EFFET DES MICELLES ET DE L'ÉLECTROLYTE SUR LA CINÉTIQUE DE L'ADSORPTION	2 - 2
EFFECT OF MICELLES AND ELECTROLYTE ON THE ADSORPTION KINETICS	153

Auteur(s) Author(s)	Nom (s) Name (s)	Prénom (s) First name (s)	Affiliation
1	DANOV	Krassimir D.	LTPH, Univ. Sofia, BG
2	VLAHOVSKA	Petia M.	LTPH, Univ. Sofia, BG
3	KRALCHEVSKY	Peter A.	LTPH, Univ. Sofia, BG

Adresse postale Mailing address	Lab. of Thermod. and Phys.-Chem. Hydrodynamics, Fac. of Chem., University of Sofia, J. Bourchier Avenue 1, Sofia 1126, Bulgaria

RÉSUMÉ

Nous proposons une approche théorique de la cinétique de l'adsorption sur l'interface dilatée d'une solution à base de micellaires. Les micelles se diffusent et libèrent simultanément des monomères pour compenser la déficience locale du surfactant. Cette théorie est appliquée à des données expérimentales pour la tension de surface dynamique de solutions micellaires de dodécylsulfate de sodium (SDS) et de sulfate de polyoxyéthylène-2 de sodium (SDP2S), mesurée par la méthode de pression maximale des bulles. On détermine les constantes de la micellization.

On présente un modèle pour la cinétique d'adsorption des surfactants ioniques de solutions, en présence d'électrolyte symétrique. L'effet exercé par les ions du champ électrique sur la diffusion des molécules chargées vers l'interface chargée est pris en compte. Le modèle est appliqué de manière à interpréter les données expérimentales pour le dodécyletrimethylebromure, le SDS et le SDP2S à l'interface entre l'eau et l'éther de pétrole, le décane et l'heptane.

ABSTRACT

A theoretical approach to the kinetics of adsorption on the expanding interface of an micellar solution is proposed. The extension of the adsorption monolayer leads to a transfer of surfactant molecules from the bulk of solution. The micelles simultaneously diffuse and release monomers to compensate the local deficiency of surfactant. The theory is applied to fit experimental data for dynamic surface tension of micellar solutions of sodium dodecyl sulfate (SDS) and sodium polyoxyethylene-2 sulfate (SDP2S) measured by the maximum bubble pressure method. The rate constants of micellization are determined.

A model for adsorption kinetics of ionic surfactants solutions in the presence of background symmetrical electrolyte is presented. The effect of the electric field due to ions on the diffusion of charged molecules toward charged interface is taken into account. The model is applied to interpret experimental data for dodecyl trimethyl bromide, SDS and SDP2S at the interface between water and petorleum ether, decane and heptane.

EFFECT OF MICELLES AND ELECTROLYTE ON THE ADSORPTION KINETICS

1. Introduction

Many processes in emulsions are accompanied by disturbances of the interfacial adsorption monolayers at the droplet surfaces. The surfactant solution has the property to damp the disturbances by diffusion of surfactant from the bulk to the interface, or by surface convection and diffusion of already adsorbed surfactant molecules throughout the interface (1,2). These processes turn out to be crucial for the *kinetic* stability of emulsions and emulsion films (2,3). Important rheological characteristics of the emulsion interfaces, such as the surface (Gibbs) elasticity, the dilatational and shear viscosities are determined in dynamic experiments (4,5). The latter can be interpreted if only the exchange of surfactant between the bulk and the interface can be quantitatively described.

Here we present solutions of two relatively complicated problems of the kinetics of surfactant adsorption, corresponding to situations appearing often in practice. The first of them is the problem about the adsorption from *micellar* surfactant solutions in the case of *large interfacial disturbances* when the boundary problem cannot be linearized. The purely numerical solution of this problem is much time consuming and inconvenient to apply when interpreting experimental data. Below we propose an analytical solution, which much accelerates the computational procedures and reveals better the physics of the underlying processes.

