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ORIGINAL CONTRIBUTION

A. Petkova
C. Dushkin

Method of the Green functions in the kinetics of adsorption from micellar surfactant solutions

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A. Petkova
Department of Chemistry
Brandeis University
Waltham, Massachusetts 02254, USA

Dr. C.D. Dushkin (✉)
Department of Life Sciences
Graduate School of Arts and Sciences
University of Tokyo
3-8-1 Komaba, Meguro-ku
Tokyo 153, Japan

Abstract The kinetics of adsorption from micellar surfactant solutions is considered theoretically from a uniform point of view. Three boundary value problems for the adsorption on flat and on spherical interface are solved analytically by means of the method of the Green functions. In this way the bulk concentration and the adsorption of surfactant monomers are expressed as functions of time. The contribution of the micelles (surfactant aggregates) to the diffusion of the monomers is accounted for as pseudo-first order reaction. The adsorption from surfactant solutions without micelles turns out to be the particular case of the problems considered here. Being general in form, the derived equations can be applied also to other practical problems in heterogeneous chemical kinetics, adsorption of gases, heat transfer, etc.

Key words Adsorption kinetics – micellar surfactant solutions – Green functions

Introduction

In this paper, we study theoretically the kinetics of adsorption from micellar surfactant solutions. The micelles, aggregates containing different number of surfactant molecules (monomers), form above the critical micelle concentration (CMC). Although only the monomers adsorb on an interface, the micelles can noticeably affect the adsorption kinetics. In nonequilibrium conditions the micelles show a peculiar behavior due to the way they form. Two relaxation processes of micellization, fast and slow, are demonstrated in homogenous water solutions both experimentally and theoretically [1, 2]. If, however, mass transfer processes like diffusion and adsorption take place simultaneously this picture becomes more complicated [3, 4]. Of importance for the adsorption kinetics is that micellization process (fast or slow) whose characteristic time τ_M is comparable in magnitude either with the time constant of adsorption τ_A (slow adsorption) or with the time constant of diffusion τ_D (slow diffusion).

One possibility for theoretical description of nonhomogeneous micellar solutions is to extend the approaches available for the kinetics of adsorption below CMC. The case of diffusion controlled adsorption, $\tau_A \ll \tau_D$, was considered by Ward and Tordai [5] and Hansen [6] assuming that the subsurface layer and the adsorption layer on the surface are in instantaneous equilibrium. The opposite case of kinetic (barrier) controlled adsorption, $\tau_A \gg \tau_D$, was studied by Baret [7] and Joos et al. [8] in dependence on the way the surfactant molecules pass from the subsurface layer onto the surface. The intermediate case of mixed adsorption, $\tau_A \sim \tau_D$, was treated in refs. [9, 10] for particular adsorption mechanism.

We showed recently [11] that the theoretical approaches used for diffusion controlled adsorption below CMC are in fact respective boundary value problems of the mathematical physics. This allowed a uniform treatment of the adsorption kinetics by the method of the Green functions. Here we extend this approach for solutions containing micelles. For this purpose, we consider the micellization kinetics as a pseudo-first order reaction which allows to linearize the diffusion equations. After that we solve the boundary value problems for flat and spherical interface. The final results of our calculations are new integral equations for the adsorption as a function of time expressed by the subsurface concentration of monomers.

Formulation of the problems and method of solution

The model system consists of two liquid phases, oil/water, or air/water, brought into contact along the dividing surface S, which can be either a plane, situated at $x = 0$, or a sphere with radius R and sphere center at $r = 0$. In the latter case the water is the outer phase surrounding an oil droplet or a gas bubble. The surfactant is soluble only in the water phase where the micelles coexist with single surfactant molecules (monomers). Only the monomers can adsorb on the dividing surface S thus providing certain adsorption Γ. The equilibrium between the adsorbed monomers and the free monomers in the subsurface layer is disturbed by producing an initial jump in the adsorption. This shifts in turn the chemical equilibrium between the monomers and the micelles in the underlying solution. The micelles start to release monomers in order to compensate the local deficiency of surfactant molecules which will influence the surfactant diffusion and, hence, the adsorption kinetics.

