# The kinetics of the surface tension of micellar surfactant solutions

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## Abstract

The effect of diffusion of polydisperse micelles on the kinetics of the surface tension is studied theoretically. It is shown that the surface properties of micellar surfactant solutions depend on which of the relaxation processes of micellization (fast or slow), has a time constant comparable with the characteristic time of diffusion. General equations, describing the diffusion of the free monomers and the micelles, are derived. They include new expressions for the source terms, accounting for the kinetics of micellization of the polydisperse micelles. Analytical solutions of these equations for the surface tension as a function of time are obtained. Since the micelles are additional sources of monomers, the relaxation of the surface tension is faster than the relaxation below the CMC. The theory allows computation of the relaxation time constants of micellization from data obtained by surface stress experiments.

## INTRODUCTION

We consider below the effect of the micelles on the surface tension kinetics of surfactant solutions at concentrations not exceeding several times the critical micelle concentration (CMC). When the interfacial monolayer is expanded, the surfactant molecules are transported to the interface by diffusion before their adsorption. Hence, the local equilibrium between the micelles and the monomers has been disturbed in some vicinity of the interface. Gradients of the micellar concentration thus appear, giving rise to a mass transfer.

In homogeneous micellar systems the species have uniform concentrations at every point in the solution. The micellization kinetics are simpler because diffusion and adsorption processes are missing. Relaxation techniques, producing small deviations from equilibrium, are usually applied to study the kinetics of micellization in such systems.

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The relaxation in a micellar solution is a consequence of two relaxation processes: a fast relaxation process with time constant $\tau_F$, followed by a slow relaxation process with characteristic time $\tau_{SL}$. Usually the two time constants, $\tau_F$ and $\tau_{SL}$, differ by several orders of magnitude ($\tau_F/\tau_{SL} \approx 10^{-2}-10^{-3}$). Aniansson and co-workers [1-3] have developed the most realistic theory of the micellization kinetics in the bulk of surfactant solutions. They considered the micelles as polydisperse particles, containing different numbers of monomers $s$. The micelles participate in a sequence of reaction steps: at each step one monomer is added to, or dissociated from, a micelle. They derived theoretical expressions for the two time constants $\tau_F$ and $\tau_{SL}$. The nature of the relaxation processes will be discussed in more detail in Section 1.

The micellization kinetics are more complicated in non-homogeneous surfactant solutions where diffusion and adsorption occur simultaneously. In this case the concentrations of the species are functions also of the space variables. As far as we know, the kinetics of adsorption from micellar solutions has been treated (both theoretically and experimentally) in only a few studies. Lucassen [4] has measured the surface elasticity modulus of micellar solutions whose surfaces are subjected to periodical perturbations. He has used the model of Kresheck et al. [5] for the kinetics of micellization to explain the experimental data. In this model the micelles are supposed to be monodisperse, i.e. containing the same number of monomers, $m$. In addition a single-step formation of a micelle by simultaneous aggregation of all $m$ monomers has been accepted. This mechanism corresponds roughly to the slow relaxation process [2]. One can conclude that the slow relaxation process of micellization has been detected in the experiment of Lucassen [4].

Using the same model, Miller [6] has solved numerically the respective diffusion equations for the monomers and the monodisperse micelles. His results are not restricted to small deviations from equilibrium. The computations are carried out for Henry's adsorption isotherm (which is not so suitable for typical surfactants above the CMC) and for Langmuir's adsorption isotherm. The numerical examples demonstrated that the adsorption relaxation in the presence of micelles is faster than the relaxation below the CMC. Recently Joos and van Hunsel [7] have used the model of the monodisperse micelles to interpret experimental data on adsorption kinetics obtained by the drop-volume method. The effect of the micelles is accounted for by an effective diffusivity of the monomers.

The monodisperse model is widely used when the diffusivity of the micelles has been determined [8-1 The apparent diffusivity of the micelles is calculated in ments from the concentration profile, measured at a fixe e solution.

Rillaerts and Joos [11] have accounted for the micellization kinetics by adding a single source term to the diffusion equation of the free monomers. This term is proportional to the concentration of the monomers, as in the pseudo-first-order reaction (PFOR) model, known from chemical kinetics. They have solved the respective boundary value problem, formulated by Ward and Tordai [12] for concentrations below the CMC. The result is an expression for the adsorption as a function of time and the subsurface concentration. These authors have also calculated the rate constant of micellization from experimental data of dynamic surface tension, measured by means of the oscillating-jet and flowing-film methods. The PFOR-model will be discussed in detail in Section 5.

Feinerman [13] has also tried to combine the theory of Aniansson and Wall with the kinetics of adsorption from micellar solutions. He has proposed two pairs of diffusion equations for the free monomers and the micelles, written separately for the fast and slow relaxation processes. To do this he has simplified the respective time constants, known from the theory of Aniansson and Wall. The source terms thus obtained are proportional to the concentration of the free monomers as in the PFOR-model. Feinerman has solved the adsorption kinetics problem of Ward and Tordai and has found two solutions for the adsorption, valid for the fast and slow relaxation processes. Very recently Feinerman and Rakita [14] have applied this theory to calculate the micellization time constant from data of the dynamic surface tension, obtained experimentally by means of the maximum bubble pressure method. More details about the equations of Feinerman [13] will be given in Sections 3 and 4.

The purpose of our study is to develop a diffusion theory of the kinetic surface tension of surfactant solutions which contain polydisperse micelles. The general diffusion equations, derived below, include new expressions for the source terms accounting for the kinetics of micellization of the polydisperse micelles. To do this we apply, in a consistent way, the ideas of Aniansson and Wall for the micellization kinetics to non-homogeneous micellar systems, where diffusion and adsorption take place simultaneously.

In Section 1 we present a brief review of the theory of Aniansson and Wall for micellization kinetics in bulk systems. The general formulation of the mathematical problem describing the diffusion of polydisperse micelles is given in Section 2. In Sections 3 and 4 we consider two special cases of diffusion, where either the slow or the fast relaxation process predominantly affects the transfer of surfactant. The respective two pairs of diffusion equations for the concentrations of the free monomers and the micelles are solved analytically and two

expressions for the kinetic surface tension are derived. In Section 5 an approximate solution for the surface tension in the frames of the PFOR-model is obtained.

## 1. RELAXATION PROCESSES WITH MICELLES

According to Aniansson and co-workers [1–3] the relaxation in a micellar solution can be thought of as a sequence of processes which can be visualized by plotting the concentration of the species $c_s$ as a function of their aggregation numbers $s$ (see Fig. 1). The size distribution can be separated into three important regions: oligomers, including the free monomers ($s = 1, 2, 3, \ldots, s_1$); rare aggregates ($s = s_1 + 1, s_1 + 2, \ldots, s_2$); and abundant micelles ($s = s_2 + 1, s_2 + 2, \ldots, s_3$). The species belonging to these regions exhibit a cooperative behavior during the relaxation in the micellar solution. The premicellar aggregates with $s = 2, 3, 4, \ldots, s_2$ are present at considerably smaller concentrations than the free monomers and the abundant micelles.

The relaxation pathway depends on the experimental method used, although the relaxation time constants are the same. As an example we shall briefly discuss here the stopped-flow method where initially two surfactant solutions (micellar and submicellar ones) are suddenly mixed. After the mixing, the concentrations of the species decrease (with respect to their values in the micellar solution) if the mixing time is shorter than $\tau_F$ (Fig. 1). The system moves towards a new equilibrium state with smaller micellar concentration but the same monomer concentration (the latter is equal to the CMC). During the fast relaxation the micelle peak moves towards smaller mean aggregation numbers without changing its height. During the slow relaxation the peak returns back to the initial location and simultaneously
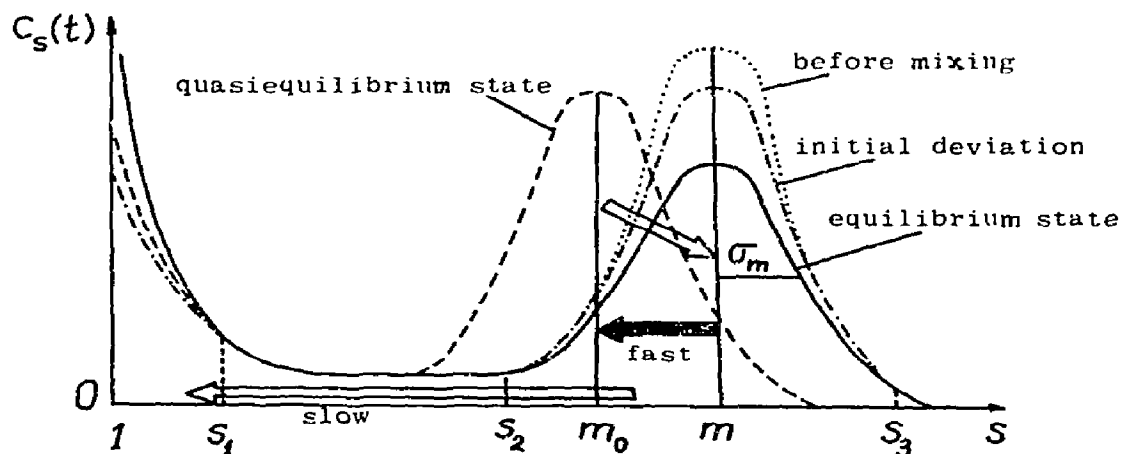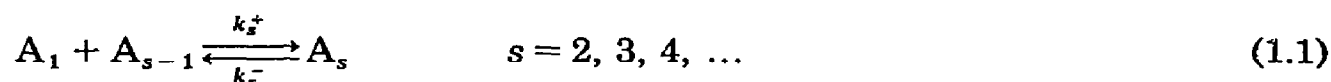


Fig. 1. Sketch of the relaxation of a micellar solution in a stopped-flow experiment.

decreases its height until the final equilibrium concentration of micelles is reached (for a more detailed discussion see Ref. [15]).