Second, we consider the problem about the adsorption from solutions of *ionic* surfactants. In this case the main difficulty arises from the non-linearity of the electro-diffusion equations. Simplified models (1) and numerical methods (6) are used to solve this problem. As reported below, we succeeded to obtain an analytical solution for the case of small deviations from equilibrium, which yields an useful expressions for the characteristic relaxation time of adsorption.

2. Adsorption from Micellar Surfactant Solutions: Non-linear Theory
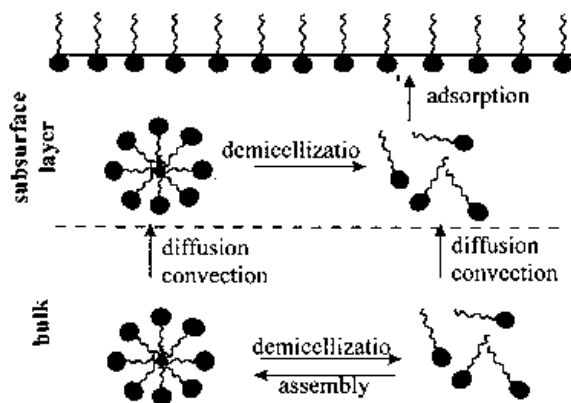

Fig. 1. Role of the micelles in the kinetics of surfactant adsorption.

At concentrations above the critical micellization concentration (CMC) the kinetics of surfactant adsorption is strongly affected (accelerated) by the presence of micelles. The micelles exist in dynamic equilibrium with the surfactant monomers in the bulk of solution. A dilatation of the surfactant adsorption monolayer leads to adsorption of monomers, which causes a transient decrease of the subsurface concentration of monomers (Fig. 1). These processes are accompanied by diffusion transport of monomers and micelles driven by the concentration gradients. The experiments on micellization show that the relaxation in micellar solution is characterized by two relaxation times. The decay of a micelle is considered as a consequence of fast and slow processes (7). The *fast* process is

$$A_m \underset{k_f^a}{\overset{k_f^d}{\longleftrightarrow}} A_{m-1} + A_1 , \qquad \text{for } m > n ,$$
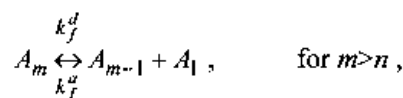
where k_f^d and k_f^a are the respective rate constants. This means that for m greater than a certain value n a micelle can easily release a monomer and transform into a micelle of aggregation number $m-1$

without destruction of the micellar aggregate. On the other hand, the *slow* process is initiated by the detachment of a monomer from a micelle of critical aggregation number n, which leads to a break of the micelle into highly unstable fractions disintegrating to monomers:

$$A_n \overset{k_s^d}{\underset{k_s^a}{\leftrightarrow}} nA_1 \ .$$
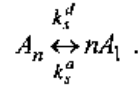
Here k_s^d and k_s^a are the dissociation and association rate constants of the slow process. The general equations describing the surfactant transport toward an expanding flat liquid interface read (8):

$$\frac{\partial c_1}{\partial t} - \dot{\alpha}x \frac{\partial c_1}{\partial x} = D_1 \frac{\partial^2 c_1}{\partial x^2} + nk_s^d c_n - nk_s^a c_1^n + k_f^d \sum_{i=n+1}^{M} c_i - k_f^a c_1 \sum_{i=n}^{M-1} c_i \ , \quad (x > 0, t > 0),$$

$$\frac{\partial c_n}{\partial t} - \dot{\alpha}x \frac{\partial c_n}{\partial x} = D_n \frac{\partial^2 c_n}{\partial x^2} - k_s^d c_n + k_s^a c_1^n + k_f^d c_{n+1} - k_f^a c_1 c_n \ , \quad (x > 0, t > 0),$$

$$\frac{\partial c_k}{\partial t} - \dot{\alpha}x \frac{\partial c_k}{\partial x} = D_k \frac{\partial^2 c_k}{\partial x^2} + k_f^d (c_{k+1} - c_k) - k_f^a c_1 (c_k - c_{k-1}) \quad (n+1 \leq k \leq M), \ (x > 0, t > 0),$$

