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Advances in Colloid and Interface Science 119 (2006) 1 – 16

ADVANCES IN COLLOID AND INTERFACE SCIENCE

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Mass transport in micellar surfactant solutions: 1. Relaxation of micelle concentration, aggregation number and polydispersity

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Available online 21 November 2005

Abstract

The surfactant transfer in micellar solutions includes transport of all types of aggregates and the exchange of monomers between them. Such processes are theoretically described by a system containing tens of kinetic equations, which is practically inapplicable. For this reason, one of the basic problems of micellar kinetics is to simplify the general set of equations without loosing the adequacy and correctness of the theoretical description. Here, we propose a model, which generalizes previous models in the following aspects. First, we do not use the simplifying assumption that the width of the micellar peak is constant under dynamic conditions. Second, we avoid the use of the quasi-equilibrium approximation (local chemical equilibrium between micelles and monomers). Third, we reduce the problem to a self-consistent system of four nonlinear differential equations. Its solution gives the concentration of surfactant monomers, total micelle concentration, mean aggregation number, and halfwidth of the micellar peak as functions of the spatial coordinates and time. Further, we check the predictions of the model for the case of spatially uniform bulk perturbations (such as jumps in temperature, pressure or concentration). The theoretical analysis implies that the relaxations of the three basic parameters (micelle concentration, mean aggregation number, and polydispersity) are characterized by three different characteristic relaxation times. Two of them coincide with the slow and fast micellar relaxation times, which are known in the literature. The third time characterizes the relaxation of the width of the micellar peak (i.e. of the micelle polydispersity). It is intermediate between the slow and fast relaxation times, in the case of not-too-low micellar concentrations. For low micelle concentrations, the third characteristic time is close to the fast relaxation time. Procedure for obtaining the exact numerical solution of the problem is formulated. In addition, asymptotic analytical expressions are derived, which compare very well with the exact numerical solution. In the second part of this study, the obtained set of equations is applied for theoretical modeling of surfactant adsorption from micellar solutions under various dynamic conditions, corresponding to specific experimental methods.
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Keywords: Micellar surfactant solutions; Kinetics of micelle association and decay; Fast and slow micellization processes; Surfactant adsorption kinetics; Dynamic surface tension

Contents

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doi:10.1016/j.cis.2005.09.002

1. Introduction

In the present series of two articles, we address some unsolved problems in the theory of adsorption from micellar surfactant solutions. In general, the diffusion and convective transport of monomers and aggregates is accompanied by release or uptake of monomers by the micelles. The first models of micellar kinetics in spatially uniform solutions have been developed by Kresheck et al. [1], and Aniansson and Wall [2]. The model [2] provides explanations of the main experimental facts, so that it is generally accepted and used as a basis for further developments. In subsequent studies, it was upgraded and applied to interpret experimental results for various micellar systems [3–11]. Detailed reviews on micellar kinetics and dynamic surface tension have been recently published by Noskov and Grigoriev [12] and Noskov [13].

The first theoretical model of surfactant adsorption from micellar solutions was proposed by Lucassen [14] and applied to interpret the tensiometric data from experimental methods with oscillating surface area [14,15]. This model uses the simplifying assumptions that the micelles are monodisperse, and that the micellization happens as a single step, which is described as a reversible reaction of order n (n is the micelle aggregation number). This nonlinear problem was linearized for the case of small perturbations [14]. Later, Miller [16] solved numerically the nonlinear problem using the assumption for monodisperse micelles. An alternative approach to the nonlinear problem, based on the von Karman's method in hydrodynamics, was proposed in [17]. A linearized model was developed by Fainerman [18] and applied to interpret dynamic surface tension data [19–21]. Joos and co-authors [22–25] developed a model, which is based on the assumption for local quasi-equilibrium between monodisperse micelles and monomers. More realistic models of the diffusion in micellar solutions, which account for the polydispersity of the micelles and for the multi-step character of the micellar process, was developed independently by Noskov [26], Johner and Joanny [27], and Dushkin et al. [28,29]. Shah and coworkers investigated the effect of the micellar kinetics on the foaminess of surfactant solutions, and its scientific and technological significance [30–32].