The effect of the micellization kinetics can be accounted for by simply adding a single source term to the diffusion equation [4, 12]

$$\frac{\partial c}{\partial t} = D\Delta c - \frac{1}{\tau_M}(c - c_e) . \tag{2.1}$$

Here, $c(\mathbf{r}, t)$ is the concentration of free monomers in the solution; c_e is their equilibrium concentration, equal to CMC; D is the monomer diffusivity; $\mathbf{r}$ is the space position vector; t is time. The differential operator Δ depends on the geometry of the dividing interface S; for plane $\Delta = \partial^2/\partial x^2$; for sphere

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} .$$

The initial condition for c in the bulk of solution is

$$c(\mathbf{r}, 0) = c_e . \tag{2.2}$$

The initial adsorption $\Gamma(0)$ just after perturbation is assumed to be zero. The boundary condition for the concentration far from S simply reads

$$c(\mathbf{r}, t) = c_e, \quad |\mathbf{r}| \to \infty . \tag{2.3}$$

Most important for the solution of the problem is the boundary condition on the dividing surface S, because it accounts for the actual mechanism of adsorption. Depending on this condition, three boundary value problems can be considered:

i) First problem (known as problem of Dirichlet) [5]

$$c(\mathbf{r}, t)|_S = \Phi(t) , \tag{2.4}$$

where $\Phi(t)$ is the subsurface concentration. Equation (2.4) corresponds to a quasi-equilibrium between the subsurface layer of the solution located near S and the adsorption layer, i.e., $\tau_A \ll \tau_D$.

ii) Second problem (problem of Neuman) [6]

$$\left.\frac{\partial c}{\partial n}\right|_S = \frac{1}{D}\frac{d\Gamma}{dt} , \tag{2.5}$$

where $\partial/\partial n = \partial/\partial x$ is for plane, $\partial/\partial n = \partial/\partial r$ is for sphere ($\mathbf{n}$ is the normal to S). Equation (2.5) states that the rate of adsorption equals the diffusion flux of monomers across S. Problems i) and ii) are closely related [11].

iii) Third problem (problem of Robin)

$$\left.\left(\frac{\partial c}{\partial n} - \frac{c}{h}\right)\right|_S = -\frac{\Gamma}{hH} , \tag{2.6}$$

where

$$H = \frac{k_a}{k_d}$$

is the Henry constant, and

$$h = \frac{D}{k_a} .$$

Equation (2.6) is derived assuming linear adsorption mechanism

$$\frac{d\Gamma}{dt} = k_a c|_S - k_d\Gamma , \tag{2.7}$$

where k_a and k_d are adsorption and desorption rate constants, respectively. Hence, Eq. (2.6) follows from (2.5) and (2.7) at $\tau_A \sim \tau_D$.

Below we will solve Eq. (2.1) using the boundary conditions formulated above. First we transform Eqs. (2.1)–(2.6) by introducing a new variable

$$u(\mathbf{r}, t) = [c(\mathbf{r}, t) - c_e]\exp\left(\frac{t}{\tau_M}\right) .$$

After that we solve the respective problems for $u(r, t)$ by means of the method of the Green functions [13, 14]. Since outline of the procedure is given in ref. [11], we give here only the final results for u:

Flat interface:

$$u(x,t) = \int_0^\infty (u\cdot G)|_{t'=0}\, dx' + D\int_0^t \left(u\frac{\partial G}{\partial x'} - G\frac{\partial u}{\partial x'}\right)\Bigg|_{x'=0} dt' \ . \tag{2.8}$$

Spherical interface:

$$u(r,t) = \int_R^\infty (u\cdot G)|_{t'=0}\, r'^2 dr' + R^2 D\int_0^t \left(u\frac{\partial G}{\partial r'} - G\frac{\partial u}{\partial r'}\right)\Bigg|_{r'=R} dt' \ . \tag{2.9}$$

Here $G(\mathbf{r},t;\mathbf{r}',t')$ is the Green function representing the concentration field in the point $\mathbf{r}$ of the solution at the moment t, which is created by an instantaneous point source of material acting in another point $\mathbf{r}'$ at the moment t'. G depends strongly on the geometry and on the boundary conditions. Different Green functions are summarized in Table 1, most of them taken from the literature [13, 14]. The Green function of the second problem for spherical interface is proposed by us. Note that the flat Green functions in Eq. (2.8) are of different dimension from the spherical functions used in Eq. (2.9).