$$\frac{d\Gamma}{dt} + \dot{\alpha}\Gamma = D_1 \frac{\partial c_1}{\partial x} \ , \quad (x = 0, t > 0), \tag{1}$$

where $\dot{\alpha}(t)$ is the rate of interfacial dilatation, t is time, x is a spatial coordinate normal to the interface, c_1 and c_k are the bulk concentrations of monomers and micelles containing k monomers, D_k is the respective diffusion coefficient, M is the aggregation number of the largest micelles, and Γ is the surfactant adsorption. To solve the problem we use appropriate *model* profiles, $c_k^*(x,t)$, $(k = 1, n,...,M)$ of the species concentrations in the bulk of solution (8,9). Thus the time consuming numerical integration of the partial differential equations [1] can be avoided. The model functions c_k^* must satisfy the following integral condition for equivalence of the model and real systems with respect to the masses of the species:

$$\int_0^\infty \left[1 - \frac{c_k^*(x,t)}{c_{k,e}} \right] dx = \int_0^\infty \left[1 - \frac{c_k(x,t)}{c_{k,e}} \right] dx = I_k(t) \qquad (k = 1, n,..., M), \tag{2}$$

where $c_k(x,t)$ denotes the *real* concentration profile and $c_{k,e}$ is the equilibrium initial concentration. The appropriate model function for the *monomer* concentration profile is defined (9) by the expression $c_1^*(x,t) = c_{1,s}(t) + \left[c_{1,e} - c_{1,s}(t) \right] \sin\left[\pi x / (2\delta) \right]$ for $x \leq \delta$ and $c_1^* = c_{1,e}$ for $x \geq \delta$, where the parameter δ is a characteristics of the diffusion layer thickness and $c_{1,s}$ is the subsurface concentration of the monomers. A similar model function for the concentration profile of the micellar aggregates $(n \leq k \leq M)$ was proposed (8), $2c_k^*(x,t) = \left[c_{k,e} + c_{k,s}(t) \right] - \left[c_{k,e} - c_{k,s}(t) \right] \cos(\pi x / \delta)$ for $x \leq \delta$ and $c_k^* = c_{k,e}$ for $x \geq \delta$, where $c_{k,s}$ is the subsurface concentration of the micelles. As shown in Refs. (8,9) these model profiles guarantee the fulfillment of the boundary condition at the interface and the smooth matching at the point $x = \delta$. The positions of the matching points and the subsurface concentrations can be determined from Eq. [2]: $I_1 = (\pi - 2)\delta(c_{1,e} - c_{1,s}) / (\pi c_{1,e})$ and $I_k = \delta(c_{k,e} - c_{k,s}) / (2c_{k,e})$. With the help of these model profiles the initial set of *partial* differential equations [1] reduce to the following set of *ordinary* differential and *algebraic* equations

$$\frac{dl_1}{dt} + \dot{\alpha}l_1 = \frac{\pi^2}{2(\pi-2)}\frac{D_1 l_1}{\delta^2} + nk_s^d \frac{c_{n,e}}{c_{1,e}}\left[l_n - l_1 G_n\left(\frac{l_1}{\delta}\right)\right] + k_f^d \sum_{k=n+1}^{M}\frac{c_{k,e}}{c_{1,e}}R_k \ , \tag{3}$$

$$\frac{dl_n}{dt} + \dot{\alpha}l_n = -k_s^d\left[l_n - l_1 G_n\left(\frac{l_1}{\delta}\right)\right] + k_f^d \frac{c_{n+1,e}}{c_{1,e}}R_{n+1} \ , \tag{4}$$

$$\frac{dl_k}{dt} + \dot{\alpha}l_k = k_f^d \frac{c_{k+1,e}}{c_{1,e}}R_{k+1} - k_f^d R_k \qquad (k = n+1,...,M) \ , \tag{5}$$

$$\Gamma(t) = \frac{A(0)}{A(t)}\Gamma(0) + c_{1,e}l_1 + \sum_{k=n}^{M}kc_{k,e}l_k \ . \tag{6}$$

