.15) is zero, and Eq. (6.1) yields  $\tau = t/t_{\text{age}}$ . Thus, Eq. (6.15) reduces to

$$\gamma \approx \gamma_{\text{eq}} + \frac{kT(\tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0)\tilde{\Gamma}_{1,\text{eq}}}{(\pi D_{\text{eff}}t)^{1/2}} \left( \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \right). \quad (6.28)$$

Then, for  $1/c_{2\infty} \rightarrow 0$  (nonionic surfactant or ionic surfactant at high concentration of added salt) and for  $\tilde{\Gamma}_1^0 \ll \tilde{\Gamma}_{1,\text{eq}}$ , Eq. (6.28) coincides with Eqs. (1.3) and (1.4). Note that in the latter case  $D_{\text{eff}} \approx D_1$ , see Eq. (6.25). In the general case of arbitrary salt concentration, Eq. (6.28), with  $D_{\text{eff}}$  given by Eqs. (6.16)–(6.23), represents a generalization of Eqs. (1.3) and (1.4). At the higher ionic strengths ( $c_{2\infty} > 1$  mM), we have  $\tilde{\Gamma}_{1,\text{eq}} \approx \Gamma_{1,\text{eq}}$ , and in addition, in Eq. (6.28)  $c_{i\infty}$  should be replaced by  $\gamma_{\pm}c_{i\infty}$ ,  $i = 1, 2$ ; see Eqs. (1.6) and (8.3).

#### 6.3.2. Maximum bubble pressure method (MBPM)

In this case, the surface tension is registered at the moment of maximum pressure. Then, in Eq. (6.15) we have to substitute  $t = t_{\text{age}}$ , which leads to

$$\begin{aligned} \gamma = \gamma_{\text{eq}} + \frac{\tilde{\Gamma}_{1,\text{eq}}kT}{(\pi D_{\text{eff}}t_{\text{age}})^{1/2}} \left( \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \right) \\ \times [(\tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0)\lambda_1 + \tilde{\Gamma}_{1,\text{eq}}\lambda], \end{aligned} \quad (6.29)$$

where

$$\lambda_1 \equiv \tau_1^{-1/2}, \quad \tau_1 \equiv \int_0^1 [\tilde{A}(\hat{t}_d)]^2 d\hat{t}_d, \quad (6.30)$$

$$\lambda \equiv \int_0^1 \frac{1}{(\tau_1 - \tau)^{1/2}} \frac{d}{dt_d} [\tilde{A}(t_d)] dt_d, \quad \tau \equiv \int_0^{t_d} [\tilde{A}(\hat{t}_d)]^2 d\hat{t}_d. \quad (6.31)$$

Here,  $\tilde{A} = A/A_0$  is the dimensionless area, and  $t_d = t/t_{\text{age}}$  is the dimensionless time;  $\hat{t}_d$  is an integration variable. The experiment shows that for a given MBPM setup,  $\tilde{A}(t_d)$  is a universal function (apparatus function), which is independent of the surfactant type and concentration, and of the bubbling period [25,36]. Consequently,  $\lambda$  and  $\lambda_1$  are constants that characterize a given MBPM tensiometer (apparatus constants).

For commercially available MBPM tensiometers (like Krüss BP2) the following relationship is satisfied [36]:

$$\frac{\tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0}{\tilde{\Gamma}_{1,\text{eq}}} \frac{\lambda_1}{\lambda} \ll 1. \quad (6.32)$$

Then, the term with  $\lambda_1$  in Eq. (6.29) is negligible and we obtain Eqs. (1.5) and (1.6). In the latter equations, we have introduced also the activity coefficient,  $\gamma_{\pm}$ , which should be taken into account for ionic strengths greater than 1 mM, see Eq. (8.3). Note that the replacement of the concentrations,  $c_{i\infty}$ , with the activities,  $\gamma_{\pm}c_{i\infty}$ , in Eqs. (6.17)–(6.23) does not change  $D_{\text{eff}}$  because  $\gamma_{\pm}$ , which appears in both the numerators and denominators of these equations, cancels. In addition, for ionic strengths  $> 1$  mM, we have  $\tilde{\Gamma}_{1,\text{eq}} \approx \Gamma_{1,\text{eq}}$ . In Section 8, Eqs. (1.5) and (1.6) are used to test the derived theoretical expressions against MBPM experimental data.

The comparison of Eqs. (1.5) and (1.6) with Eq. (6.28) indicates that the dynamic surface tension detected by MBPM becomes identical with the dynamic surface tension of an *immobile* interface of age  $t_u \equiv t_{\text{age}}/\lambda^2$  that has been initially clean ( $\Gamma_1^0 = 0$ ). Consequently, the dynamic surface tensions measured by different MBPM tensiometers (with different apparatus constants,  $\lambda$ ) become physically comparable if the experimental data are plotted as  $\gamma$  vs  $t_u$ . In other words, the  $\gamma(t_u)$  curves measured for the same solution by different MBPM apparatuses must coincide. This fact can be utilized for introduction of a universal time-scale for the MBPM tensiometers; see Ref. [36] for details.

### 7. Stationary interfacial expansion

In the case of stationary expansion ( $\dot{\alpha} = \text{const}$ ), expression for the dynamic surface tension,  $\gamma$ , cannot be deduced as a special case of Eq. (6.15). Therefore, this case is considered separately in the present section.