The first term in the right side of (2.8) and (2.9) gives the effect of the initial condition for u, while the second term accounts for the boundary condition on S. These equations allow to treat the adsorption problems, formulated above, from a uniform point of view. The functions u, and hence, the concentration profiles $c(\mathbf{r},t)$, can be derived by inserting there the boundary conditions (2.4)–(2.6) and the respective Green functions from Table 1. Below, we summarize the theoretical results for the bulk surfactant concentration and the adsorption obtained by us for flat and spherical interface.

Flat interface

First problem

Using (2.3), (2.4) and (2.8), as well as the respective Green function from Table 1, we found for the bulk surfactant concentration

$$c(x,t) = c_e - \frac{c_e}{2}\exp\left(-\frac{x^2}{4Dt} - \frac{t}{\tau_M}\right) \cdot\left[\mathrm{E}\left(\frac{x}{2\sqrt{Dt}} + \sqrt{\frac{t}{\tau_M}}\right) + \mathrm{E}\left(\frac{x}{2\sqrt{Dt}} - \sqrt{\frac{t}{\tau_M}}\right)\right] + \frac{x}{2\sqrt{D}}\int_0^t \frac{\Phi(t')}{(t-t')^{3/2}}\exp\left[-\frac{x^2}{4D(t-t')} - \frac{t-t'}{\tau_M}\right]dt' \ , \tag{3.1}$$

where

$$\mathrm{E}(z) = \exp(z^2)\,\mathrm{erfc}(z)$$

$$\mathrm{erfc}(z) = 1 - \mathrm{erf}(z) = 1 - \frac{2}{\sqrt{\pi}}\int_0^z \exp(z'^2)\, dz' \ .$$

To obtain the adsorption Γ, we combined (3.1) and (2.5) and carried out the integration on t as in ref. [5]. The final

Table 1 Green functions of the boundary value problems

	Flat Green functions	Spherical Green functions
First problem	$\frac{1}{2\sqrt{\pi D(t-t')}}\left\{\exp\left[-\frac{(x-x')^2}{4D(t-t')}\right] - \exp\left[-\frac{(x+x')^2}{4D(t-t')}\right]\right\}$	$\frac{1}{2rr'\sqrt{\pi D(t-t')}}\left\{\exp\left[-\frac{(r-r')^2}{4D(t-t')}\right] - \exp\left[-\frac{(r+r'-2R)^2}{4D(t-t')}\right]\right\}$
Second problem	$\frac{1}{2\sqrt{\pi D(t-t')}}\left\{\exp\left[-\frac{(x-x')^2}{4D(t-t')}\right] + \exp\left[-\frac{(x+x')^2}{4D(t-t')}\right]\right\}$	$\frac{1}{2rr'\sqrt{\pi D(t-t')}}\left\{\exp\left[-\frac{(r-r')^2}{4D(t-t')}\right] + \exp\left[-\frac{(r+r'-2R)^2}{4D(t-t')}\right]\right\}$ $-\frac{1}{Rrr'}\exp\left[-\frac{(r+r'-2R)^2}{4D(t-t')}\right]\cdot\mathrm{E}\left[\frac{r+r'-2R}{2\sqrt{D(t-t')}} + \frac{\sqrt{D(t-t')}}{R}\right]$
Third problem	$\frac{1}{2\sqrt{\pi D(t-t')}}\left\{\exp\left[-\frac{(x-x')^2}{4D(t-t')}\right] + \exp\left[-\frac{(x+x')^2}{4D(t-t')}\right]\right\}$ $-\frac{1}{h}\exp\left[-\frac{(x+x')^2}{4D(t-t')}\right]\cdot\mathrm{E}\left[\frac{x+x'}{2\sqrt{D(t-t')}} + \frac{\sqrt{D(t-t')}}{h}\right]$	$\frac{1}{2rr'\sqrt{\pi D(t-t')}}\left\{\exp\left[-\frac{(r-r')^2}{4D(t-t')}\right] + \exp\left[-\frac{(r+r'-2R)^2}{4D(t-t')}\right]\right\}$ $-\frac{1}{brr'}\exp\left[-\frac{(r+r'-2R)^2}{4D(t-t')}\right]\cdot\mathrm{E}\left[\frac{r+r'-2R}{2\sqrt{D(t-t')}} + \frac{\sqrt{D(t-t')}}{b}\right]$

result is

$$\Gamma(t) = c_e\sqrt{D\tau_M}\left[\left(\frac{1}{2}+\frac{t}{\tau_M}\right)\mathrm{erf}\left(\sqrt{\frac{t}{\tau_M}}\right)\right.$$
$$\left.+\sqrt{\frac{t}{\pi\tau_M}}\exp\left(-\frac{t}{\tau_M}\right)\right]-\sqrt{\frac{D}{\tau_M}}\int_0^t \Phi(t')\,\mathrm{erf}\left(\sqrt{\frac{t-t'}{\tau_M}}\right)dt'$$
$$-\sqrt{\frac{D}{\pi}}\int_0^t \frac{\Phi(t')}{\sqrt{t-t'}}\exp\left(\frac{t-t'}{\tau_M}\right)dt'\ . \tag{3.2}$$