Despite the advance in this field, some unsolved questions remain. In the case, when the deviations from equilibrium are not small, the available theories are using unjustifiable assumptions and are describing the kinetics of adsorption only in a limited number of situations [13]. In addition, depending on the used experimental method and specific surfactant, the measured experimental dynamic surface tension of *micellar* solutions follows different functional dependencies: inverse square root of time [21–23], or exponential decay [25,33,34]. Although some encouraging steps in theory have been made [23,25,33,34], a general theoretical picture is still missing, and it is not clear why different functional dependencies are observed under different experimental conditions. An additional challenge to the theory comes from the necessity to interpret the data for the dynamic surface tension of micellar solutions measured by different experimental methods [35], such as the maximum bubble pressure tensiometry [21,36,37], the inclined plate method [25,33], the dynamic drop volume method [22,23], the stripe method [24,25], the oscillatory methods [14,15], the overflowing cylinder method [38,39], etc.

In an attempt to resolve a part of the above problems, here we present a general derivation of the mass balances in a micellar solution avoiding most of the approximations and simplifying assumptions used in previous studies. First, a basic system of four nonlinear mass-balance equations is derived for multi-step micellization (Section 2). We do not use the simplifying assumption for constant width of the micellar peak and, in the general case we do not linearize the equations for small perturbations. The linearized equations are derived in Section 3, as a special case.

The model is further applied to analyze the evolution of a micellar system, which is subjected to spatially uniform perturbations. As a result, we arrive at the non-trivial conclusion that there are three (rather than two) micelle relaxation times (Section 4). The third characteristic time describes the relaxation of the width of the micellar peak. Its existence is not in conflict with the previous works on micellar relaxation kinetics. From the viewpoint of applications, the measurement of the third characteristic time would allow one to determine the rate constant of the fast micellization process. At the next step, in the second part of this study [40] we apply the

developed theoretical model to investigate the complicated dynamics of adsorption from micellar solutions.

2. Nonlinear theory of the mass transfer in micellar solutions

2.1. General set of equations

According to the theory by Aniansson and Wall [2], the association and dissociation of surfactant aggregates proceeds in unitary steps, described by the following set of reactions:

$$A_1 + A_{s-1} \underset{k_s^-}{\overset{k_s^+}{\leftrightarrow}} A_s \qquad (s = 2, 3, 4, \ldots) \tag{2.1}$$

Here A_1 and A_s denote, respectively, a surfactant monomer and an aggregate of s monomers; k_s^+ and k_s^- are the rate constants of association and dissociation, respectively. The above reaction mechanism implies the following balance equations for the monomers and aggregates [2,26,29]:

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_1 = -2J_2 - \sum_{s=3}^{\infty} J_s \tag{2.2}$$

$$\frac{\mathrm{d}c_s}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_s = J_s - J_{s+1} \qquad (s = 2, 3, 4, \ldots) \tag{2.3}$$

Here, c_s is the number concentration of the aggregates A_s ($s=1,2,3,\ldots$); t is time; ∇ is the spatial gradient operator; $\mathbf{I}_s$ is the diffusion flux of the respective component ($s=1,2,\ldots$); J_s is the flux due to the respective reaction ($s=2,3,\ldots$), see Eq. (2.7), and $\mathrm{d}/\mathrm{d}t$ is the material time derivative:

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla \tag{2.4}$$

$\mathbf{v}$ is the mean mass velocity ($\nabla\cdot\mathbf{v}=0$ for an incompressible fluid). In general, the flux $\mathbf{I}_s$ expresses the relative motion of the component s with respect to the mean mass velocity [41]:

$$\mathbf{I}_s \equiv c_s(\mathbf{v}_s - \mathbf{v}) \qquad (s = 1, 2, 3, \ldots) \tag{2.5}$$

where $\mathbf{v}_s$ is the velocity of component s. As a next step, one can postulate the Fick's law of diffusion:

$$\mathbf{I}_s = -D_s \nabla c_s \qquad (s = 1, 2, 3, \ldots) \tag{2.6}$$

where D_s is the diffusivity of the respective component. The reaction flux J_s accounts for the micelle association and dissociation. In accordance with the reaction mechanism, Eq. (2.1), this flux is given by the expression:

$$J_s \equiv k_s^+ c_1 c_{s-1} - k_s^- c_s \qquad (s = 2, 3, 4, \ldots) \tag{2.7}$$