Stationary expansion is experimentally realized with the strip method [30,31], and the overflowing cylinder method [32–35]. It could be realized also by a Langmuir trough. Because we are dealing with a stationary process, all derivatives  $\partial c_i/\partial t$  and  $d\Gamma_i/dt$ ,  $i = 1, 2, 3$ , in the diffusion equations and the respective boundary conditions are equal to zero. The characteristic length of the outer region is now  $L_d = (D_1/\dot{\alpha})^{1/2}$ . After that, the analysis of the stationary problem is completely analogous to that in Sections 3–5; see also Ref. [17]. The counterparts of Eqs. (5.5), (5.6), (5.15), and (5.16), written in terms

of dimensional variables for small deviations from equilibrium, are:

$$-\dot{\alpha}x \frac{\partial c_1}{\partial x} = a_{11} \frac{\partial^2 c_1}{\partial x^2} + a_{13} \frac{\partial^2 c_3}{\partial x^2}, \quad (7.1)$$

$$-\dot{\alpha}x \frac{\partial c_3}{\partial x} = a_{31} \frac{\partial^2 c_1}{\partial x^2} + a_{33} \frac{\partial^2 c_3}{\partial x^2}, \quad (7.2)$$

$$\tilde{\Gamma}_{1,\text{eq}} \dot{\alpha} = \left( a_{11} \frac{\partial c_1}{\partial x} + a_{13} \frac{\partial c_3}{\partial x} \right)_{x=0}, \quad (7.3)$$

$$0 = \left( a_{31} \frac{\partial c_1}{\partial x} + a_{33} \frac{\partial c_3}{\partial x} \right)_{x=0} \quad (7.4)$$

( $\tilde{\Gamma}_{3,\text{eq}} \approx 0$ ). The coefficients  $a_{ij}$  are defined by Eq. (6.11). In Appendix C, the linear boundary problem (7.1)–(7.4) is solved, expressions for  $\Delta c_{1b}$  and  $\Delta c_{3b}$  are derived, and finally Eq. (6.14) is used to determine  $\gamma$ . The result is

$$\gamma = \gamma_{\text{eq}} + kT \tilde{\Gamma}_{1,\text{eq}}^2 \left( \frac{\pi \dot{\alpha}}{2D_{\text{eff}}} \right)^{1/2} \left( \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \right), \quad (7.5)$$

where  $D_{\text{eff}}$  is defined by Eqs. (6.16)–(6.23). Equation (7.5) does not contain the time,  $t$ , as it should be for a stationary process. As discussed above, for nonionic surfactants and for ionic surfactants at high salt concentrations the term  $1/c_{2\infty}$  in Eq. (7.5) disappears and  $D_{\text{eff}} = D_1$ . In addition, for nonionic surfactants  $\tilde{\Gamma}_{1,\text{eq}} = \Gamma_1$ . For ionic surfactants, at ionic strengths  $\geq 1$  mM one could use the approximation  $\tilde{\Gamma}_{1,\text{eq}} \approx \Gamma_1$ , and the activity coefficient,  $\gamma_{\pm}$ , should be taken into account, see Eq. (8.3).

In summary, the expressions for the dynamic surface tension in the cases of nonstationary and stationary interfacial expansion, Eqs. (6.15) and (7.5), are different, however the expression for the effective diffusivity,  $D_{\text{eff}}$ , is the same; see Eqs. (6.16)–(6.23).

In some methods with stationary interfacial expansion, like the overflowing cylinder method, the dynamic surfactant adsorption  $\Gamma_1(\dot{\alpha})$  is directly registered by ellipsometry [32] or neutron reflection [33]. To derive an expression for  $\Gamma_1(\dot{\alpha})$ , we consider the case of small deviations of the adsorption from its equilibrium value:

$$\Gamma_1 - \Gamma_{1,\text{eq}} \approx h_{1a} \Delta c_{1b} + h_{2a} (\Delta c_{1b} + \Delta c_{3b}), \quad (7.6)$$

where the identity  $\Delta c_{2b} = \Delta c_{1b} + \Delta c_{3b}$  has been used;  $h_{1a}$  and  $h_{2a}$  are the so called adsorption lengths:

$$h_{ia} \equiv \left( \frac{\partial \Gamma_1}{\partial c_{i\infty}} \right)_{\text{eq}}, \quad i = 1, 2. \quad (7.7)$$

The derivatives in Eq. (7.7) have to be calculated from the equilibrium adsorption isotherm. With the help of Eqs. (6.16), (B.20), (C.8), and (C.9) (see Appendices B and C), one can represent Eq. (7.6) in the form:

$$\frac{\Gamma_1}{\Gamma_{1,\text{eq}}} \approx 1 - \left( \frac{\pi \dot{\alpha} q^2}{2D_{\text{eff}}} \right)^{1/2} \left[ \left( \frac{a_{33}}{a^{1/2}} + 1 \right) h_{1a} + \left( \frac{a_{33} - a_{31}}{a^{1/2}} + 1 \right) h_{2a} \right]. \quad (7.8)$$

The parameters taking part in Eq. (7.8) are defined by Eqs. (6.16)–(6.23).

## 8. Comparison of theory and experiment

To test the derived theoretical expressions, we will use experimental data for dynamic surface tension from Ref. [36]. The data are obtained by means of the maximum bubble pressure method (MBPM) for sodium dodecyl sulfate (SDS) + added 10 and 100 mM NaCl, as well as for dodecyl-trimethyl ammonium bromide (DTAB) + added 5 and 100 mM NaBr; the temperature was  $T = 27$  °C. The raw experimental data for  $\gamma(t_{\text{age}})$  are fitted by means of the equation [36]

$$\gamma = \gamma_{\text{eq}} + \frac{s_{\gamma}}{a_{\gamma} + (t_{\text{age}})^{1/2}}, \quad (8.1)$$

where  $\gamma_{\text{eq}}$ ,  $a_{\gamma}$ , and  $s_{\gamma}$  have been determined as adjustable parameters. Using the values of  $s_{\gamma}$ , determined in Ref. [36], we calculate the equilibrium adsorption,  $\Gamma_{1,\text{eq}}$ , with the help of our Eq. (1.6)

$$\Gamma_{1,\text{eq}}^2 = \frac{(\pi D_{\text{eff}})^{1/2} c_{1\infty} c_{2\infty} \gamma_{\pm}}{(c_{1\infty} + c_{2\infty}) kT \lambda} s_{\gamma}. \quad (8.2)$$

In our computations, we used the value  $\lambda = 6.074$  for the apparatus constant, which was determined in [36] by numerical solution of the integral in Eq. (6.31) substituting the experimental dependence  $\tilde{A}(t_d)$ . The activity coefficient,  $\gamma_{\pm}$ , was calculated from the known semiempirical formula [56]