When micelles are absent in the solution ($\tau_M \to \infty$) Eq. (3.2) transforms into the equation of Ward and Tordai [5]. Equation (3.2) was published first by Rillaerts and Joos [12]. The case $\Phi = 0$ is known from the paper of Dankwerts [15] describing the absorption of gas in a liquid in the presence of first order chemical reaction.

Second problem

In this case the monomer concentration, obtained from (2.3), (2.5) and (2.8), reads

$$c(x,t) = c_e - \frac{1}{\sqrt{\pi D}}\int_0^t \frac{d\Gamma}{dt}\frac{1}{\sqrt{t-t'}}$$
$$\times\exp\left[-\frac{x^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right]dt'\ . \tag{3.3}$$

The subsurface concentration follows from (3.3) at $x = 0$

$$\Phi(t) = c_e - \frac{1}{\sqrt{\pi D}}\int_0^t \frac{d\Gamma}{dt}\frac{1}{\sqrt{t-t'}}\exp\left(-\frac{t-t'}{\tau_M}\right)dt'\ . \tag{3.4}$$

Equation (3.4) relates the adsorption Γ with the subsurface concentration Φ. In the limit $\tau \to \infty$ Eq. (3.4) gives the respective equation of Hansen [6]. Since (3.4) can be inverted to Eq. (3.2) [16], both the first and the second boundary value problems lead to one and the same result for the adsorption.

Third problem

The concentration profile follows from Eqs. (2.3), (2.6), and (2.8)

$$c(x,t) = c_e + c_e\exp\left(-\frac{x^2}{4Dt}-\frac{t}{\tau_M}\right)\cdot\left\{\frac{D\tau_M}{D\tau_M-h^2}\mathrm{E}\left(\frac{x}{2\sqrt{Dt}}+\frac{\sqrt{Dt}}{h}\right)-\frac{1}{2}\left[\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}-h}\mathrm{E}\left(\frac{x}{2\sqrt{Dt}}+\sqrt{\frac{t}{\tau_M}}\right)\right.\right.$$
$$\left.\left.+\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}+h}\mathrm{E}\left(\frac{x}{2\sqrt{Dt}}-\sqrt{\frac{t}{\tau_M}}\right)\right]\right\}+\frac{1}{hH}\left\{\sqrt{\frac{D}{\pi}}\int_0^t\frac{\Gamma(t')}{\sqrt{t-t'}}\exp\left[-\frac{x^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right]dt'\right.$$
$$\left.-\frac{D}{h}\int_0^t\Gamma(t')\exp\left[-\frac{x^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right]\cdot\mathrm{E}\left[\frac{x}{2\sqrt{D(t-t')}}+\frac{\sqrt{D(t-t')}}{h}\right]dt'\right\}. \tag{3.5}$$

We obtained from (3.5) the subsurface concentration at $x = 0$

$$\Phi(t) = c_e + c_e\exp\left(-\frac{t}{\tau_M}\right)\cdot\left\{\frac{D\tau_M}{D\tau_M-h^2}\mathrm{E}\left(\frac{\sqrt{Dt}}{h}\right)\right.$$
$$\left.-\frac{1}{2}\left[\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}-h}\mathrm{E}\left(\sqrt{\frac{t}{\tau_M}}\right)+\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}+h}\mathrm{E}\left(\sqrt{\frac{t}{\tau_M}}\right)\right]\right\}$$
$$+\frac{1}{hH}\left\{\sqrt{\frac{D}{\pi}}\int_0^t\frac{\Gamma(t')}{\sqrt{t-t'}}\exp\left(\frac{t-t'}{\tau_M}\right)dt'\right.$$
$$\left.-\frac{D}{h}\int_0^t\Gamma(t')\exp\left(-\frac{t-t'}{\tau_M}\right)\cdot\mathrm{E}\left[\frac{\sqrt{D(t-t')}}{h}\right]dt'\right\}. \tag{3.6}$$

It should be noted that at $\tau_M \to \infty$ both Eqs. (3.5) and (3.6) transforms into the respective equations at concentration below CMC, published in ref. [11].