Aniansson and Wall have accepted the following reaction mechanism of formation of aggregates

$$A_1 + A_{s-1} \underset{k_s^-}{\overset{k_s^+}{\rightleftharpoons}} A_s \qquad s = 2, 3, 4, \ldots \qquad (1.1)$$

where $A_s$ is the symbol of one $s$-mer, $k_s^+$ and $k_s^-$ are the rate constants of association and dissociation respectively. To solve the system of kinetic equations corresponding to (1.1) Aniansson and Wall have made the following assumptions. (i) The size distribution of the abundant micelles is broad enough to be considered as continuous. A gaussian size distribution

$$c(s) = c_{max} \exp \left[ - \frac{(s - m)^2}{2\sigma_m^2} \right] \qquad (1.2)$$

has been assumed with a mean aggregation number $m$ and dispersion $\sigma_m$. In addition, the sums in the micellar region have been replaced by integrals over $s$. (ii) The dissociation rate constant of an elementary reaction in the micellar region does not depend on $s$, i.e. one can write $k_s^- \approx k_m^- = $ const. (iii) The reaction set can be cut off at some value $s_1$, because the concentrations of the micelles with larger $s$ vanish.

Following these assumptions, Aniansson and Wall have obtained

$$\frac{1}{\tau_F} = \frac{k_m^-}{\sigma_m^2} (1 + \sigma_m^2 \beta_m) \qquad (1.3)$$

for the relaxation time of the fast process, where

$$k_m^- = \sum_{s_2+1}^{s_3} k_s^- \bar{c}_s / \bar{c}_m \qquad (1.4a)$$

$$\bar{c}_m = \sum_{s_2+1}^{s_3} \bar{c}_s \qquad m = \sum_{s_2+1}^{s_3} s\bar{c}_s / \bar{c}_m \qquad (1.4b)$$

$k_m^-$ is the mean dissociation rate constant of the micelles; $\beta_m = \bar{c}_m / \bar{c}_1$; $\bar{c}_1$ is the concentration of the free monomers (for non-ionic surfactants $\bar{c}_1 \approx $ CMC); $\bar{c}_m$ is the total concentration of the micelles $(\bar{c}_m \approx (\bar{c} - \bar{c}_1)/m\bar{c}_1)$; $\bar{c}_s$ is the $s$-mer concentration; $\bar{c}$ is the total surfactant concentration; $m$ is the mean aggregation number of the abundant micelles. (The bars denote equilibrium values.)

For the slow relaxation time the authors of Refs [1–3] have derived respectively

$$\frac{1}{\tau_{SL}} = \frac{1}{R\bar{c}_1\,\beta_m}\,\frac{n_2\beta_n + m_2\beta_m}{n_2\beta_n + \sigma_m^2\beta_m} \tag{1.5}$$

where

$$m_2 = m^2 + \sigma_m^2 = \sum_{s_2+1}^{s_3} s^2\bar{c}_s/\bar{c}_m \tag{1.6a}$$

$$n = \sum_1^{s_1} s\bar{c}_s/\bar{c}_n \qquad n_2 = n^2 + \sigma_n^2 = \sum_1^{s_1} s^2\bar{c}_s/\bar{c}_n \tag{1.6b}$$

$$\bar{c}_n = \sum_1^{s_1} \bar{c}_s$$

$$R = \sum_{s_1}^{s_2} (k_s^-\,\bar{c}_s)^{-1} \tag{1.6c}$$

where $m_2$ and $n_2$ are the second mathematical moments of the micellar and oligomer size distributions; $\sigma_n$ and $n$ are the dispersion and the mean aggregation number of the oligomers; $\bar{c}_n$ is the total oligomer concentration; $\beta_n = \bar{c}_n/\bar{c}_1$; $R$ is termed the resistance of the transition region.

Although the theory of Aniansson and Wall explains satisfactorily a number of experimental data for homogeneous systems, it is too complicated for direct application to more sophisticated diffusion problems in non-homogeneous micellar systems, where adsorption–desorption processes are also important. That is why we re-examined recently [16] this theory by means of the mathematical method of matched asymptotic expansions [17]. The ratio $\tau_F/\tau_{SL}$ was used as a small parameter when solving the kinetic problem. Three different types of solutions for the concentrations of the free monomers and of the micelles were found: inner, outer and matched solutions. The inner solutions are valid during the fast relaxation process. The outer solutions describe the relaxation during the slow process. The matched solutions are uniformly valid over the whole time interval.

The asymptotic solutions obtained in Ref. [16] refer to uniform micellar solutions, where diffusion and adsorption are absent. In the present paper we shall consider the case when concentration gradients and diffusion exist. We shall again use the method of the matched asymptotic expansions to solve the respective diffusion equations of the species. The theory is developed for the case of a non-ionic surfactant. Nevertheless, the main features of the diffusion theory

proposed here can be valid also for ionic surfactants, as is the theory of Aniansson and Wall.

## 2. DIFFUSION EQUATIONS

We shall study the relaxation of the surface tension of a flat air/water interface with time. Consider an adsorption layer which is in equilibrium with the adjacent solution (the equilibrium adsorption is $\bar{\Gamma}$, while the surface tension is $\bar{\sigma}$). If initially the layer is expanded (or compressed), as in the surface stress–relaxation methods [18–20], an initial non-equilibrium adsorption $\Gamma_0$ is established (the corresponding surface tension is $\sigma_0$). Immediately surfactant monomers will start to adsorb onto the surface to compensate the perturbation there. We propose that the total area of the adsorption layer does not change during the relaxation. The adsorption is supposed to be diffusion controlled. This means (i) the diffusion is much faster than the adsorption and (ii) the adsorption layer and the subsurface layer are in a state of instantaneous (quasi)equilibrium during the relaxation.

The characteristic time of the experiment should be of the order of the diffusion time constant $\tau_D$ in order to observe any relaxation of the surface tension caused by the surfactant diffusion. Generally, $\tau_D$ can be expressed as $\tau_D = \delta_D^2/D_1$, where $\delta_D$ is the characteristic length of diffusion and $D_1$ is the diffusivity of surfactant monomers. Since $D_1 \approx 5 \cdot 10^{-6}$ cm$^2$ s$^{-1}$ for most surfactants, $\tau_D$ will be determined predominantly by $\delta_D$. The last quantity may be the derivative $\partial \bar{\Gamma}/\partial \bar{c}_1$ (see below) or some other quantity of linear dimension, characterizing the width of the region where the diffusion takes place. $\tau_D$ can vary over fairly large limits: $10^{-5}$–$10^2$ s, depending on the type of the surfactant. These values cover the whole interval of $\tau_F$ and $\tau_{SL}$ observed experimentally [3]. We shall consider separately the following two cases: (i) $\tau_D$ of the order of $\tau_F$, and (ii) $\tau_D$ of the order of $\tau_{SL}$.

Consider a semi-infinite solution occupying the space with $x > 0$ (the dividing surface solution/air is placed at $x = 0$). The starting point of our considerations is the following set of equations corresponding to the reaction mechanism (1.1):

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} - 2j_2 - \sum_{3}^{s_3} j_s \tag{2.1a}$$

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} + j_s - j_{s+1} \qquad s = 2, 3, 4, \ldots, s_3 \tag{2.1b}$$

$$j_s = k_s^+ c_1 c_{s-1} - k_s^- c_s \qquad s = 2, 3, 4, \ldots, s_3 \tag{2.2}$$

$$\sum_{1}^{s_3} c_s = c \tag{2.3}$$

where $c_s(x, t)$ is the $s$-mer concentration; $D_s$ is the diffusivity of one $s$-mer; $j_s(x, t)$ is the total rate of the $s$th reaction, i.e. the chemical (pseudo)flux. Note that the total surfactant concentration $c(x, t)$ is not equal to the equilibrium value, $\bar{c}$, in the mass balance of the monomers (2.3), because of the diffusion and adsorption processes.