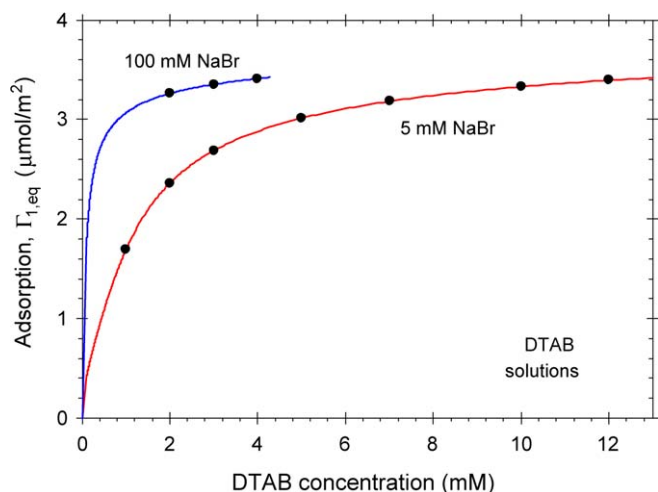
$$\log \gamma_{\pm} = - \frac{AZ^2 \sqrt{I}}{1 + Bd_i \sqrt{I}} + bI \quad (8.3)$$

stemming from the Debye–Hückel theory;  $I = Z^2 c_{2\infty}$  is the ionic strength of the solution; the logarithm in Eq. (8.3) is decimal;  $d_i$  is the diameter of the ion,  $A$ ,  $B$ , and  $b$  are parameters, which are tabulated in [56]; for our experimental conditions, we used the values  $A = 0.5115 \text{ M}^{-1/2}$ ,  $Bd_i = 1.316 \text{ M}^{-1/2}$ , and  $b = 0.055 \text{ M}^{-1}$ .

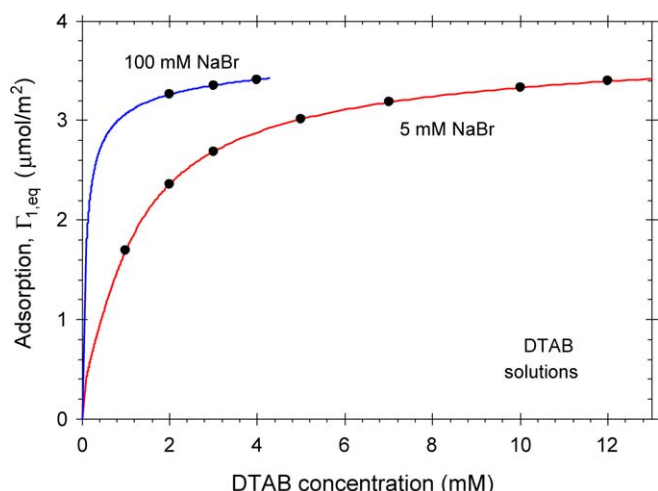
The values of the surfactant diffusivity are  $D_1 = 5.5 \times 10^{-10} \text{ m}^2/\text{s}$  for SDS [57] and  $D_1 = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$  for DTAB [36]. The diffusivities of the  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  ions were calculated from the radii of the hydrated ions [58] with the help of the Stokes–Einstein formula substituting  $\eta = 0.852 \text{ mPa s}$  for the viscosity of water at  $T = 27$  °C. Thus, for the system SDS + NaCl we obtain  $D_2 = 7.18 \times 10^{-10} \text{ m}^2/\text{s}$  and  $D_3 = 7.83 \times 10^{-10} \text{ m}^2/\text{s}$ , whereas for the system DTAB + NaBr we have  $D_2 = 7.83 \times 10^{-10} \text{ m}^2/\text{s}$  and  $D_3 = 7.18 \times 10^{-10} \text{ m}^2/\text{s}$  (the hydrated  $\text{Cl}^-$ , and  $\text{Br}^-$  ions have practically the same size). Afterwards,  $D_{\text{eff}}$  was calculated by means of Eqs. (6.16)–(6.23) as a function of  $c_{1\infty}$  and  $c_{2\infty}$ . The points in Fig. 2 represent the values of  $\Gamma_{1,\text{eq}}$ , obtained from the experimental  $s_{\gamma}$  and Eq. (8.2), as described above. (As mentioned earlier, for the investigated solutions the difference between  $\tilde{\Gamma}_{1,\text{eq}}$  and  $\Gamma_{1,\text{eq}}$  is of the order of 1–2%, and is negligible.)

The solid lines  $\Gamma_{1,\text{eq}}$  vs  $c_{1\infty}$  in Fig. 2 are calculated independently from the fits of equilibrium experimental surface tension data,  $\gamma_{\text{eq}}$  vs  $c_{1\infty}$ , by means of the van der Waals adsorption model using the full system of equations in Refs. [20,47]. The parameters of this model,  $K_1$ ,  $K_{\text{St}}$ ,  $\Gamma_{\infty}$ , and  $\beta$ , determined from the fits are tabulated in [36]. Then, we computed  $\Gamma_{1,\text{eq}}$  by solving numerically the respective system of equations for various





(a)

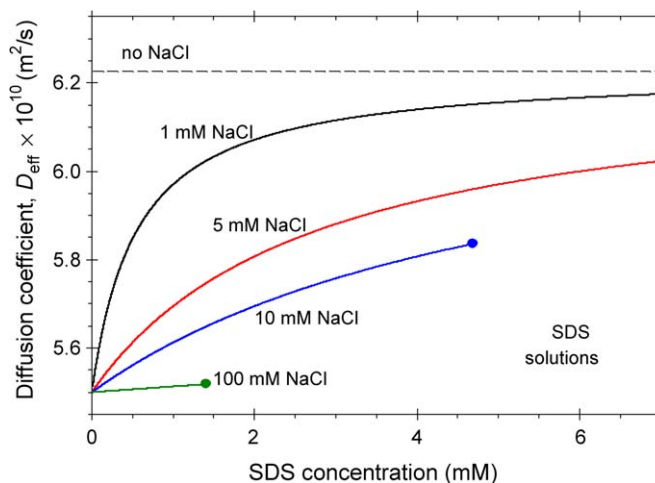


(b)