Spherical interface

First problem

We obtained the concentration in the water phase, surrounding a spherical particle with radius R from (2.3), (2.4), (2.9) and the respective Green function from Table 1

$$c(r,t) = c_e - \frac{c_e}{2}\frac{R}{r}\exp\left[-\frac{(r-R)^2}{4Dt}-\frac{t}{\tau_M}\right]$$
$$\times\left[\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}}+\sqrt{\frac{t}{\tau_M}}\right)+\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}}-\sqrt{\frac{t}{\tau_M}}\right)\right]$$
$$+\frac{r-R}{2\sqrt{D}}\frac{R}{r}\int_0^t\frac{\Phi(t')}{(t-t')^{3/2}}$$
$$\times\exp\left[-\frac{(r-R)^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right]dt'\ . \tag{4.1}$$

By inserting (4.1) into (2.5) and integrating on t as in ref. [11], we found for the adsorption

$$\begin{aligned}\Gamma(t) = {} & c_e\sqrt{D\tau_M}\left[\left(\frac{1}{2}+\frac{t}{\tau_M}\right)\operatorname{erf}\left(\sqrt{\frac{t}{\tau_M}}\right)+\sqrt{\frac{t}{\pi\tau_M}}\exp\left(-\frac{t}{\tau_M}\right)\right] \\ & -\sqrt{\frac{D}{\tau_M}}\int_0^t \Phi(t')\operatorname{erf}\left(\sqrt{\frac{t-t'}{\tau_M}}\right)dt' \\ & -\sqrt{\frac{D}{\pi}}\int_0^t \frac{\Phi(t')}{\sqrt{t-t'}}\exp\left(\frac{t-t'}{\tau_M}\right)dt' \\ & -\frac{D}{R}\left[c_e t+\int_0^t \Phi(t')\,dt'\right]. \qquad (4.2)\end{aligned}$$

It is seen that Eq. (3.2) follows from (4.2) at $R \to \infty$.

Second problem

The integration of Eq. (2.9) at the boundary conditions (2.3) and (2.5) leads to the following equation for the bulk concentration

$$\begin{aligned}c(r,t) = {} & c_e - \frac{1}{\sqrt{\pi D}}\frac{R}{r}\int_0^t \frac{d\Gamma}{dt}\frac{1}{\sqrt{t-t'}} \\ & \cdot\exp\left[-\frac{(r-R)^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right]dt' \\ & +\frac{1}{r}\int_0^t \frac{d\Gamma}{dt}\exp\left[-\frac{(r-R)^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right] \\ & \cdot\mathrm{E}\left[\frac{r-R}{2\sqrt{D(t-t')}}+\frac{\sqrt{D(t-t')}}{R}\right]dt'. \qquad (4.3)\end{aligned}$$

For the subsurface concentration $\Phi(t) = c(R,t)$, we derived respectively

$$\begin{aligned}\Phi(t) = {} & c_e - \frac{1}{\sqrt{\pi D}}\int_0^t \frac{d\Gamma}{dt}\frac{1}{\sqrt{t-t'}}\exp\left(-\frac{t-t'}{\tau_M}\right)dt' \\ & +\frac{1}{R}\int_0^t \frac{d\Gamma}{dt}\exp\left(-\frac{t-t'}{\tau_M}\right)\mathrm{E}\left[\frac{\sqrt{D(t-t')}}{R}\right]dt'. \qquad (4.4)\end{aligned}$$

Since the last term in the right side of Eq. (4.4) accounting for the effect of curvature vanishes at $R \to \infty$, Eq. (4.4) reduces to (3.4).