The boundary and the initial conditions are the following:

$$\frac{d\Gamma}{dt} = D_1 \frac{\partial c_1}{\partial x}\bigg|_{x=0} \tag{2.4}$$

$$\Gamma = \bar{\Gamma} + (\partial\bar{\Gamma}/\partial\bar{c}_1)(c_1 - \bar{c}_1)|_{x=0} \tag{2.5}$$

$$\frac{\partial c_s}{\partial x}\bigg|_{x=0} = 0 \qquad s = 2, 3, 4, \ldots, s_3 \tag{2.6}$$

$$c_s(\infty, t) = \bar{c}_s \qquad s = 1, 2, 3, \ldots, s_3 \tag{2.7a}$$

$$c_s(x, 0) = \bar{c}_s \qquad s = 1, 2, 3, \ldots, s_3 \tag{2.7b}$$

$$\Gamma(0) = \Gamma_0 \tag{2.8}$$

Equation (2.4) is the surface mass balance; Eqn (2.5) is an expansion of the adsorption $\Gamma(t)$ at small deviations from equilibrium. The derivative $\partial\bar{\Gamma}/\partial\bar{c}_1$ should be calculated at the CMC [4]. Equation (2.6) means that all aggregates ($s \geqslant 2$) do not adsorb while Eqn (2.7a) implies that the equilibrium concentrations of the species are not disturbed far from the interface. Equations (2.7b) and (2.8) are the respective initial conditions, valid at the moment $t = 0$. An expansion similar to (2.5) can be written also for the surface tension $\sigma(t)$

$$\sigma = \bar{\sigma} + (\partial\bar{\sigma}/\partial\bar{c}_1)(c_1 - \bar{c}_1)|_{x=0} \tag{2.9a}$$

It follows from (2.5) and (2.9a) that the respective deviations from the equilibrium quantities are connected by means of the relationship

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} = \frac{\Delta\Gamma(t)}{\Delta\Gamma(0)} = \frac{\Delta c_1(0, t)}{\Delta c_1(0, 0)} \tag{2.9b}$$

where $\Delta\sigma = \sigma - \bar{\sigma}$, $\Delta\Gamma = \Gamma - \bar{\Gamma}$ and $\Delta c_1 = c_1 - \bar{c}_1$.

To solve the set (2.1) containing many partial differential equations we shall follow the asymptotic approach, developed in Ref. [16] for systems without diffusion terms. First, we group the equations describing the cooperative behavior of the aggregates in the three distinct regions (oligomers, rare aggregates and abundant micelles). Second,

we scale the terms in an appropriate way to distinguish the role which every term plays during the mass transfer. Third, we expand the concentrations $c_s$ and the fluxes $j_s$ into power series of the small parameter

$$\epsilon = \tau_F/\tau_{SL} \ll 1 \tag{2.10}$$

Fourth we reduce the number of the source terms in the right-hand side of Eqns (2.1) as explained in Ref. [16]. Finally, we obtain a system of two diffusion equations for the concentrations of the free monomers and of the micelles. The application of this procedure is demonstrated below.

We scale time by $\tau_D$, which is the diffusion time constant of the free monomers. The space variable, $x$, is scaled by the respective diffusion length (see Eqn (2.5))

$$\delta_D = \partial \bar{\Gamma}/\partial \bar{c}_1$$

It is clear that the kinetic terms $\partial c_s/\partial t$ and $d\Gamma/dt$ and the diffusion terms $D_s \partial^2 c_s/\partial x^2$ and $D_1 \partial c_1/\partial x$ must be of the same order of magnitude. However, the bulk diffusion equations ought to be consistent with the boundary conditions (2.4) and (2.5). That is why the diffusion time $\tau_D$ must be

$$\tau_D = \frac{1}{D_1} \left( \frac{\partial \bar{\Gamma}}{\partial \bar{c}_1} \right)^2 \tag{2.11}$$

Very important is the scaling of the fluxes $j_s$. Based on the kinetic theory of micellization one can introduce two characteristic fluxes

$$J_F = \bar{c}_1/\tau_F \quad \text{and} \quad J_{SL} = \bar{c}_1/\tau_{SL} \tag{2.12}$$

(their meaning is discussed in detail in Ref. [16]). We scale the fluxes $j_s$, having $s = 2, 3, 4, \ldots, s_1$ (oligomer region) and $s = s_2 + 1, s_2 + 2, \ldots, s_3$ (micelle region), by $J_F$. The fluxes with $s = s_1 + 1, s_1 + 2, \ldots, s_2$ (transition region) are scaled by $J_{SL}$.

In accordance with Eqn (2.2) $j_s$ can be written in the form

$$j_s = k_s^- \bar{c}_s [\xi_1 (1 + \xi_{s-1}) + \xi_{s-1} - \xi_s] \qquad s = 2, 3, 4, \ldots, s_3 \tag{2.13}$$

where

$$\xi_s(x, t) = (c_s - \bar{c}_s)/\bar{c}_s \qquad s = 1, 2, 3, \ldots, s_3 \tag{2.14}$$

is the relative deviation of the $s$-mer concentration, $c_s(x, t)$, from equilibrium. The equilibrium mass action law

$$k_s^+/k_s^- = \bar{c}_s/\bar{c}_1 \bar{c}_{s-1} \qquad s = 2, 3, 4, \ldots, s_3$$

is used when deriving Eqns (2.13). At small deviations from equilibrium $(|\xi_s| \ll 1)$ the product $\xi_1 \xi_{s-1} \ll 1$ can be omitted.

## 3. DIFFUSION AFFECTED BY THE SLOW RELAXATION PROCESS

### 3.1 Bulk diffusion equations

Following the scaling procedure, described in Section 2, we write the diffusion equations (2.1) for $\tau_D \approx \tau_{SL}$ in the following dimensionless form:

$$\epsilon \left( \frac{\partial \xi_1}{\partial T} - \frac{\partial^2 \xi_1}{\partial X^2} \right) = -\alpha \left( 2J_2 + \sum_3^{s_1} J_s + \sum_{s_2+1}^{s_3} J_s \right) - \epsilon\alpha \sum_{s_1+1}^{s_2} J_s \tag{3.1a}$$

$$\epsilon\beta_s \left( \frac{\partial \xi_s}{\partial T} - d_s \frac{\partial^2 \xi_s}{\partial X^2} \right) = \alpha(J_s - J_{s+1}) \qquad s = 2, 3, 4, \dots, s_1 - 1 \tag{3.1b}$$

$$\epsilon\beta_{s_1} \left( \frac{\partial \xi_{s_1}}{\partial T} - d_{s_1} \frac{\partial^2 \xi_{s_1}}{\partial X^2} \right) = \alpha J_{s_1} - \epsilon\alpha J_{s_1+1} \tag{3.1c}$$

$$\beta_s \left( \frac{\partial \xi_s}{\partial T} - d_s \frac{\partial^2 \xi_s}{\partial X^2} \right) = \alpha(J_s - J_{s+1}) \qquad s = s_1 + 1, s_1 + 2, \dots, s_2 - 1 \tag{3.1d}$$

$$\epsilon\beta_{s_2} \left( \frac{\partial \xi_{s_2}}{\partial T} - d_{s_2} \frac{\partial^2 \xi_{s_2}}{\partial X^2} \right) = \epsilon\alpha J_{s_2} - \alpha J_{s_2+1} \tag{3.1e}$$

$$\epsilon\beta_s \left( \frac{\partial \xi_s}{\partial T} - d_s \frac{\partial^2 \xi_s}{\partial X^2} \right) = \alpha(J_s - J_{s+1}) \qquad s = s_2 + 1, s_2 + 2, \dots, s_3 \tag{3.1f}$$

where $d_s = D_s/D_1$; $\beta_s = \bar{c}_s/\bar{c}_1$; $T = t/\tau_D$ and $X = x/\delta_D$; $J_s = j_s/J_F$ $(s = 2, 3, \dots, s_1$ and $s = s_2 + 1, s_2 + 2, \dots, s_3)$ and $J_s = j_s/J_{SL}$ $(s = s_1 + 1, s_1 + 2, \dots, s_2)$. $\alpha = \tau_D/\tau_{SL} \approx 1$ is the Damköhler number. This number is an important characteristic of the mass transfer in reacting systems, giving the ratio between the diffusion and the reaction terms.

Let us expand the functions in Eqns (3.1) in power series of the small parameter $\epsilon$ (2.10)

$$\xi_s(X, T; \epsilon) = \sum_{k=0}^{\infty} \epsilon^k \xi_s^{(k)}(X, T)$$

$$J_s(X, T; \epsilon) = \sum_{k=0}^{\infty} \epsilon^k J_s^{(k)}(X, T) \tag{3.2}$$

If we substitute the above expansions for $\xi_s$ and $J_s$ in Eqns (3.1) and

set equal the coefficients at $\epsilon^0$, we find the zeroth-order equations

$$J_s^{(0)} = 0, \qquad s = 2, 3, 4, \ldots, s_1; s_2 + 1, s_2 + 2, \ldots, s_3 \tag{3.3}$$

$$\beta_s\left(\frac{\partial \xi_s^{(0)}}{\partial T} - d_s\frac{\partial^2 \xi_s^{(0)}}{\partial X^2}\right) = \alpha(J_s^{(0)} - J_{s+1}^{(0)}) \qquad s = s_1 + 1, s_1 + 2, \ldots, s_2 \tag{3.4}$$

Equation (3.3) means that the reactions (1.1) have reached equilibrium state in the oligomer and micelle regions due to the fast relaxation process. Bearing in mind that the rare aggregates obey the equilibrium conditions $\beta_s \ll 1 (s = s_1 + 1, s_1 + 2, \ldots, s_2)$, Eqn (3.4) gives

$$J_s^{(0)} = J^{(0)} \qquad s = s_1 + 1, s_1 + 2, \ldots, s_2 \tag{3.5}$$

where the flux $J^{(0)}(x, t)$ does not depend on $s$.