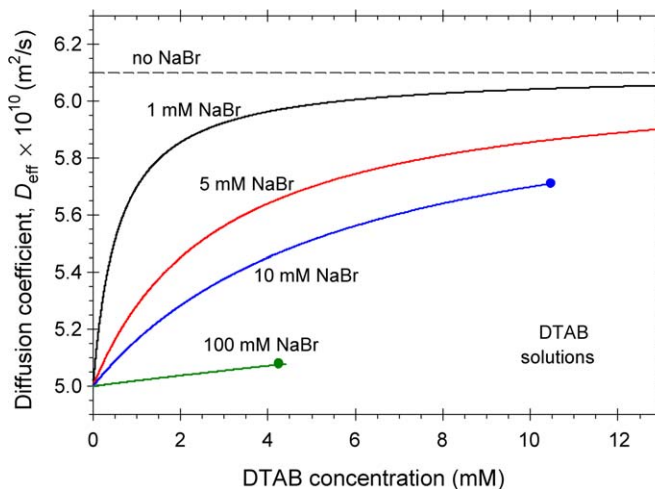
Fig. 2. Plot of the equilibrium surfactant adsorption,  $\Gamma_{1,\text{eq}}$ , vs the surfactant concentration,  $c_{1,\infty}$ , for various salt concentrations,  $c_{3,\infty}$ , denoted in the figure: (a) SDS + NaCl; (b) DTAB + NaBr. The points are calculated by means of Eq. (8.2) from the experimental  $s_\gamma$  measured by MBPM in Ref. [36]. The solid lines are calculated independently from fits of surface tension data,  $\gamma_{\text{eq}}$  vs  $c_{1,\infty}$ , by means of the van der Waals adsorption model (see the text).

$c_{1,\infty}$ ; see Ref. [36]. The lines  $\Gamma_{1,\text{eq}}(c_{1,\infty})$  calculated in this way from  $\gamma_{\text{eq}}$  are in excellent agreement with the points, which are obtained in a completely independent manner from the MBPM data for  $s_\gamma$ ; see Fig. 2. Note that the points and the lines in Fig. 2 have been plotted directly as calculated by the two different procedures, and their agreement is not a result of fit. This agreement confirms the validity of the equations derived in the present paper: Eqs. (1.5) and (1.6) for the dynamic surface tension,  $\gamma(t_{\text{age}})$ , and Eqs. (6.16)–(6.23) for the effective diffusivity  $D_{\text{eff}}(c_{1,\infty}, c_{3,\infty})$ .

Figs. 3a and 3b illustrate the dependence of  $D_{\text{eff}}$  on the surfactant and salt concentrations,  $c_{1,\infty}$  and  $c_{3,\infty}$ , in the range below the CMC. The curves are calculated by means of Eqs. (6.16)–(6.23) using the values of  $D_1$ ,  $D_2$ , and  $D_3$  for SDS and DTAB (see above). Because the latter equations are valid for  $c_{1,\infty} \leq \text{CMC}$ , the calculated curves end at the CMC. At very low surfactant concentrations,  $c_{1,\infty} \rightarrow 0$ , in the presence of salt ( $c_{3,\infty} > 0$ ), the effective diffusivity approaches its limiting



(a)



(b)

Fig. 3. Dependence of  $D_{\text{eff}}$  on the surfactant concentration,  $c_{1,\infty}$ , for various salt concentrations,  $c_{3,\infty}$ , denoted in the figure. The curves are calculated by means of Eqs. (6.16)–(6.23) using the values of  $D_1$ ,  $D_2$ , and  $D_3$  for (a) SDS and (b) DTAB (see the text). The end points of some curves correspond to the CMC.

value for diluted solutions,  $D_{\text{eff}} \rightarrow D_1$ . One sees that  $D_{\text{eff}}$  increases with the rise of  $c_{1,\infty}$ , except the case without added salt ( $c_{3,\infty} = 0$ ), for which  $D_{\text{eff}}$  is a constant given by Eq. (6.27). On the other hand,  $D_{\text{eff}}$  decreases with the rise of salt concentration,  $c_{3,\infty}$ , and becomes  $\approx D_1$  for  $c_{3,\infty} = 100$  mM; see Eq. (6.25). Note that the salt concentration affects the dynamic surface tension,  $\gamma$ , also through  $\Gamma_{1,\text{eq}}$  and through the factor  $(1/c_{1,\infty} + 1/c_{2,\infty})$  in Eqs. (1.6) and (7.5).

In the case of MBPM, the applicability of the developed theory is determined by the applicability of Eq. (8.1). Our experiments [36] showed that Eq. (8.1) provides excellent fits of MBPM data everywhere except for the earliest surface ages at low surfactant concentrations. The values of  $s_\gamma$  determined from the fits are found to agree very well with Eq. (1.6) for concentrations below the CMC, where this equation is valid. In other words, despite some approximations used in the present paper, the derived theoretical expressions are applicable to a wide and practically important range of surfactant concentrations; see Ref. [36] for details.

## 9. Summary and conclusions

We derived analytical asymptotic expressions for the dynamic surface tension of ionic surfactant solutions in the general case of nonstationary interfacial expansion. Because the diffusion layer is much wider than the electric double layer, the equations contain a small parameter; see Eq. (3.1). The resulting perturbation problem is singular and it is solved by means of the method of matched asymptotic expansions. It turns out that the “inner” region represents a quasistatic electric double layer (Section 4), while the “outer” region is an electroneutral solution (Section 5). The concentrations of the ionic species vary in the outer region because of the diffusion process. This leads to the nontrivial fact that the electric potential is different from zero in the electroneutral outer region, see Eq. (5.3). The derived general expression for the dynamic surface tension, Eq. (6.15), is simplified for the special cases of immobile interface, Eq. (6.28), and maximum-bubble-pressure tensiometry, Eqs. (1.5) and (1.6). The case of stationary interfacial expansion is also considered (Section 7). The effective diffusivity of the ionic surfactant,  $D_{\text{eff}}$ , which appears in the derived theoretical expressions, essentially depends on the concentrations of surfactant and nonamphiphilic salt; see Eqs. (6.16)–(6.23), and Fig. 3. To test the theory, the derived equations are applied to calculate the surfactant adsorption from MBPM experimental data. The results are compared with the adsorption determined independently from fits of equilibrium surface tension isotherms. Excellent agreement between the two sets of data is observed (Fig. 2), which confirms the validity of the derived theoretical expressions. The results could find application for interpretation of data obtained by MBPM and other experimental methods for investigating interfacial dynamics; see, e.g., Ref. [36].