Third problem

The equation for the bulk concentration was derived from Eqs. (2.3), (2.6) and (2.9)

$$\begin{aligned}c(r,t) = {} & c_e + c_e\frac{b}{h}\frac{R}{r}\exp\left(-\frac{(r-R)^2}{4Dt}-\frac{t}{\tau_M}\right) \\ & \times\left\{\frac{D\tau_M}{D\tau_M-b^2}\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}}+\frac{\sqrt{Dt}}{b}\right)\right. \\ & -\frac{1}{2}\left[\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}-b}\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}}+\sqrt{\frac{t}{\tau_M}}\right)\right. \\ & \left.\left.+\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}+b}\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}}-\sqrt{\frac{t}{\tau_M}}\right)\right]\right\} \\ & +\frac{1}{hH}\frac{R}{r}\left\{\sqrt{\frac{D}{\pi}}\int_0^t \frac{\Gamma(t')}{\sqrt{t-t'}}\right. \\ & \times\exp\left[-\frac{(r-R)^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right]dt' \\ & -\frac{D}{b}\int_0^t \Gamma(t')\exp\left[-\frac{(r-R)^2}{4D(t-t')}-\frac{t-t'}{\tau_M}\right] \\ & \left.\times\mathrm{E}\left[\frac{r-R}{2\sqrt{D(t-t')}}+\frac{\sqrt{D(t-t')}}{b}\right]dt'\right\}, \qquad (4.5)\end{aligned}$$

where

$$\frac{1}{b}=\frac{1}{h}+\frac{1}{R}.$$

The subsurface concentration follows from Eq. (4.5) at $r = R$

$$\begin{aligned}\Phi(t) = {} & c_e + c_e\frac{b}{h}\exp\left(-\frac{t}{\tau_M}\right)\cdot\left\{\frac{D\tau_M}{D\tau_M-b^2}\mathrm{E}\left(\frac{\sqrt{Dt}}{b}\right)\right. \\ & \left.-\frac{1}{2}\left[\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}-b}\mathrm{E}\left(\sqrt{\frac{t}{\tau_M}}\right)+\frac{\sqrt{D\tau_M}}{\sqrt{D\tau_M}+b}\mathrm{E}\left(-\sqrt{\frac{t}{\tau_M}}\right)\right]\right\} \\ & +\frac{1}{hH}\left\{\sqrt{\frac{D}{\pi}}\int_0^t \frac{\Gamma(t')}{\sqrt{t-t'}}\exp\left(-\frac{t-t'}{\tau_M}\right)dt'\right. \\ & \left.-\frac{D}{b}\int_0^t \Gamma(t')\exp\left(-\frac{t-t'}{\tau_M}\right)\cdot\mathrm{E}\left[\frac{\sqrt{D(t-t')}}{b}\right]dt'.\right. \qquad (4.6)\end{aligned}$$

For flat interface ($R \gg h$, i.e., $b = h$) Eq. (4.6) reduces to (3.6).

As previously, all equations derived in this section give in the limit $\tau_M \to \infty$ their spherical analogues from ref. [11].

Discussion

The equations for the adsorption $\Gamma(t)$ and the subsurface concentration $\Phi(t)$ derived by us can be applied to calculate the surface tension of micellar solutions as a function of time. Below we discuss particular cases of the respective equations as well as limitations of the theoretical model for the kinetics of adsorption.

Early time approximation

The function $\Phi(t)$ can be obtained experimentally [17] as the concentration of a surfactant solution of equilibrium surface tension equal to the nonequilibrium one at time t. Besides, a model subsurface concentration can also be used to obtain an explicit time dependence of Γ (an example for flat interface is given in ref. [18]).

If the adsorption is diffusion controlled, the surfactant molecules can be thought to instantaneously adsorb on an empty surface ($t \geq 0$). Hence, no monomers can accumulate in the subsurface layer at the early stage of adsorption. By setting $\Phi(t) = 0$ in (3.2) or (4.2) the respective integrals disappear and the equations for Γ become much simpler. Similarly, the adsorption prevails initially over the desorption in the mixed kinetics described as the third problem. Assuming $\Gamma \cong 0$ the integral terms in (3.6) and (4.6) can be neglected which allows to calculate $\Phi(t)$.

The early time approximation holds for short time intervals which usually cannot be accessed experimentally. Especially for micellar solutions where the adsorption kinetics is additionally accelerated by the micellization. That is why the integral terms should also be kept for more adequate description of the relaxation process. A procedure to calculate numerically such terms at concentrations *below* CMC is proposed in ref. [19]. Using an additional relation between Γ and Φ

$$\Gamma(t) = \Gamma[\Phi(t)] \tag{5.1}$$

representing an adsorption isotherm of general type, e.g. Langmurian, one can solve the respective integral equations. Since the numerical computations of $\Gamma(t)$ *above* CMC turned out to be rather tedious, we restrict ourselves with qualitative considerations on the effect of the micelles based on an explicit dependence of the adsorption on time.