In Eq. [6] $A(t)$ is the interfacial area (which is supposed to be a known function of t) and the functions used for the definitions of the sources in the kinetic equations are defined by expressions

$$R_k = l_k - l_1 - l_{k-1} + \frac{3\pi-4}{3(\pi-2)}\frac{l_1}{\delta}l_{k-1} \qquad (k = n+1,...,M), \qquad R_{M+1} \equiv 0 \ , \tag{7}$$

$$G_n(y) = \frac{2}{\pi y}\int_0^{\pi/2}\left\{1-\left[\left(1-\frac{\pi y}{\pi-2}\right)+\frac{\pi y}{\pi-2}\sin x\right]^n\right\}dx \ . \tag{8}$$

Eqs. [3-8] together with the adsorption isotherm (say the Langmuir isotherm) form a closed set of equations for determining the unknown functions. The system can be solved numerically; it is convenient to tabulate the special function $G_n(y)$ in the computer memory.
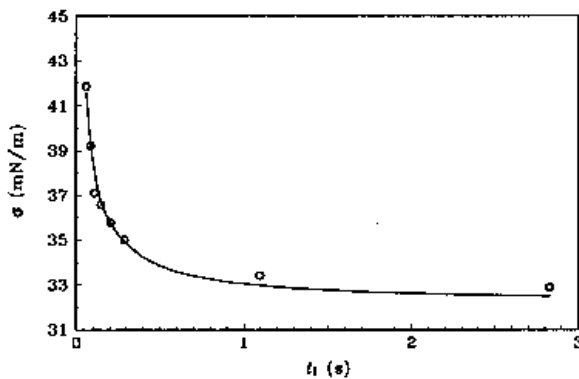

Fig. 2. Dynamic surface tension of SDS at concentration 1.25×10^{-3} mol/l.

The above theory is applied for interpretation of dynamic surface tension data for the adsorption from solutions of sodium dodecyl sulfate (SDS), Fig. 2. The maximum bubble pressure method (MBPM) is used. An empirical adsorption isotherm of SDS was used with a value $\overline{M} \approx 80$ of the mean aggregation number of the micelles (8). As an example, a numerical fit of data is shown in Fig. 2. The diffusion coefficient of the SDS monomers calculated from experimental data below CMC is $D_1 \approx 5 \times 10^{-10}$ m^2/s, which is close to the value determined by other authors (10). This value of D_1 has been further used to fit the data for concentrations above CMC. The diffusion coefficients of the micelles are taken to be the same, $D_k \approx 1.4 \times 10^{-10}$ m^2/s. The rate constants of the slow and fast relaxation processes, determined from the best fit are $k_s^d = 68$ s^{-1} and $k_f^d = 1130$ s^{-1}. The determined aggregation number of the critical micelle is $n = 74$; the polydispersity of the micelles is of the order of $(\overline{M} - n)/\overline{M} \approx 6\%$.

3. Adsorption Kinetics of Ionic Surfactants

The process of adsorption of an *ionic* surfactant is accompanied with a growth of the surface charge density and the surface potential with time. In its own turn, the presence of surface
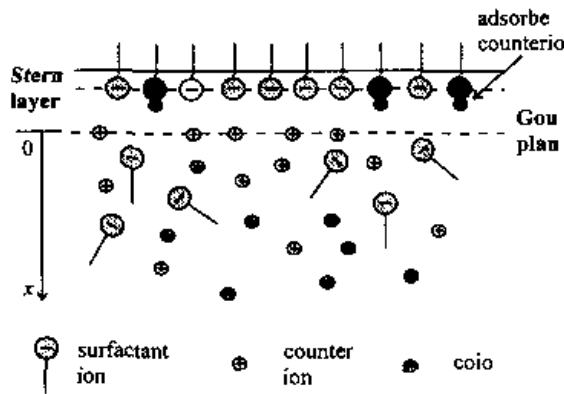
Fig. 3. Adsorption from anionic surfactant solution