## Acknowledgments

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## Appendix A. Derivation of Eqs. (5.12)–(5.14)

Let us consider the plane  $x = b$ , which is situated in the transition zone between the outer and inner regions ( $\kappa^{-1} \ll b \ll L_d$ ). We will formally consider  $b$  as a boundary between the two regions (Fig. 1). Next, we integrate the diffusion equations (2.3)–(2.5) with respect to  $x$  from 0 to  $b$ , and sum up the resulting expressions with the boundary conditions (2.8)–(2.10). Thus, we obtain

$$\frac{d}{dt}(\Gamma_i + \Lambda_{ib}) + \dot{\alpha}(\Gamma_i + \Lambda_{ib}) = D_i \left( \frac{\partial c_i}{\partial x} + c_i \frac{\partial \Phi}{\partial x} \right)_{x=b}, \quad (\text{A.1})$$

$$\Lambda_{ib} \equiv \int_0^b (c_i - c_{ib}) dx, \quad c_{ib} \equiv c_i|_{x=b}, \quad i = 1, 2, 3. \quad (\text{A.2})$$

Here, we have not used the approximation  $\Gamma_3 \approx 0$ ; to derive Eq. (A.1), we applied integration by parts:

$$\int_0^b x \frac{\partial c_i}{\partial x} dx = b c_{ib} - \int_0^b c_i dx = -\Lambda_{ib}. \quad (\text{A.3})$$

Because the region  $0 < x < b$  contains the electric double layer, we have  $\Lambda_{ib} \approx \Lambda_i$ . Consequently,  $\Gamma_i + \Lambda_{ib} \approx \tilde{\Gamma}_i$ , see Eq. (2.15). Finally, in Eq. (A.1) we introduce dimensionless variables by means of Eq. (3.2), and take into account the fact that  $\tilde{b} \equiv b/L_d \ll 1$ . As a result, we obtain Eqs. (5.12)–(5.14).

## Appendix B. Derivation of Eq. (6.15)

We seek  $L[\Delta c_1]$  in the form:

$$L[\Delta c_1] = X_1 \exp(-\nu_1 y) + X_2 \exp(-\nu_2 y), \quad (\text{B.1})$$

where  $y \geq 0$ ;  $X_1$  and  $X_2$  are unknown coefficients;  $\nu_1$  and  $\nu_2$  are the two positive roots of the characteristic equation of the system (6.7) and (6.8); see Eqs. (B.9)–(B.12). Substituting Eq. (B.1) into Eq. (6.7), we obtain

$$L[\Delta c_3] = \left( \frac{s}{t_{\text{age}} \nu_1^2} - a_{11} \right) \frac{X_1}{a_{13}} \exp(-\nu_1 y) + \left( \frac{s}{t_{\text{age}} \nu_2^2} - a_{11} \right) \frac{X_2}{a_{13}} \exp(-\nu_2 y). \quad (\text{B.2})$$

Furthermore, substituting Eqs. (B.1) and (B.2) into the boundary condition, Eq. (6.10), we derive a connection between  $X_1$  and  $X_2$ :

$$\left( \frac{s}{t_{\text{age}} \nu_1^2} - \frac{a}{a_{33}} \right) \nu_1 X_1 + \left( \frac{s}{t_{\text{age}} \nu_2^2} - \frac{a}{a_{33}} \right) \nu_2 X_2 = 0, \quad (\text{B.3})$$

where, as usual,  $a = a_{11}a_{33} - a_{13}a_{31}$ ; see Eq. (6.18). Next, we transform the left-hand side of Eq. (6.9):

$$\begin{aligned} L \left[ \frac{d}{d\tau} \left( \tilde{\Gamma}_1 \frac{A}{A_0} \right) \right] &= sL \left[ \tilde{\Gamma}_1 \frac{A}{A_0} \right] - \tilde{\Gamma}_1^0 \\ &= sL \left[ \left( \tilde{\Gamma}_1 - \tilde{\Gamma}_{1,\text{eq}} \right) \frac{A}{A_0} \right] \\ &\quad + \tilde{\Gamma}_{1,\text{eq}} \left( sL \left[ \frac{A}{A_0} \right] - 1 \right) + \tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0 \\ &\approx \tilde{\Gamma}_{1,\text{eq}} L \left[ \frac{d}{d\tau} \frac{A}{A_0} \right] + \tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0. \end{aligned} \quad (\text{B.4})$$

At the last step, we neglected the term with  $(\tilde{\Gamma}_1 - \tilde{\Gamma}_{1,\text{eq}})$  for small deviations from equilibrium. Substituting Eqs. (B.1), (B.2), and (B.4) into the boundary condition, Eq. (6.9), we obtain

$$\frac{X_1}{\nu_1} + \frac{X_2}{\nu_2} = -\frac{t_{\text{age}}}{s} Y, \quad (\text{B.5})$$

where

$$Y \equiv \frac{\tilde{\Gamma}_{1,\text{eq}}}{t_{\text{age}}} L \left[ \frac{d}{d\tau} \frac{A}{A_0} \right] + \frac{\tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0}{t_{\text{age}}}. \quad (\text{B.6})$$

With the help of Eq. (B.5), we represent Eq. (B.3) in the form:

$$v_1 X_1 + v_2 X_2 = -\frac{a_{33}}{a} Y. \quad (\text{B.7})$$

Next, from Eqs. (B.5) and (B.7) we derive

$$\begin{aligned} X_1 &= \frac{v_1}{v_2^2 - v_1^2} \left( \frac{a_{33}}{a} - \frac{t_{\text{age}} v_2^2}{s} \right) Y, \\ X_2 &= \frac{v_2}{v_2^2 - v_1^2} \left( \frac{t_{\text{age}} v_1^2}{s} - \frac{a_{33}}{a} \right) Y. \end{aligned} \quad (\text{B.8})$$

To determine  $v_1$  and  $v_2$ , we substitute  $L[\Delta c_i] = C_i \exp(-vy)$ ,  $i = 1, 3$ , in Eqs. (6.7) and (6.8). Thus, we obtain a homogeneous linear system for  $C_1$  and  $C_3$ , and consider its characteristic equation:

$$\left( a_{11} - \frac{1}{\mu^2} \right) \left( a_{33} - \frac{1}{\mu^2} \right) - a_{13} a_{31} = 0, \quad (\text{B.9})$$

$$\frac{1}{\mu^2} \equiv \frac{s}{t_{\text{age}} v^2}. \quad (\text{B.10})$$

Equation (B.9) represents a quadratic equation for  $1/\mu^2$ , whose solution is:

$$\left( \frac{1}{\mu^2} \right)_{1,2} = \frac{1}{2} \{ (a_{11} + a_{33}) \pm [(a_{11} + a_{33})^2 - 4a_{13} a_{31}]^{1/2} \}. \quad (\text{B.11})$$