In general $J^{(0)}$ is not equal to zero, i.e. the reactions (1.1) in the region of the rare aggregates, $s_1 < s \leqslant s_2$, are out of chemical equilibrium. Since $\tau_{SL} \approx \tau_D$, this deviation from equilibrium is due to diffusion. In fact $J^{(0)}$ is connected with the process of step-by-step disintegration of the micelles. This process gives rise to the series of unstable rare aggregates, whose consecutive decomposition produces monomers, thus making up for the lack of monomers due to adsorption. As a matter of fact, $J^{(0)}$ is related to the slow relaxation process (see Fig. 1).

Equations (2.13), (3.3a) and (3.4) give (at $\xi_1 \xi_{s-1} \approx 0$)

$$\xi_1^{(0)} - \xi_{s-1}^{(0)} - \xi_s^{(0)} = 0 \qquad s = 2, 3, 4, \ldots, s_1; s_2 + 1, s_2 + 2, \ldots, s_3 \tag{3.6a}$$

$$\xi_1^{(0)} - \xi_{s-1}^{(0)} - \xi_s^{(0)} = (J_{SL}/k_s^- \bar{c}_s)J^{(0)} \qquad s = s_1 + 1, s_1 + 2, \ldots, s_2 \tag{3.6b}$$

To transform Eqns (3.6) we follow the procedure of Aniansson and Wall [1]. First, Eqn (3.6a) is summed from 2 to $s$ to yield

$$s\xi_1^{(0)} - \xi_s^{(0)} = 0 \qquad s = 1, 2, 3, \ldots, s_1; s_2 + 1, s_2 + 2, \ldots, s_3 \tag{3.7}$$

After that, Eqn (3.6a) is summed for $2 < s \leqslant s_1$, Eqn (3.6b) for $s_1 + 1 < s \leqslant s_2$ and Eqn (3.6a) for $s_2 + 1 \leqslant s$, and then the three resulting equations are summed again to yield

$$s\xi_1^{(0)} - \xi_s^{(0)} = RJ_{SL}J^{(0)} \qquad s = s_1 + 1, s_1 + 2, \ldots, s_2 \tag{3.8}$$

where $R$ is given by Eqn (1.6c). Further, each of Eqns (3.7) and (3.8) is multiplied by $\bar{c}_s$ and then they are summed for all admissible values of $s$. The results are

$$n\xi_1^{(0)} - \xi_n^{(0)} = 0 \tag{3.9a}$$

$$m\xi_1^{(0)} - \xi_m^{(0)} = RJ_{SL}J^{(0)} \tag{3.9b}$$

where

$$\xi_n = \sum_1^{s_1} \bar{c}_s \xi_s / \bar{c}_n \qquad\qquad \xi_m = \sum_{s_2+1}^{s_3} \bar{c}_s \xi_s / \bar{c}_n$$

$\xi_n$ and $\xi_m$ are the relative deviations from equilibrium of the total concentrations of the oligomers and micelles respectively. After that each of Eqns (3.7) and (3.8) is multiplied by $s\bar{c}_s$ and then summed in a similar way. The results are

$$n_2 \xi_1^{(0)} - \Xi_n^{(0)} = 0 \tag{3.9c}$$

$$m_2 \xi_1^{(0)} - \Xi_m^{(0)} = mRJ_{\mathrm{SL}} J^{(0)} \tag{3.9d}$$

where

$$\Xi_n = \sum_1^{s_1} s\bar{c}_s \xi_s / \bar{c}_n \qquad\qquad \Xi_m = \sum_{s_2+1}^{s_3} s\bar{c}_s \xi_s / \bar{c}_n$$

$\Xi_n$ and $\Xi_m$ are the relative deviations from equilibrium of the total numbers of monomers aggregated in oligomers and micelles respectively.

Finally we neglect the concentrations of the intermediate species $(s = s_1 + 1, s_1 + 2, \ldots, s_2)$ in Eqn (2.3) which then becomes

$$\beta_n \Xi_n^{(0)} + \beta_m \Xi_m^{(0)} = \beta \xi^{(0)} \tag{3.9e}$$

where

$$\xi = (c - \bar{c})/\bar{c}$$

is the relative deviation of the total surfactant concentration from equilibrium $(\beta = \bar{c}/\bar{c}_1)$.

The terms in $\epsilon$ in Eqns (3.1) yield

$$\frac{\partial \xi_1^{(0)}}{\partial T} - \frac{\partial^2 \xi_1^{(0)}}{\partial X^2} = -\alpha(s_2 - s_1)J^{(0)} - \alpha\left(2J_2^{(1)} + \sum_3^{s_1} J_s^{(1)} + \sum_{s_2+1}^{s_3} J_s^{(1)}\right) \tag{3.10a}$$

$$\beta_s\left(\frac{\partial \xi_s^{(0)}}{\partial T} - d_s \frac{\partial^2 \xi_s^{(0)}}{\partial X^2}\right) = \alpha(J_s^{(1)} - J_{s+1}^{(1)}) \qquad s = 2, 3, 4, \ldots, s_1 - 1 \tag{3.10b}$$

$$\beta_{s_1}\left(\frac{\partial \xi_{s_1}^{(0)}}{\partial T} - d_{s_1} \frac{\partial^2 \xi_{s_1}^{(0)}}{\partial X^2}\right) = \alpha(J_{s_1}^{(1)} - J^{(0)}) \tag{3.10c}$$

$$\beta_{s_2}\left(\frac{\partial \xi_{s_2}^{(0)}}{\partial T} - d_{s_2} \frac{\partial^2 \xi_{s_2}^{(0)}}{\partial X^2}\right) = \alpha(J^{(0)} - J_{s_2+1}^{(1)}) \tag{3.10d}$$

$$\beta_s\left(\frac{\partial \xi_s^{(0)}}{\partial T} - d_s \frac{\partial^2 \xi_s^{(0)}}{\partial X^2}\right) = \alpha(J_s^{(1)} - J_{s+1}^{(1)}) \qquad s = s_2 + 1, s_2 + 2, \ldots, s \tag{3.10e}$$

Similar equations can also be derived for $\zeta_s^{(1)}$ in the region of the rare aggregates $s_1 < s \leqslant s_2$.

Let us first multiply each of Eqns (3.10) by $s$ and sum them. The result is

$$\beta_n\left(\frac{\partial \Xi_n^{(0)}}{\partial T} - d_n\frac{\partial^2 \Xi_n^{(0)}}{\partial X^2}\right) + \beta_m\left(\frac{\partial \Xi_m^{(0)}}{\partial T} - d_m\frac{\partial^2 \Xi_m^{(0)}}{\partial X^2}\right) = 0 \qquad (3.11a)$$

where it has been supposed that $d_s$ is approximately constant in both the oligomer and micelle regions, and equal to

$$d_n = D_n/D_1 = \sum_1^{s_1} \beta_s d_s/\beta_n$$

or $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (3.11b)$

$$d_m = D_m/D_1 = \sum_{s_2}^{s_3} \beta_s d_s/\beta_m$$

respectively. $D_n$ and $D_m$ are the mean diffusivities of the oligomers and micelles. Although the deviations from the equilibrium size distribution are small, $s_1$, $s_2$ and $s_3$ in principal can depend on $x$ and $t$ during relaxation (see Fig. 1). That is why, when deriving Eqn (3.11a), we have performed the differentiations in Eqns (3.10) as follows:

$$\sum_{s_2}^{s_3} \frac{\partial}{\partial t}(sc_s) \approx \frac{\partial}{\partial t}\int_{s_2}^{s_3} sc(s)\,ds + s_2 c(s_2)\frac{\partial s_2}{\partial t} - s_3 c(s_3)\frac{\partial s_3}{\partial t} \qquad (3.12a)$$

$$\sum_{s_2}^{s_3} \frac{\partial}{\partial x}(sc_s) \approx \frac{\partial}{\partial x}\int_{s_2}^{s_3} sc(s)\,ds + s_2 c(s_2)\frac{\partial s_2}{\partial x} - s_3 c(s_3)\frac{\partial s_3}{\partial x} \qquad (3.12b)$$

The last two terms in each of Eqns (3.12) can be neglected, because at the ends of the size distribution $c(s_2) \approx 0$ and $c(s_3) \approx 0$. If we sum Eqns (3.10d) and (3.10e), we obtain an equation for the micelle concentration

$$\beta_m\left(\frac{\partial \zeta_m^{(0)}}{\partial T} - d_m\frac{\partial^2 \zeta_m^{(0)}}{\partial X^2}\right) = \alpha_J J^{(0)} \qquad (3.13)$$

It was supposed again that $d_s \approx d_m = \text{const}$ for all $s_2 < s \leqslant s_3$. Our aim below is to reduce the system of equations (3.9), (3.11) and (3.13) to two equations for the functions $\zeta_1^{(0)}$ and $\zeta_m^{(0)}$.