charge leads to formation of an electrical double layer (EDL) inside the solution. The charged surface repels the new-coming surfactant molecules (Fig. 3), which results in a deceleration of the adsorption process. We consider an aqueous solution of symmetrical $(z{:}z)$ ionic surfactant in the presence of additional common z:z electrolyte. The transport of the surfactant ions is strongly affected by the electric field due to the non-uniform ionic distribution in the EDL. This is accounted for by the electromigration terms in the transport equations of each charged species $(i = 1, 2$ and 3 for the surfactant ions, counterions and coions, respectively), of charge z_i and diffusion coefficient D_i:
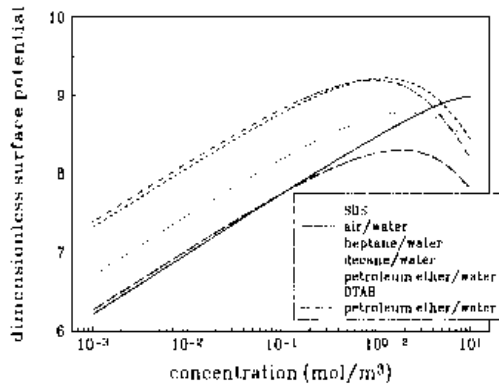
$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial x}\left(\frac{\partial c_i}{\partial x} + \frac{z_i}{k_B T} c_i \frac{\partial \psi}{\partial x}\right) \quad (i = 1,2,3) \ , \qquad \frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi}{\varepsilon}\left[z_1 c_1 + z_2 c_2 + z_3 c_3\right] \ . \qquad [9]$$

Here ψ denotes electrical potential, $c_i(x,t)$ are the bulk concentrations of the respective ions; k_B is the Boltzmann constant, T is absolute temperature, ε is dielectric permittivity. Since both the surfactant and the salt are symmetrical electrolytes, one has $z_1 = -z_2 = z_3 \equiv z$. The boundary conditions for Eq. [9] stem from the interfacial mass balances and the electroneutrality condition for the solution as a whole:

$$\frac{d\Gamma_i}{dt} = D_i\left(\frac{\partial c_i}{\partial x} + \frac{z_i}{k_B T} c_i \frac{\partial \psi}{\partial x}\right) \text{ at } x{=}0 \quad (i = 1,2,3) \ ; \qquad \int_0^\infty \left[z c_1 + (-z)c_2 + z c_3\right] dx + z\Gamma_1 + (-z)\Gamma_2 = 0 \ .$$

It is assumed that coions do not adsorb, $\Gamma_3 \equiv 0$. In addition, the adsorptions of surfactant ions, Γ_1, and counterions, Γ_2, are related: $\Gamma_2 = \theta\Gamma_1$ with θ being the occupancy of the Stern layer with adsorbed counterions $(0 \le \theta \le 1)$. To close the set of equations we use also the equilibrium connection between surface charge and surface potential and an adsorption isotherm due to Borwankar and Wasan (11):

$$\Gamma_1^e = \frac{4c_2^\infty}{(1-\theta)\kappa}\sinh\left(\frac{\phi_s^e}{2}\right) \ , \qquad \Gamma_1^e \exp\left(-B\Gamma_1^e / \Gamma_1^\infty\right)/\left(\Gamma_1^e - \Gamma_1^\infty\right) = Kc_1^\infty \exp\left(-\phi_s^e\right) \ , \qquad [10]$$

where the superscript "e" refers to the equilibrium state, κ is the inverse Debye screening length: $\kappa = 8\pi z^2 c_2^\infty / \left(\varepsilon k_B T\right)$; $\phi_s^e = z\psi_s^e /\left(k_B T\right)$ is the dimensionless surface potential; Γ_1^∞ is the adsorption in a closely packed monolayer, the parameter B accounts for the interactions between the adsorbed molecules, K has meaning of equilibrium constant of the adsorption-desorption process.