After equivalent transformations, using Eqs. (6.16)–(6.23), one can prove that

$$\begin{aligned} & (D_{21}^{(+)} c_{1\infty} + D_{23}^{(+)} c_{3\infty})^2 [(a_{11} + a_{33})^2 - 4a_{13} a_{31}] \\ &= [(D_1 D_{32}^{(-)} + D_2 D_{31}^{(-)}) c_{1\infty} + (D_2 D_{13}^{(-)} + D_3 D_{12}^{(-)}) c_{3\infty}]^2 \\ &+ 8D_2^2 (D_{13}^{(-)})^2 c_{1\infty} c_{3\infty} > 0, \end{aligned} \quad (\text{B.12})$$

where  $D_{ij}^{(\pm)} = D_i \pm D_j$ . In other words, the discriminant in Eq. (B.11) is positive, and because  $a > 0$ , we have two positive roots,  $\mu_1$  and  $\mu_2$ . Then, the quantities  $v_i = (s/t_{\text{age}})_i^{1/2}$ ,  $i = 1, 2$ , are also positive; see Eq. (B.10).

In view of Eq. (6.14), we consider the expression:

$$Z = -L \left[ \frac{\Delta c_{1b}}{c_{1\infty}} + \frac{\Delta c_{1b} + \Delta c_{3b}}{c_{2\infty}} \right]. \quad (\text{B.13})$$

Having in mind Eq. (6.13), we set  $y = 0$  in Eqs. (B.1) and (B.2), and substitute the result into Eq. (B.13). Thus, in view of Eq. (B.10), we obtain

$$\begin{aligned} -Z &= \left[ \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \left( \frac{1}{a_{13} \mu_1^2} + \frac{a_{13} - a_{11}}{a_{13}} \right) \right] X_1 \\ &+ \left[ \frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}} \left( \frac{1}{a_{13} \mu_2^2} + \frac{a_{13} - a_{11}}{a_{13}} \right) \right] X_2. \end{aligned} \quad (\text{B.14})$$

The Viète's formulas for Eq. (B.9) read:

$$\frac{1}{\mu_1^2} + \frac{1}{\mu_2^2} = a_{11} + a_{33}, \quad \frac{1}{\mu_1^2} \frac{1}{\mu_2^2} = a. \quad (\text{B.15})$$

Further, with the help of Eqs. (B.8), (B.10), and (B.15) we derive

$$X_1 + X_2 = - \left( \frac{a_{33}}{a} + \frac{1}{a^{1/2}} \right) \frac{Q}{\mu_1 + \mu_2}, \quad (\text{B.16})$$

$$\frac{X_1}{\mu_1^2} + \frac{X_2}{\mu_2^2} = - \left( \frac{a_{11}}{a^{1/2}} + 1 \right) \frac{Q}{\mu_1 + \mu_2}, \quad (\text{B.17})$$

$$Q \equiv (t_{\text{age}}/s)^{1/2} Y. \quad (\text{B.18})$$

Using Eqs. (B.16) and (B.17), we express Eq. (B.14) in the form:

$$\begin{aligned} Z &= \left[ \frac{1}{c_{1\infty}} \left( \frac{a_{33}}{a} + \frac{1}{a^{1/2}} \right) \right. \\ &\left. + \frac{1}{c_{2\infty}} \left( \frac{a_{33} - a_{31}}{a} + \frac{1}{a^{1/2}} \right) \right] \frac{Q}{\mu_1 + \mu_2}. \end{aligned} \quad (\text{B.19})$$

Next, with the help of Eq. (B.15), we derive

$$\begin{aligned} (\mu_1 + \mu_2)^2 &= \mu_1^2 \mu_2^2 \left( \frac{1}{\mu_1^2} + \frac{1}{\mu_2^2} + \frac{2}{\mu_1 \mu_2} \right) \\ &= \frac{a_{11} + a_{33} + 2a^{1/2}}{a}. \end{aligned} \quad (\text{B.20})$$

Substituting  $\mu_1 + \mu_2$  from Eq. (B.20) into Eq. (B.19), after some transformations we obtain

$$Z = \frac{Q}{(a_{11} + a_{33} + 2a^{1/2})^{1/2}} \frac{c_{1\infty} + c_{2\infty}}{c_{1\infty} c_{2\infty} q}, \quad (\text{B.21})$$

where  $q$  is defined by Eq. (6.17).

Combining Eqs. (B.6), (B.18), and (B.21), we derive

$$Z = \frac{c_{1\infty} + c_{2\infty}}{c_{1\infty} c_{2\infty}} \left\{ \frac{\tilde{\Gamma}_{1,\text{eq}}}{(D_{\text{eff}} t_{\text{age}} s)^{1/2}} L \left[ \frac{d}{d\tau} \frac{A}{A_0} \right] + \frac{\tilde{\Gamma}_{1,\text{eq}} - \tilde{\Gamma}_1^0}{(D_{\text{eff}} t_{\text{age}} s)^{1/2}} \right\}, \quad (\text{B.22})$$

where the effective diffusion coefficient,  $D_{\text{eff}}$ , is defined by Eq. (6.16). Finally, we apply inverse Laplace transformation to Eq. (B.22), and in view of Eqs. (B.13) and (6.14) we obtain Eq. (6.15) for the dynamic surface tension.