If $\Xi_n^{(0)}$ and $\Xi_m^{(0)}$ are expressed from Eqns (3.9c) and (3.9d) and then

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substituted in Eqns (3.9e) and (3.11a), one obtains

$$J^{(0)} = \frac{1}{m\beta_m R J_{SL}} [(n_2\beta_n + m_2\beta_m)\xi_1^{(0)} - \beta\xi^{(0)}]$$ (3.14a)

$$\beta\left(\frac{\partial\xi^{(0)}}{\partial T} - d_m\frac{\partial^2\xi^{(0)}}{\partial X^2}\right) - n_2\beta_n(d_n - d_m)\frac{\partial^2\xi_1^{(0)}}{\partial X^2} = 0$$ (3.14b)

Further we substitute $J^{(0)}$ from Eqn (3.14a) into (3.9b), and the result for $\xi_m^{(0)}$ into (3.13). In this way we obtain the expression

$$\beta\left(\frac{\partial\xi^{(0)}}{\partial T} - d_m\frac{\partial^2\xi^{(0)}}{\partial X^2}\right) - (n_2\beta_n + \sigma_m^2\beta_m)\left(\frac{\partial\xi_1^{(0)}}{\partial T} - d_m\frac{\partial^2\xi_1^{(0)}}{\partial X^2}\right) = m\alpha J^{(0)}$$ (3.14c)

Finally we subtract Eqn (3.14b) from (3.14c) and substitute the flux $J^{(0)}$, as given by (3.9b). The result, together with Eqn (3.13), represents the final system of two diffusion equations for the concentrations of the ̃ee monomers and the micelles:

$$\frac{\partial\xi_1}{\partial t} = D_1^*\frac{\partial^2\xi_1}{\partial x} - \frac{m}{R\bar{c}_1(n_2\beta_n + \sigma_m^2\beta_m)}(m\xi_1 - \xi_m)$$ (3.15a)

$$\frac{\partial\xi_m}{\partial t} = D_m\frac{\partial^2\xi_m}{\partial x} + \frac{1}{R\bar{c}_1\beta_m}(m\xi_1 - \xi_m)$$ (3.15b)

The superscripts (0) have been omitted. The functions $\xi_1$ and $\xi_m$ are the respective relative deviations of the concentrations of the species from equilibrium. The constants in (3.15) are given by Eqns (1.4b) and (1.6).

Here we have introduced an effective diffusivity of the monomers $D_1^*$ given by

$$D_1^* = \frac{D_n n_2\beta_n + D_m\sigma_m^2\beta_m}{n_2\beta_n + \sigma_m^2\beta_m} \approx D_1\frac{n_2\beta_n + d_m\sigma_m^2\beta_m}{n_2\beta_n + \sigma_m^2\beta_m}$$ (3.16)

If micelles are absent ($\beta_m = 0$, $R \to \infty$, $D_1^* = D_1$), Eqn (3.15a) transforms into the well-known Fick's equation. $D_1^*$ exhibits a weak dependence on the surfactant concentration due to the polydispersity of the micelles. Indeed, if the micelles were monodisperse, i.e. $\sigma_m = 0$, then $D_1^*$ would be identical to $D_1$.

The source term in the right-hand side of Eqn (3.15a) increases strongly with the surfactant concentration. In this way the micelles will generally accelerate the relaxation of the monomer concentration and hence of the surface tension.

The equations derived by Feinerman [13], corresponding to the physical situation considered in this Section, differ from Eqns (3.15). The

right-hand sides of Feinerman's equations for the diffusion of micelles and monomers contain the same single source term $(c_1 - \bar{c}_1)/\tau_{SL}$, depending only on the concentration of the free monomers as in the PFOR-model (see below). Instead of the effective diffusivity $D_1^*$, the common monomer diffusivity $D_1$ appears in his equation for the free monomer diffusion.

Now we shall try to solve the system (3.15) by means of the Laplace transformation and to obtain an expression for the time dependence of the surface tension.

## 3.2 Kinetic surface tension

The boundary conditions (2.4)–(2.8), written in a dimensionless form for the concentrations of the free monomers and the micelles, read

$$\frac{\partial \xi_1}{\partial T} = \frac{\partial \xi_1}{\partial X}\bigg|_{x=0} \tag{3.17a}$$

$$\xi_1(\infty, T) = 0 \tag{3.17b}$$

$$\xi_1(X, 0) = 0 \tag{3.17c}$$

$$\xi_1(0, 0) = \xi \tag{3.17d}$$

$$\frac{\partial \xi_m}{\partial X}\bigg|_{x=0} = 0 \tag{3.17e}$$

$$\xi_m(\infty, T) = 0 \tag{3.17f}$$

$$\xi_m(X, 0) = 0 \tag{3.17g}$$

where $\xi_{10} = \xi_1(0, 0)$ is connected by the initial jump of the surface tension by means of Eqns (2.9a) and (2.14). Equations (3.17e)–(3.17g) are derived by summation of Eqns (2.6)–(2.7). Equations (3.17) remain the same in the case when the diffusion is affected by the fast relaxation process, because the boundary conditions (2.4)–(2.8) do not contain reaction terms explicitly.

To derive an expression for the surface tension $\sigma(t)$ we first transform Eqns (3.15) and the boundary conditions (3.17) by using the Laplace transformation (see the Appendix). After that we calculate the image of the subsurface concentration, which is related to the surface tension by Eqn (2.9b). In this way we obtain the Laplace image $\sigma_L(p)$ of the

kinetic surface tension

$$\frac{\Delta\sigma_L(p)}{\Delta\sigma(0)} = \left\{ q + \left[ \frac{1}{d_1^*}(\alpha+q) \right]^{1/2} \right.$$

$$\times \left\{ \left[ q^{1/2} + \left(\frac{d_m}{d_1^*}\right)^{1/2}(\alpha+q)^{1/2} \right]^2 + \alpha\frac{d_n-d_m}{d_1^*}\frac{n_2\beta_n}{(n_2\beta_n+m_2\beta_m)} \right\}^{1/2}$$

$$\times \left. \left[ q + \alpha\frac{(n_2\beta_n+\sigma_m^2\beta_m)}{(n_2\beta_n+m_2\beta_m)} + \left(\frac{d_m}{d_1^*}\right)^{1/2}(\alpha+q)^{1/2} \right]^{-1} \right\}^{-1} \tag{3.}$$

where $q = p\tau_D$ ($p$ is the parameter of transformation) and $d_1^* = D_1^*/D_1$. The other constants in Eqn (3.18) are given by Eqns (1.4b), (1.5), (1.6) and (3.11b). If the micelles are monodisperse the constants become: $\beta_n = 1$, $d_n = 1$ and $n_2 = 1$; $\sigma_m = 0$ and $m_2 = m^2$; $d_1^* = 1$; $R = (k_m^- \bar{c}_m)^{-1}$; $1/\tau_{SL} = k_m^-(1 + m^2\beta_m)$. Equation (3.18) can not be inverted in a simple way to its original $\sigma(t)$. Special cases of Eqn (3.18) will be discussed in Section 5.