Explicit time dependence

Let us assume a linear relation between the subsurface concentration and the adsorption

$$\Gamma(t) = H\Phi(t)\,. \tag{5.2}$$

Equation (5.2) is a consequence of (2.7) which is valid commonly below CMC. Nevertheless, the more general expression (5.1) acquires the same form, if $\Gamma(\Phi)$ is expanded in series with respect to c_e (small deviations from equilibrium [4]).

Here we give only the results for spherical interface: bulk surfactant concentration

$$\begin{aligned}\frac{c(r,t)}{c_e} = 1 - \frac{1}{2Q}\frac{R}{r}\exp\left[-\frac{(r-R)^2}{4Dt} - \frac{t}{\tau_M}\right] &\times\left[(1+Q)\,\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}} + \frac{1+Q}{2}\sqrt{\frac{t}{\tau_M}}\right)\right.\\ &\left.-(1-Q)\,\mathrm{E}\left(\frac{r-R}{2\sqrt{Dt}} + \frac{1-Q}{2}\sqrt{\frac{t}{\tau_M}}\right)\right]\end{aligned} \tag{5.3}$$

and adsorption

$$\begin{aligned}\frac{\Gamma(t)}{\Gamma_e} = 1 - \frac{1}{2Q}\exp\left(-\frac{t}{\tau_M}\right)&\left[(1+Q)\,\mathrm{E}\left(\frac{1+Q}{2}\sqrt{\frac{t}{\tau_M}}\right)\right.\\ &\left.-(1-Q)\,\mathrm{E}\left(\frac{1-Q}{2}\sqrt{\frac{t}{\tau_M}}\right)\right],\end{aligned} \tag{5.4}$$

where

$$Q = \sqrt{1 + 4\left(\frac{\tau_D}{\tau_M} - \frac{H}{R}\right)}$$

$$\tau_D = \frac{H^2}{D}\,. \tag{5.5}$$

At $R \gg H$ Eqs. (5.3) and (5.4) are counterparts of the respective equations for flat interface derived in ref. [4]. Particular case of Eq. (5.4) is the equation of Frish and Mysels [20] referring to concentrations *below* CMC ($\tau_D/\tau_M \to 0$). Other particular cases depending on the parameter Q can also be obtained as for flat interface [18].

In view of the above equations, the effect of the micelles on the kinetics of adsorption is accounted for by the parameter τ_D/τ_M. The adsorption increases with increasing the ratio τ_D/τ_M. Therefore, the smaller the micellization time τ_M, the faster the relaxation of the adsorption (τ_D does not change sufficiently above CMC). In general, τ_M decreases with increasing of the surfactant concentration [1], i.e., of the number of micelles. The micelles appear like bulk sources of material, which supply the interface with additional amount of surfactant monomers [18, 21]. Same trends predict also the integral equations for the adsorption derived in the third section as proven for their early time approximation.

The adsorption on a spherical drop is affected in addition by the interfacial curvature. In general, $\Gamma(t)$ increases faster at smaller drop radius R, because the surfactant molecules more effectively reach the interface at $R \sim H$.

The computations by Eq. (5.4) showed that above CMC the micelles enhance additionally the adsorption despite the drop radius.

Effect of polydispersity of micelles

The source term on the right-hand side of Eq. (2.1) corresponds to micellization kinetics described as a pseudo-first order reaction of single characteristic time τ_M. In this case the reaction rate is linearly proportional to the monomer concentration which allows to solve analytically the respective adsorption problems. Despite the theoretical and experimental verification of this assumption [4, 12, 18], the real micellization kinetics is more complicated. Two relaxation processes of time constants differing by order of magnitude have been found to exist in the micellar solutions [1]. Hence, a more realistic way is to consider separately the diffusion in these two cases. A set of two equations (one for the diffusion of free monomers and the second one for the diffusion of micelles) should be used instead of a single equation. Such equations are coupled through source terms containing both the monomer concentration and the micelle concentration [3, 4]. They contain also parameters accounting for the micelle size distribution: mean aggregation number, dispersion, etc. Unfortunately, it is not possible to find an analytical solution of a set of partial differential equations, even linear, using classical methods such as the Green functions or the Laplace transformation.

In conclusion, the theoretical model presented here treats the adsorption kinetic problems from a uniform point of view. The obtained results can be applied to interpret the kinetics of the surface tension of micellar solutions as well as to other practical problems in the mass and heat transfer.

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