### Appendix C. Derivation of Eq. (7.5)

Substituting  $\partial c_i / \partial x = C_i \exp(-\mu^2 \dot{\alpha} x^2 / 2)$ ,  $i = 1, 3$ , in Eqs. (7.1) and (7.2), we obtain a homogeneous linear system for  $C_1$  and  $C_3$ , whose characteristic equation coincides with Eq. (B.9). Consequently, Eqs. (B.11), (B.15), and (B.20), which are direct corollaries from Eq. (B.9), hold also in the present case. As proven in Appendix B, this characteristic equation has two positive roots,  $\mu_1$  and  $\mu_2$ ; see Eq. (B.12). Consequently, the general form of  $\partial c_1 / \partial x$  is

$$\frac{\partial c_1}{\partial x} = X_1 \exp\left(-\mu_1^2 \dot{\alpha} \frac{x^2}{2}\right) + X_2 \exp\left(-\mu_2^2 \dot{\alpha} \frac{x^2}{2}\right), \quad (\text{C.1})$$

where  $X_1$  and  $X_2$  are unknown constants. Substituting Eq. (C.1) into Eq. (7.1) and integrating, we obtain

$$\begin{aligned} \frac{\partial c_3}{\partial x} &= \left( \frac{1}{\mu_1^2} - a_{11} \right) \frac{X_1}{a_{13}} \exp\left(-\mu_1^2 \dot{\alpha} \frac{x^2}{2}\right) \\ &+ \left( \frac{1}{\mu_2^2} - a_{11} \right) \frac{X_2}{a_{13}} \exp\left(-\mu_2^2 \dot{\alpha} \frac{x^2}{2}\right). \end{aligned} \quad (\text{C.2})$$

The substitution of Eqs. (C.1) and (C.2) into the boundary conditions, Eq. (7.4), yields:

$$\left(\frac{1}{\mu_1^2} - \frac{a}{a_{33}}\right)X_1 + \left(\frac{1}{\mu_2^2} - \frac{a}{a_{33}}\right)X_2 = 0. \quad (\text{C.3})$$

Another connection between  $X_1$  and  $X_2$  can be derived by substitution of Eqs. (C.1) and (C.2) into Eq. (7.3):

$$\frac{X_1}{\mu_1^2} + \frac{X_2}{\mu_2^2} = \tilde{\Gamma}_{1,\text{eq}}\dot{\alpha}. \quad (\text{C.4})$$

From Eqs. (C.3) and (C.4) we obtain

$$X_1 = \frac{\tilde{\Gamma}_{1,\text{eq}}\dot{\alpha}}{\mu_2^2 - \mu_1^2} \left( \mu_1^2 \mu_2^2 - \frac{a_{33}}{a} \mu_1^2 \right),$$

$$X_2 = \frac{\tilde{\Gamma}_{1,\text{eq}}\dot{\alpha}}{\mu_2^2 - \mu_1^2} \left( -\mu_1^2 \mu_2^2 + \frac{a_{33}}{a} \mu_2^2 \right). \quad (\text{C.5})$$

Integrating Eqs. (C.1) and (C.2) from 0 to  $\infty$ , we derive

$$\Delta c_{1b} = -\frac{\pi^{1/2}}{(2\dot{\alpha})^{1/2}} \left( \frac{X_1}{\mu_1} + \frac{X_2}{\mu_2} \right), \quad (\text{C.6})$$

$$\Delta c_{3b} = -\frac{\pi^{1/2}}{(2\dot{\alpha})^{1/2}} \left[ \left( \frac{1}{a_{13}\mu_1^2} - \frac{a_{11}}{a_{13}} \right) \frac{X_1}{\mu_1} + \left( \frac{1}{a_{13}\mu_2^2} - \frac{a_{11}}{a_{13}} \right) \frac{X_2}{\mu_2} \right], \quad (\text{C.7})$$

where  $\Delta c_{ib} = c_i|_{x=0} - c_{i\infty}$ . Next, we substitute  $X_1$  and  $X_2$  from Eq. (C.5) into Eqs. (C.6) and (C.7), and transform the result with the help of Eq. (B.15):

$$\Delta c_{1b} = -\tilde{\Gamma}_{1,\text{eq}} \left( \frac{\pi\dot{\alpha}}{2} \right)^{1/2} \left( \frac{a_{33}}{a} + \frac{1}{a^{1/2}} \right) \frac{1}{\mu_1 + \mu_2}, \quad (\text{C.8})$$

$$\Delta c_{3b} = \tilde{\Gamma}_{1,\text{eq}} \left( \frac{\pi\dot{\alpha}}{2} \right)^{1/2} \frac{a_{31}}{a} \frac{1}{\mu_1 + \mu_2}. \quad (\text{C.9})$$

Finally, we express  $\mu_1 + \mu_2$  from Eq. (B.20), and substitute Eqs. (C.8) and (C.9) into Eq. (6.14). As a result, we obtain Eq. (7.5).