## 4. DIFFUSION AFFECTED BY THE FAST RELAXATION PROCESS

### 4.1 Bulk diffusion equations

When $\tau_D \approx \tau_F$ the Damköhler number for the fast process, $\alpha = \tau_D/\tau_F \approx 1$, appears in Eqns (3.1). The respective diffusion equations read

$$\frac{\partial\xi_1}{\partial T} - \frac{\partial^2\xi_1}{\partial X^2} = -\alpha\left(2J_2 + \sum_3^{s_1} J_s + \sum_{s_2+1}^{s_3} J_s\right) - \epsilon\alpha\sum_{s_1+1}^{s_2} J_s \tag{4.1a}$$

$$\beta_s\left(\frac{\partial\xi_1}{\partial T} - d_s\frac{\partial^2\xi_s}{\partial X^2}\right) = \alpha(J_s - J_{s+1}) \qquad s = 2, 3, 4, \ldots, s_1-1 \tag{4.1b}$$

$$\beta_{s_1}\left(\frac{\partial\xi_{s_1}}{\partial T} - d_{s_1}\frac{\partial^2\xi_{s_1}}{\partial X^2}\right) = \alpha J_{s_1} - \epsilon\alpha J_{s_1+1} \tag{4.1c}$$

$$\beta_s\left(\frac{\partial\xi_s}{\partial T} - d_s\frac{\partial^2\xi_s}{\partial X^2}\right) = \epsilon\alpha(J_s - J_{s+1}) \qquad s = s_1+1, s_1+2, \ldots, s_2-1 \tag{4.1d}$$

$$\beta_{s_2}\left(\frac{\partial\xi_{s_2}}{\partial T} - d_{s_2}\frac{\partial^2\xi_{s_2}}{\partial X^2}\right) = \epsilon\alpha J_{s_2} - \alpha J_{s_2+1} \tag{4.1e}$$

$$\beta_s \left( \frac{\partial \xi_s}{\partial T} - d_s \frac{\partial^2 \xi_s}{\partial X^2} \right) = \alpha (J_s - J_{s+1}) \qquad\qquad s = s_2 + 1, s_2 + 2, \ldots, s_3 \qquad (4.1f)$$

If one substitutes the asymptotic expansions (3.2) in Eqns (4.1) and set equal to the coefficients at $\epsilon^0$, one obtains

$$\frac{\partial \xi_1^{(0)}}{\partial T} - \frac{\partial^2 \xi_1^{(0)}}{\partial X^2} = -\alpha \int_{-\infty}^{+\infty} J^{(0)}(s)\, \mathrm{d}s \qquad\qquad (4.2a)$$

$$\frac{\partial \xi_{s_2}^{(0)}}{\partial T} - d_{s_2} \frac{\partial^2 \xi_{s_2}^{(0)}}{\partial X^2} = -\alpha J_{s_2+1}^{(0)} \qquad\qquad (4.2b)$$

$$\frac{\partial \xi_s^{(0)}}{\partial T} - d_s \frac{\partial^2 \xi_s^{(0)}}{\partial X^2} = \alpha (J_s^{(0)} - J_{s+1}^{(0)}) \qquad\qquad s = s_2 + 1, s_2 + 2, \ldots, s_3 \qquad (4.2c)$$

Here we have neglected the concentrations of the oligomers $\xi_s$ corresponding to $2 \leqslant s \leqslant s_1$. The equations for the rare aggregates ($s_1 < s \leqslant s_2$) are omitted, because they are not important for our further considerations. In the right-hand side of Eqn (4.2a) we have replaced the summation by integration. It will be shown that in view of Eqn (1.2) the main contribution to this integral is given by the micellar region: $s_2 \leqslant s \leqslant s_3$. That is why one can extend the limits of integration to infinity. The flux $J^{(0)}(s)$ can be written as

$$J^{(0)}(s) = \tau_F k_m^- \beta(s) \left\{ \xi_1^{(0)} [1 + \xi^{(0)}(s)] - \frac{\partial}{\partial s} \xi^{(0)}(s) \right\} \qquad (4.3)$$

where $\beta(s) = \bar{c}(s)/\bar{c}_1$ (for definition of $\bar{c}(s)$ see Eqn (1.2)). Equation (4.3) follows from Eqns (2.12) and (2.13), where we have set $\xi_s \approx \xi_{s-1}$ in parentheses and also $\xi_s - \xi_{s-1} \approx \partial \xi(s)/\partial s$, as in Ref. [2].

Summing Eqns (4.2e) and (4.2f) and assuming that $d_s \approx d_m$ for all $s_2 \leqslant s \leqslant s_3$ we obtain the following equation for the micelles

$$\frac{\partial \xi_m^{(0)}}{\partial T} - d_m \frac{\partial^2 \xi_m^{(0)}}{\partial X^2} = 0 \qquad\qquad (4.4a)$$

(note, that $J_{s_3} \approx 0$). Let us multiply each of Eqns (4.2b) and (4.2c) by $s$ and sum them. The result is

$$\frac{\partial \Xi_m^{(0)}}{\partial T} - d_m \frac{\partial^2 \Xi_m^{(0)}}{\partial X^2} = -\alpha \int_{-\infty}^{+\infty} s\, \mathrm{d}J^{(0)}(s) \approx \alpha \int_{-\infty}^{+\infty} J^{(0)}(s)\, \mathrm{d}s \qquad (4.4b)$$

($d_s \approx d_m$ for all $s_2 \leqslant s \leqslant s_3$; $J(\infty) \approx J(-\infty) \approx 0$). To derive Eqn (4.4b) we carried out [ ]fferentiation by using Eqns (3.12). Finally, by using

Eqn (1.2) we integrate the flux (4.3). The result is

$$\int\limits_{-\infty}^{+\infty} J^{(0)}(s)\, ds = \tau_F k_m^- \beta_m \left( \xi_1^{(0)} + \frac{m}{\sigma_m^2} \xi_m^{(0)} - \frac{1}{\sigma_m^2} \Xi_m^{(0)} \right) \tag{4.5}$$

The substitution of Eqn (4.5) into Eqns (4.2a) and (4.4b), along with Eqn (4.4a), leads to the final set of diffusion equations for the case when the fast relaxation process affects the diffusion

$$\frac{\partial \xi_1}{\partial t} = D_1 \frac{\partial^2 \xi_1}{\partial x^2} - k_m^- \beta_m \left( \xi_1 + \frac{m}{\sigma_m^2} \xi_m - \frac{1}{\sigma_m^2} \Xi_m \right) \tag{4.6a}$$

$$\frac{\partial \xi_m}{\partial t} = D_m \frac{\partial^2 \xi_m}{\partial x^2} \tag{4.6b}$$

$$\frac{\partial \Xi_m}{\partial t} = D_m \frac{\partial^2 \Xi_m}{\partial x^2} + k_m^- \left( \xi_1 + \frac{m}{\sigma_m^2} \xi_m - \frac{1}{\sigma_m^2} \Xi_m \right) \tag{4.6c}$$

The superscripts (0) have been omitted. The constants are defined by Eqns (1.4). Equation (4.6a) describes the diffusion of the free monomers; Eqn (4.6b) describes the diffusion of the micelles, while Eqn (4.6c) concerns the transport of the monomers, aggregated in micelles. In our case the solution of Eqn (4.6b) at the boundary conditions (3.17e)–(3.17g) is

$$\xi_m = 0 \tag{4.7}$$

This means that the total micellar concentration is kept constant during the relaxation. Nevertheless, the different components belonging to the fraction of micelles can take part in the diffusion process. Therefore, the total number of monomers aggregated in micelles at a given point, i.e. $\Xi_m$, can vary. For example, when the interfacial adsorption layer is expanded, the concentration of the micelles of lower aggregation number will be higher close to the interface than in the bulk of solution.

Locally, the deficiency of monomers is simultaneously compensated by the diffusion and the direct exchange of material between the fractions of the micelles and of the free monomers. These two processes have comparable rates. However, they are not reactions transforming the micelles into rare aggregates (see Fig. 1), because the reaction chain with the rare aggregates is activated during the slow relaxation process. The peak of the micelles in a given layer of the solution will have a constant height, but will somehow be shifted in comparison with the peak in the underlying layer situated close to the interface.

Although locally the total number of the micelles can remain constant (Eqn (4.7)), diffusion of micellar fractions from and towards the solution takes place.

From Eqns (4.6) and (4.7) one finally obtains

$$\frac{\partial \xi_1}{\partial t} = D_1 \frac{\partial^2 \xi_1}{\partial x^2} - k_m^- \beta_m \left( \xi_1 - \frac{1}{\sigma_m^2} \Xi_m \right) \qquad (4.8a)$$

$$\frac{\partial \Xi_m}{\partial t} = D_m \frac{\partial^2 \Xi_m}{\partial x^2} + k_m^- \left( \xi_1 - \frac{1}{\sigma_m^2} \Xi_m \right) \qquad (4.8b)$$

The respective equations of Feinerman [13] for the micelles and the monomers contain one and the same single source term $k_m^- c_m (c_1 - \bar{c}_1)/\bar{c}_1 \sigma_m^2$ (written in our notation). Note, that $c_m(x, t)$ in this term is a function of $x$ and $t$, while our Eqn (4.7) yields $c_m = \bar{c}_m$.

## 4.2 Kinetic surface tension

To solve the set of equations (4.8) we use Eqns (3.17a)–(3.17d) as boundary conditions for the function $\xi_1$. The boundary conditions for the function $\Xi_m$ are

$$\left. \frac{\partial \Xi_m}{\partial X} \right|_{x=0} = 0 \qquad (4.9a)$$

$$\Xi_m(\infty, T) = 0 \qquad (4.9b)$$

$$\Xi_m(X, 0) = 0 \qquad (4.9c)$$

Equations (4.9) can be derived by multiplying Eqns (2.6)–(2.7) by $s$ and summing them. Solving this set we obtain the Laplace image of the surface tension (see the Appendix)

$$\frac{\Delta \sigma_L(p)}{\Delta \sigma(0)} = \left\{ q + (\alpha + q)^{1/2} \left\{ \left[ q^{1/2} + d_m^{1/2}(\alpha + q)^{1/2} \right]^2 + \alpha(1 - d_m)\frac{1}{1 + \sigma_m^2 \beta_m} \right\}^{1/2} \right.$$

$$\left. \times \left[ q + \alpha \frac{1}{1 + \sigma_m^2 \beta_m} + d_m^{1/2}(\alpha + q)^{1/2} \right]^{-1} \right\}^{-1} \qquad (4.10)$$

Equation (4.10) is a counterpart of Eqn (3.18) for the fast relaxation

process. The original of Eqn (4.10) can be found in some special cases, considered in the next Section.