Fig. 4 represents the dimensionless equilibrium surface potential, ϕ_s^e, of SDS solutions for the interfaces water/air, water/decane, water/heptane and water/petroleum ether, as well as for the interface between petroleum ether and aqueous solution of dodecyl trimethyl amonium bromide (DTAB). The curves are calculated by means of Eq. [10] for surfactant solutions without electrolyte. The differences between the curves demonstrate an effect of the nature of the oil phase. The surface potential increases with the increase of the polarity (and the dielectric constant) of the non-aqueous phase. The maximum of the surface potential can be attributed to the fact that after the formation of a dense adsorption

monolayer a further addition of ionic surfactant (which is an electrolyte) rather suppresses the electric double layer, than increases the adsorption and the surface charge.

In the case of small initial deviation from equilibrium we present the solution of the problem as a perturbation over the equilibrium state. The resulting set of partial differential equations has an analytical solution in terms of hypergeometric functions (12). We found the long time asymptotics of the solution in the form:

$$\frac{\sigma_e - \sigma(t)}{\sigma_e - \sigma(0)} = \frac{\Gamma_1^e - \Gamma_1(t)}{\Gamma_1^e - \Gamma_1(0)} = \sqrt{\frac{t_r}{\pi t}}, \quad t \gg t_r, \quad [11]$$

where $\sigma(t)$ and σ_e denote the surface tension and its equilibrium value; t_r is the relaxation time. If there is *no* additional electrolyte in the surfactant solution, the relaxation time is given by the expression

Fig. 4. Dimensionless surface potential vs. bulk surfactant concentration

$$t_r = \frac{1}{D_*}\left(\frac{\partial \Gamma_1}{\partial c_1^\infty}\right)_{\phi_s^e}^2 \left[\frac{1}{2} + \frac{1}{2}\exp(-\phi_s^e) + \lambda\exp\left(-\frac{3\phi_x^e}{2}\right)\right]^{-2} , \quad \lambda \equiv \frac{\kappa}{2}\left(\frac{\partial \Gamma_1}{\partial c_1^\infty}\right)_{\phi_s^e} \frac{1-\theta}{\exp(-\phi_s^e)} , \quad [12]$$

where the effective diffusion coefficient of the surfactant ions is $D_* \equiv 2D_1 D_2 / (D_1 + D_2)$. A formal transition to electroneutral surface, $\phi_s^e \rightarrow 0$, $\theta \rightarrow 1$, reduces Eq. [12] to the well known formula for the non ionic surfactant relaxation time with an effective diffusivity D_* instead of D_1. The difference between D_* and D_1 accounts for the electrolytic dissociation of the ionic surfactant.

To illustrate the effect of the electrostatic interactions on the relaxation of the interfacial tension we calculated the dependence of t_r on the bulk concentration for the same systems as in Fig. 4. The general trend is that the electrostatic effect (the rise of ϕ_s^e, Fig. 4) increases the adsorption time and decelerates the process of adsorption (see Fig. 5). In addition, the higher the surfactant concentration the shorter the relaxation time. As seen, the relaxation time depends on the nature of the non-aqueous phase (air, heptane, decane, petroleum ether).

Fig. 5. Plot of the relaxation time, t_r, vs. the bulk surfactant concentration.

In the case of ionic surfactant solution *with* added common electrolyte Eq. [11] holds again, but along with another, more complicated, expression for the relaxation time:

$$t_r = \frac{1}{D_{eff}}\left(\frac{\partial \Gamma_1}{\partial c_1^\infty}\right)_{\phi_s^e}^2 , \quad x_s \equiv \frac{c_{\text{surfactant}}}{c_{\text{surfactant}} + c_{\text{electrolyte}}} , \quad \frac{1}{D_{**}} \equiv \frac{1}{2}\left(\frac{x_s}{D_1} + \frac{1}{D_2} + \frac{1-x_s}{D_3}\right) , \quad [13]$$

where the effective diffusion coefficient of the surfactant ions reads

$$\frac{1}{D_{eff}} = \left[\frac{x_s}{\sqrt{D_{**}}} + \frac{1-x_s}{2}\left(1+\exp\left(-\phi_s^e\right)\right)\sqrt{\frac{1-x_s}{D_1} + \frac{x_s}{D_3}} \right]^2 \times \left[\frac{1}{2} + \frac{1}{2}\exp\left(-\phi_s^e\right) + x_s\lambda\exp\left(-\frac{3\phi_s^e}{2}\right) \right]^{-2}$$

