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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.

Keywords: Adsorption dynamics; Dynamic surface tension; Expanding interfaces; Ionic surfactants; Maximum bubble pressure method

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 approach 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, $c_{1\mathrm{s}}(t)$:

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

where t is time; $c_{1\infty}$ is the bulk surfactant concentration; Γ_1^0 and $\Gamma_{1,\mathrm{eq}}$ 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:

$$\gamma - \gamma_{\mathrm{eq}} = -kT\Gamma_{1,\mathrm{eq}}\frac{c_{1\mathrm{s}} - c_{1\infty}}{c_{1\infty}}, \tag{1.2}$$

where γ_{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

$$\gamma = \gamma_{\mathrm{eq}} + \frac{s_{\gamma,0}}{t^{1/2}}, \tag{1.3}$$

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

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

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:

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

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

where t_{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); λ 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_{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 DS$^-$, component 2 is Na$^+$, and component 3 is 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:

$$c_{2\infty} = c_{1\infty} + c_{3\infty}. \tag{2.1}$$

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 ψ. It is convenient to introduce the dimensionless electric potential, $\Phi = Ze\psi/(kT)$, where e is the electronic charge; because Z and ψ have the same sign, we have $\Phi \geqslant 0$.

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

$$\dot{\alpha}(t) \equiv \frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}t}. \tag{2.2}$$

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