## References

- [1] S.S. Dukhin, G. Kretzschmar, R. Miller, Dynamics of Adsorption at Liquid Interfaces, Elsevier, Amsterdam, 1995.
- [2] A. Bonfillon, F. Sicoli, D. Langevin, J. Colloid Interface Sci. 168 (1994) 497–504.
- [3] S.S. Dukhin, R. Miller, G. Kretzschmar, Colloid Polym. Sci. 261 (1983) 335–339.
- [4] R. Miller, S.S. Dukhin, G. Kretzschmar, Colloid Polym. Sci. 263 (1985) 420–423.
- [5] S.S. Dukhin, R. Miller, Colloid Polym. Sci. 269 (1991) 923–928.
- [6] R. Miller, G. Kretzschmar, S.S. Dukhin, Colloid Polym. Sci. 272 (1994) 548–553.
- [7] R.P. Borwankar, D.T. Wasan, Chem. Eng. Sci. 43 (1988) 1323–1337.
- [8] D.O. Johnson, K.J. Stebe, J. Colloid Interface Sci. 168 (1994) 21–31.
- [9] D.O. Johnson, K.J. Stebe, J. Colloid Interface Sci. 182 (1996) 526–538.
- [10] A. Bonfillon, D. Langevin, Langmuir 10 (1994) 2965–2971.
- [11] C.A. McLeod, C.J. Radke, Langmuir 10 (1994) 3555–3566.
- [12] S.S. Datwani, K.J. Stebe, J. Colloid Interface Sci. 219 (1999) 282–297.
- [13] P.M. Vlahovska, K.D. Danov, A. Mehreteab, G. Broze, J. Colloid Interface Sci. 192 (1997) 194–206.
- [14] K.D. Danov, P.M. Vlahovska, P.A. Kralchevsky, G. Broze, A. Mehreteab, Colloids Surf. A 156 (1999) 389–411.
- [15] K.D. Danov, V.L. Kolev, P.A. Kralchevsky, G. Broze, A. Mehreteab, Langmuir 16 (2000) 2942–2956.
- [16] J.K. Ferri, S.Y. Lin, K.J. Stebe, J. Colloid Interface Sci. 241 (2001) 154–168.
- [17] D.S. Valkovska, G.C. Shearman, C.D. Bain, R.C. Darton, J. Eastoe, Langmuir 20 (2004) 4436–4445.
- [18] A.W. Cross, G.G. Jayson, J. Colloid Interface Sci. 162 (1994) 45–51.
- [19] S.B. Johnson, S.J. Drummond, P.J. Scales, S. Nishimura, Langmuir 11 (1995) 2367–2375.
- [20] P.A. Kralchevsky, K.D. Danov, G. Broze, A. Mehreteab, Langmuir 15 (1999) 2351–2365.
- [21] R.S. Hansen, J. Phys. Chem. 64 (1960) 637–641.
- [22] L.K. Filippov, J. Colloid Interface Sci. 164 (1994) 471–482.
- [23] R. Daniel, J.C. Berg, J. Colloid Interface Sci. 237 (2001) 294–296.
- [24] K.J. Mysels, Langmuir 2 (1986) 428–432.
- [25] T.S. Horozov, C.D. Dushkin, K.D. Danov, L.N. Arnaudov, O.D. Velev, A. Mehreteab, G. Broze, Colloids Surf. A 113 (1996) 117–126.
- [26] V.B. Fainerman, R. Miller, Adv. Colloid Interface Sci. 108–109 (2004) 287–301.
- [27] R. Nagarajan, D.T. Wasan, J. Colloid Interface Sci. 159 (1993) 164–173.
- [28] T.S. Horozov, K.D. Danov, P.A. Kralchevsky, I.B. Ivanov, R.P. Borwankar, A local approach in interfacial rheology: Theory and experiment, in: Proc. First World Congress on Emulsions, vol. 2, Paris, 1993, paper 3-20-137.
- [29] C.A. McLeod, C.J. Radke, J. Colloid Interface Sci. 160 (1993) 435–448.
- [30] E. Rillaerts, P. Joos, J. Colloid Interface Sci. 88 (1982) 1–7.
- [31] P. Joos, Dynamic Surface Phenomena, VSP BV, AH Zeist, The Netherlands, 1999.
- [32] S. Manning-Benson, C.D. Bain, R.C. Darton, J. Colloid Interface Sci. 189 (1997) 109–116.
- [33] S. Manning-Benson, S.W.R. Parker, C.D. Bain, J. Penfold, Langmuir 14 (1998) 990–996.
- [34] C.D. Bain, S. Manning-Benson, R.C. Darton, J. Colloid Interface Sci. 229 (2000) 247–256.
- [35] T. Battal, G.C. Shearman, D.S. Valkovska, C.D. Bain, R.C. Darton, J. Eastoe, Langmuir 19 (2003) 1244–1248.
- [36] N.C. Christov, K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, The maximum bubble pressure method: Universal surface age and transport mechanisms in surfactant solutions, Langmuir 22 (2006), in press.
- [37] J.Th.G. Overbeek, Electrochemistry of the double layer, in: H.R. Kruyt (Ed.), Colloid Science, vol. 1, Elsevier, Amsterdam, 1953.
- [38] F. van Voorst Vader, Th.F. Erkens, M. van den Tempel, Trans. Faraday Soc. 60 (1964) 1170–1177.
- [39] L.D. Landau, E.M. Lifshitz, Electrodynamics of Continuous Medium, Pergamon, Oxford, 1960.
- [40] S. Hachisu, J. Colloid Interface Sci. 33 (1970) 445–454.
- [41] D.G. Hall, Colloids Surf. A 90 (1994) 285–288.
- [42] M. Van Dyke, Perturbation Methods in Fluid Mechanics, Academic Press, New York, 1964.
- [43] L.E. Fraenkel, Proc. Cambridge Philos. Soc. 65 (1969) 209–284.
- [44] A.H. Nayfeh, Perturbation Methods, Wiley, New York, 1973.
- [45] J.W. Gibbs, The Scientific Papers of J.W. Gibbs, vol. 1, Dover, New York, 1961.
- [46] S. Ono, S. Kondo, Molecular theory of surface tension in liquids, in: S. Flügge (Ed.), Handbuch der Physik, vol. 10, Springer-Verlag, Berlin, 1960, p. 134.
- [47] V.L. Kolev, K.D. Danov, P.A. Kralchevsky, G. Broze, A. Mehreteab, Langmuir 18 (2002) 9106–9109.
- [48] K.D. Danov, P.A. Kralchevsky, I.B. Ivanov, Equilibrium and dynamics of surfactant adsorption monolayers and thin liquid films, in: G. Broze (Ed.), Handbook of Detergents, Part A: Properties, Dekker, New York, 1999, pp. 303–418.
- [49] R. Taylor, R. Krishna, Multicomponent Mass Transfer, Wiley, New York, 1993, p. 45.
- [50] K.D. Danov, P.A. Kralchevsky, N.D. Denkov, K.P. Ananthapadmanabhan, A. Lips, Adv. Colloid Interface Sci. 119 (2006) 17–33.

- [51] K.D. Danov, P.A. Kralchevsky, K.P. Ananthapadmanabhan, A. Lips, *Colloids Surf. A* 282–283 (2006) 143–161.
- [52] T. Horozov, L. Arnaudov, *J. Colloid Interface Sci.* 219 (1999) 99–109.
- [53] T. Horozov, L. Arnaudov, *J. Colloid Interface Sci.* 222 (2000) 146–155.
- [54] R. van den Bogaert, P. Joos, *J. Phys. Chem.* 83 (1979) 2244–2248.
- [55] G. Geeraerts, P. Joos, *Colloids Surf. A* 90 (1994) 149–154.
- [56] R.A. Robinson, R.H. Stokes, *Electrolyte Solutions*, second ed., Dover, New York, 2002.
- [57] N. Kamenka, B. Lindman, B. Brun, *Colloid Polym. Sci.* 252 (1974) 144–152.
- [58] J.N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1992.