The exact numerical solutions of the diffusion problems based on Eqns (3.15) and (4.8) will be published in a forthcoming paper [21].

## 5. PSEUDO-FIRST ORDER REACTION MODEL

Let us consider the special case when the micellar solution represents a quasi-closed system, i.e. the condition

$$c(x, t) \approx \bar{c} \tag{5.1}$$

is fulfilled at every instant, i.e. $\xi \approx 0$. In other words, the total surfactant concentration remains constant, although the concentrations of the individual species (s-mers) can vary. In this case two additional relationships follow from the mass balance (2.3).

(i) When $\tau_D$ is of the order of $\tau_{SL}$, then

$$(n_2 \beta_m + \sigma_m^2 \beta_m) \xi_1 + m \beta_m \xi_m = 0 \tag{5.2}$$

Equation (5.2) can be derived if $J^{(0)}$, $\Xi_n^{(0)}$ and $\Xi_m^{(0)}$ are eliminated from (3.9b)–(3.9e) at $\xi^{(0)} = 0$.

(ii) When $\tau_D$ is of the order of $\tau_F$, then

$$\xi_1 + \beta_m \Xi_m = 0 \tag{5.3}$$

Equation (5.3) is a direct result from (2.3) and (5.1).

However, one can multiply each of Eqns (2.1) by $s$, sum them and take into account (2.3), written at $c \approx \bar{c}$. In this manner one obtains the following relationship for the diffusivities:

$$D_m \approx D_n \approx D_1^* \approx D_1 \tag{5.4}$$

Equation (5.1) is a corollary of Eqn (5.4). It implies that the micelles and the free monomers must have approximately equal diffusivities in order to ensure the constancy of the total surfactant concentration during the micellization. In reality $D_m$ is considerably smaller than $D_1$. However, this hypothesis can be useful for some estimates, as demonstrated below.

Equations (5.2) and (5.3) reduce the sets of two diffusion equations, derived in Sections 3 and 4, to single equations for the concentration of the free monomers. In view of Eqn (5.4), Eqns (3.15) and (4.8) reduce to one and the same equation

$$\frac{\partial \xi_1}{\partial t} = D_1 \frac{\partial^2 \xi_1}{\partial x^2} - \frac{1}{\tau_M} \xi_1 \tag{5.5}$$

where $\tau_M$ is either $\tau_F$ or $\tau_{SL}$. The effect of the micelles on the diffusion of the free monomers is given by the source term in the right-hand side of (5.5). In this approximation the micelles diffuse as fast as the free monomers do (see Eqn (5.4)). That is why the micelles appear like sources of monomers rather than as surfactant carriers. Equation (5.5) could be postulated at once, assuming that the micellization kinetics can be described in the frames of the PFOR-model. This model is widely used in chemical kinetics (see e.g. Ref. [22]). According to the PFOR-model every complicated reaction (or reaction set) can be described roughly as a pseudo-first order reaction, if the deviations from equilibrium are small. The reverse characteristic time, $1/\tau_M$, is not yet a rate constant of an elementary first-order reaction, but is a complex function of the rate constants of the real reaction mechanism as well as of the concentrations. Equation (5.5) is a generalization of the statements of the PFOR-model for a diffusion problem.

The equation used by Rillaerts and Joos [11] is similar to Eqn (5.5), but instead of $1/\tau_M$ (cf. Eqns (1.3) or (1.5)) a simple reaction rate constant is used.

Solving Eqn (5.5) at the boundary conditions (2.4), (2.5), (2.7) and (2.8) (at $s = 1$) we find the Laplace image of the surface tension

$$\frac{\Delta\sigma_L(p)}{\Delta\sigma(0)} = \frac{1}{q + (q + \alpha)^{1/2}} \tag{5.6}$$

The same equation as Eqn (5.6) follows from both Eqn (3.18) and Eqn (4.8), if $d_m \approx d_n \approx 1$. The original of (5.6) is

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} = \frac{1}{2G}\exp\left(-t/\tau_M\right)$$

$$\times \left\{ (1 + G)E\left[\frac{1 + G}{2}\left(\frac{t}{\tau_D}\right)^{1/2}\right] - (1 - G)E\left[\frac{1 - G}{2}\left(\frac{t}{\tau_D}\right)^{1/2}\right] \right\} \tag{5.7}$$

where $E(z) = \exp(z^2)\operatorname{erfc}(z)$, $\operatorname{erf}(z) = 1 - \operatorname{erfc}(z)$ is the error function and $G = (1 + 4\alpha)^{1/2}$.

Three particular cases can be considered. If $\alpha \ll 1$, i.e. if the diffusion term in Eqn (5.5) is much smaller than the source term, Eqn (5.7) reduces to

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} \approx E\left[\left(\frac{t}{\tau_D}\right)^{1/2}\right] + \alpha\left\{1 - 2\left(\frac{t}{\pi\tau_D}\right)^{1/2} + \frac{3}{2}\left(\frac{t}{\tau_D}\right)E\left[\left(\frac{t}{\tau_D}\right)^{1/2}\right]\right\} \tag{5.8}$$

In the opposite case ($\alpha \gg 1$) Eqn (5.5) reduces to the simple kinetic

equation

$$\frac{\partial \xi_1}{\partial t} = -\frac{1}{\tau_M} \xi_1 \qquad (5.9a)$$

which has a solution $\xi_1(0, t) = \xi_1(0, 0) \exp(-t/\tau_M)$. In view of Eqn (2.9b) for the surface tension one obtains

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} \approx \exp(-\alpha(t/\tau_D)) \qquad (5.9b)$$

Finally, for solutions without micelles ($\tau_M \to \infty$, $\alpha \to 0$, $G = 1$) both Eqns (5.7) and (5.8) transform into

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} = E\left[\left(\frac{t}{\tau_D}\right)^{1/2}\right] \qquad (5.10)$$

Equation (5.10) has been utilized recently in Refs [18–20].

Finally, we give the solution for the bulk concentration profile stemming from Eqn (5.5)

$$\frac{\Delta c_1(x, t)}{\Delta c_1(0, 0)} = \frac{1}{2G} \exp\left(-\frac{x^2}{4D_1 t} - \frac{t}{\tau_M}\right)$$

$$\times \left\{(1 + G)E\left[\frac{x}{2(D_1 t)^{1/2}} + \frac{1 + G}{2}\left(\frac{t}{\tau_D}\right)^{1/2}\right]\right.$$

$$\left. - (1 - G)E\left[\frac{x}{2(D_1 t)^{1/2}} + \frac{1 - G}{2}\left(\frac{t}{\tau_D}\right)^{1/2}\right]\right\} \qquad (5.11)$$

In agreement with Eqn (2.9b) at $x = 0$, Eqn (5.11) transforms into Eqn (5.7). Similar concentration profiles have been obtained in other diffusion problems having a similar mathematical description [23–25]. For example this is the case when a solute, absorbing into a liquid at a constant surface concentration, reacts chemically with the liquid.

In Fig. 2 we have represented the effect of the micellization kinetics on the surface tension. The theoretical curves are calculated from Eqns (5.8) and (5.10) at different values of the Damköhler number $\alpha$. The values of $E(z)$ are computed by numerical integration of $\mathrm{erf}(z)$ for $z \leqslant 10^{1/2}$ or by means of the approximate formula

$$E(z) \approx \frac{1}{\pi^{1/2} z}\left[1 + \sum_{k=1}^{6} (-1)^k \frac{1.3.5 \ldots (2k + 1)}{(2z^2)^k}\right]$$

for $z > 10^{1/2}$. It is seen that when increasing the effect of the micelles (when increasing $\alpha$) the surface tension relaxes more quickly. It is known from experiment [3] that the relaxation time constants $\tau_F$ and
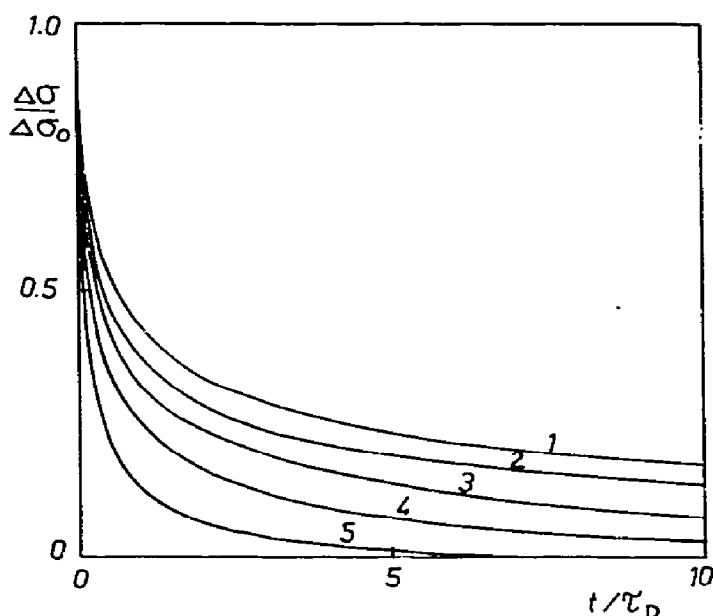
Fig. 2. Effect of the micellization kinetics on the surface tension at different values of the Damköhler number $\alpha$: curve 1, $\alpha = 0$ (no micelles); curve 2, $\alpha = 0.01$; curve 3, $\alpha = 0.05$; curve 4, $\alpha = 0.1$; curve 5, $\alpha = 0.5$.