One can check that for $x_s = 1$, i.e. in the limiting case without additional electrolyte, Eq. [13] reduces to Eq. [12], as it should be expected. On the other hand, for $x_s \to 0$, i.e. for a great amount of added electrolyte, one obtains $D_{eff} \to D_1$ and Eq. [13] reduces to the common expression for the relaxation time of a nonionic surfactant, see e.g. Ref. (1). In other words, the theory predicts that in solutions of high ionic strength the ionic surfactants diffuse and adsorb like nonionic surfactants, which is understandable from a physical viewpoint.

4. Conclusions

A new analytical approach to the kinetic theory of adsorption at the expanding interface of a micellar surfactant solution is developed. It is successfully applied to process experimental data for dynamic surface tension obtained by means of the maximum bubble pressure method (Fig. 2). The rate constant of the fast and slow processes in the relaxation kinetics of micellization are determined as adjustable parameters from the best fit.

Exact analytical expressions for the characteristic relaxation time, t_r, of adsorption of ionic surfactants from non-micellar solutions is derived, see Eqs. [11]-[13]. These expressions allow us to quantify the influence of the electrostatic interactions and added salt on the kinetics of surfactant adsorption. In agreement with the physical insight, the theory predicts an acceleration of the surfactant adsorption with the decrease of the surface electric potential and with the increase of the electrolyte concentration.

References

1. S. S. Dukhin, G. Kretzschmar, and R. Miller (1995) *Dynamics of Adsorption at Liquid Interfaces*, Elsevier, Amsterdam.
2. I. B. Ivanov and D. S. Dimitrov (1988) in: *Thin Liquid Films* (Ed. I. B. Ivanov), M. Dekker, New York, p. 379.
3. P. A. Kralchevsky, K. D. Danov, and N. D. Denkov (1997) Chemical physics of colloid systems and interfaces, in: *Handbook of Surface and Colloid Chemistry* (Ed. K. S. Birdi), CRC Press, London.
4. R. Nagarajan and D. T. Wasan (1993) *J. Colloid Interface Sci.* **159**, 164.
5. T. S. Horozov, K. D. Danov, P. A. Kralchevsky, I. B. Ivanov, and R. P. Borwankar (1993), A local approach in interfacial rheology, *Proceedings of the First World Congress on Emulsions*, Vol. 2, Paris, p. 137.
6. C. MacLeod and C. Radke (1994) *Langmuir* **10**, 3555.
7. E. A. G. Aniansson and S. N. Wall (1975) *J. Phys. Chem.* **79**, 857.
8. K. D. Danov, P. M. Vlahovska, T. S. Horozov, C. D. Dushkin, P. A. Kralchevsky, A. Mehreteab, and G. Broze (1996) *J. Colloid Interface Sci.* **183**, 223.
9. P. A. Kralchevsky, Y. S. Radkov, and N. D. Denkov (1993) *J. Colloid Interface Sci.* **161**, 361.
10. N. Kamenka, B. Lindman, and B. Brun (1974) *Colloid & Polym. Sci.* **252**, 144.
11. R. P. Borwankar and D. T. Wasan (1988) *Chem. Engng. Sci.* **43**, 1323.
12. P. M. Vlahovska, K. D. Danov, A. Mehreteab, and G. Broze (1997) Adsorption kinetics of ionic surfactant with detailed account for the electrostatic interactions. I. No added electrolyte. *J. Colloid Interface Sci.* - in press.