$\tau_{SL}$ decrease (and therefore $\alpha$ increases), when the micellar concentration increases (see also Eqns (1.3) and (1.5)). Hence, the more concentrated the surfactant solution, the faster the relaxation of the surface tension. This conclusion is also supported experimentally [26].

CONCLUSIONS

In this paper we developed a diffusion theory of the kinetics of adsorption and surface tension of micellar surfactant solutions. To account for the effect of the micelles on the surface properties we incorporated the predictions of the theory of Aniansson and Wall for the kinetics of micellization in the mass transfer equations. As a model experiment we considered the stress relaxation techniques, where initially a small perturbation in the surfactant adsorption layer is created. The deviation from equilibrium is restored by the adsorption and diffusion of the free surfactant monomers. The micelles are considered as polydisperse particles, which can form or distintegrate in order to compensate the local deviation of the monomer concentration from equilibrium. The two relaxation processes of micellization are taken into account. During the fast process the micelles release only a few monomers, while during the slow process they entirely disintegrate. The process whose time constant is comparable with the diffusion time constant has the greater effect on the mass transfer.

We considered two cases of interest: diffusion rate comparable with the rate of the fast or the slow relaxation process. The realization of one of them in an experiment depends on the type of surfactant used or on the dynamics of the particular experiment. To solve the diffusion equations of the species, we utilized an asymptotic mathematical method. In this way two equations describing the diffusion of the free monomers and of the micelles have been derived. The parameters contained in these equations represent collective characteristics of the micelle size distribution and of the micellar reaction chain. The set of equations has been solved for $\tau_D \approx \tau_F$ and $\tau_D \approx \tau_{SL}$ and the Laplace image of the surface tension has been obtained. An approximate solution for the surface tension as a function of time has been found in the frames of the PFOR-model. In agreement with experiment the theory predicts faster surface tension relaxation at higher surfactant concentration.

## ACKNOWLEDGMENT

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## APPENDIX

### A.1  Diffusion affected by the slow process

The Laplace images of (3.15) are

$$\frac{d^2 \xi_{1L}}{dX^2} = a_1 \xi_{1L} + a_m \xi_{mL} \tag{A.1a}$$

$$\frac{d^2 \xi_{mL}}{dX^2} = b_1 \xi_{1L} + b_m \xi_{mL} \tag{A.1b}$$

where $\xi_{1L}$ and $\xi_{mL}$ are the Laplace images of $\xi_1$ and $\xi_m$. We have introduced the following notation:

$$a_1 = (q/d_1^*) - ma_m \qquad a_m = - \frac{\alpha m}{(d_n n_2 \beta_n + d_m \sigma_m^2 \beta_m)/(RJ_{SL})}$$

$$b_1 = - \alpha m/(d_m \beta_m RJ_{SL}) \qquad b_m = (q/d_m) - (b_1/m)$$

The respective images of the boundary conditions (3.17a) and (3.17e) are:

$$\frac{d\xi_{1L}}{dX}\bigg|_{x=0} = q\xi_1(0, q) - \xi_{10} \tag{A.2a}$$

$$\frac{d\xi_{mL}}{dX}\bigg|_{x=0} = 0 \tag{A.2b}$$

The solution of (A.1) for the functions $\xi_{1L}(X, q)$ and $\xi_{mL}(X, q)$ is

$$\xi_{1L} = F_1 \exp(-\lambda_1 X) + F_2 \exp(-\lambda_2 X) \tag{A.3a}$$

$$\xi_{mL} = B_1 \exp(-\lambda_1 X) + B_2 \exp(-\lambda_2 X) \tag{A.3b}$$

(see, e.g. Ref. [27]). Here $\lambda_1(q)$ and $\lambda_2(q)$ are the two positive roots of the characteristic equation

$$\lambda^4 - (a_1 + b_m)\lambda^2 + \Delta = 0 \tag{A.4}$$

where $\Delta = a_1 b_m - a_m b_1$. (According to (3.17b) and (3.17f), the functions $\xi_{1L}$ and $\xi_{mL}$ should vanish as $x \to \infty$). The roots of (A.4) are

$$\lambda_1 = [(a_1 + b_m + M^{1/2})/2]^{1/2} \qquad \lambda_2 = [(a_1 + b_m - M^{1/2})/2]^{1/2}$$

where $M = (a_1 - b_m)^2 + 4a_m b_1$ is the discriminant. $\lambda_1$ and $\lambda_2$ are connected by the relationships

$$\lambda_1^2 \lambda_2^2 = \Delta = q(q + \alpha)/d_1^* d_m \qquad\qquad\qquad\qquad (A.5a)$$

$$(\lambda_1 + \lambda_2)^2 = a_1 + b_m + 2\Delta^{1/2} \qquad\qquad\qquad\qquad (A.5b)$$

To determine the coefficients $F_k(q)$ and $B_k(q)$ ($k = 1, 2$) in Eqns (A.3), we substitute Eqns (A.3) into Eqns (A.1) and (A.2) and obtain

$$F_2 = -\lambda_1(\lambda_1^2 - a_1)F_1/\lambda_2^2(\lambda_2^2 - a_1) \qquad\qquad\qquad\qquad (A.6a)$$

$$B_1 = (\lambda_1^2 - a_1)F_1/a_m \qquad\qquad\qquad\qquad (A.6b)$$

$$B_2 = -\lambda_1(\lambda_1^2 - a_1)F_1/\lambda_2 a_m \qquad\qquad\qquad\qquad (A.6c)$$

$$F_1 = \xi_{10} \frac{\lambda_2(\lambda_2 - a_1)}{\lambda_2 - \lambda_1}[q(\lambda_1^2 + \lambda_2^2 + \lambda_1\lambda_2 - a_1) + \lambda_1\lambda_2(\lambda_1 + \lambda_2)]^{-1} \qquad (A.7)$$

Finally Eqns (A.3a), (A.6a) and (A.7) give the Laplace image of the bulk concentration $\xi_{1L}(X, p)$. Setting $X = 0$ there and using Eqn (2.9b), we obtain the image of the surface tension

$$\frac{\Delta\sigma_L(p)}{\Delta\sigma(0)} = (\lambda_1^2 + \lambda_2^2 + \lambda_1\lambda_2 - a_1)[q(\lambda_1^2 + \lambda_2^2 + \lambda_1\lambda_2 - a_1) + \lambda_1\lambda_2(\lambda_1 + \lambda_2)]^{-1}$$

$$= (b_m + \Delta^{1/2})[q(b_m + \Delta^{1/2}) + \Delta^{1/2}(a_1 + b_m + 2\Delta^{1/2})]^{-1} \qquad (A.8)$$

After some algebra Eqn (A.8) transforms into Eqn (3.18).

## A.2 Diffusion affected by the fast process

The Laplace transformation of Eqns (4.8) is

$$\frac{d\xi_{1L}}{dX^2} = a_1\xi_{1L} + a_m\Xi_{mL} \qquad\qquad\qquad\qquad (A.9a)$$

$$\frac{d^2\Xi_{mL}}{dX^2} = b_1\xi_{1L} + b_m\Xi_{mL} \qquad\qquad\qquad\qquad (A.9b)$$

where

$$a_1 = q - \sigma_m^2 a_m \qquad\qquad a_m = -\alpha\tau_F k_m^- \beta_m/\sigma_m^2$$

$$b_1 = -\alpha\tau_F k_m^-/d_m \qquad\qquad b_m = (q/d_m) - (b_1/\sigma_m^2)$$

The boundary condition for the free monomer concentration $\xi_{1L}(X, q)$ remains the same, while the condition for the concentration of the aggregated monomers $\Xi_{mL}(X, q)$ is

$$\frac{\mathrm{d}\Xi_{mL}}{\mathrm{d}X}\bigg|_{x=0} = 0$$

(cf. Eqn (4.10a)). We solve the set (A.9) in the same way as the set (A.1). The only difference is that $\Delta = q(q + \alpha_F)/d_m$ in this case. The Laplace image of the surface tension has the same form as Eqn (A.8), which finally gives Eqn (4.11).