At equilibrium, all reaction fluxes, J_s, are equal to zero, and Eq. (2.7) reduces to the mass action law connecting the respective equilibrium concentrations:

$$\frac{k_s^+}{k_s^-} = \frac{c_{s,\mathrm{eq}}}{c_{1,\mathrm{eq}} c_{s-1,\mathrm{eq}}} \qquad (s = 2, 3, 4, \ldots) \tag{2.8}$$

Here and hereafter, the subscript "eq" denotes the equilibrium value of the respective quantity. The balance equation for the total amount of surfactant (the total number of surfactant molecules per unit volume), c_{tot}, can be obtained by multiplying Eq. (2.3) by s, and summing up all equations for $s \geq 1$:

$$\frac{\mathrm{d}c_{\mathrm{tot}}}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_{\mathrm{tot}} = 0 \tag{2.9}$$

$$c_{\mathrm{tot}} \equiv \sum_{s=1}^{\infty} s c_s, \qquad \mathbf{I}_{\mathrm{tot}} \equiv \sum_{s=1}^{\infty} s \mathbf{I}_s \tag{2.10}$$

where $\mathbf{I}_{\mathrm{tot}}$ is the total flux of surfactant. Note that the reaction fluxes disappear from Eq. (2.9), which is due to the conservation of the total number of surfactant molecules in the system.

2.2. Real and model micelle size distributions

In the theory by Aniansson and Wall [2], the micelle size distribution exhibits three different regions (Fig. 1): (i) Region of the monomers and oligomers, Ω_{o} ($1 \leq s \leq n_{\mathrm{o}}$); (ii) Region of the rare aggregates, Ω_{r} ($n_{\mathrm{o}} < s < n_{\mathrm{r}}$), and (iii) Region of the abundant micelles, Ω_{m} ($s \geq n_{\mathrm{r}}$). In the region Ω_{r}, the aggregate concentration is assumed to be relatively small (Fig. 1). In the region Ω_{m}, the peak of the micelle size distribution is usually described by a Gaussian curve [2]:

$$c_s = \frac{C_{\mathrm{m}}}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(s-m)^2}{2\sigma^2}\right] \qquad (s \geq n_{\mathrm{r}}) \tag{2.11}$$

Here C_{m} is the total concentration of the abundant micelles; m is their mean aggregation number; σ^2 is the dispersion of the Gaussian distribution, which characterizes the polydispersity of the abundant micelles. It is assumed that Eq. (2.11) holds under both equilibrium and dynamic conditions. In the latter case, the parameters in Eq. (2.11) depend on the spatial coordinate, $\mathbf{r}$, and time, t, i.e., we have: $C_{\mathrm{m}}(\mathbf{r},t)$, $m(\mathbf{r},t)$ and $\sigma(\mathbf{r},t)$.

To determine C_{m}, m, and σ , we will impose three conditions for equivalence of the model Gaussian distribution, Eq. (2.11), to the real micelle size distribution. For this goal, we will require the zeroth, first and second moments of the size distribution of the abundant micelles ($s \geq n_{\mathrm{r}}$) to be identical for

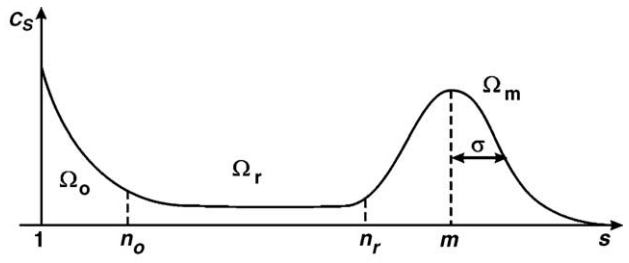

Fig. 1. Sketch of the typical size distribution of aggregates in a surfactant solution; c_s and s are the aggregate concentration and aggregation number; Ω_{o} Ω_{r} and Ω_{m} are, respectively, the regions of oligomers, rare aggregates and abundant micelles; n_{o} and n_{r} represent boundaries between the regions; $s=m$ corresponds to the peak in the region Ω_{m}.

the real and model systems. The following relations take place (see Appendix A):

$$\sum_{s\geq n_r} c_s \approx C_{\mathrm{m}} \tag{2.12}$$

$$\sum_{s\geq n_r} s c_s \approx m C_{\mathrm{m}} \tag{2.13}$$

$$\sum_{s\geq n_r} s^2 c_s \approx \left(m^2+\sigma^2\right) C_{\mathrm{m}} \tag{2.14}$$

To obtain the latter three equations, we have substituted the Gaussian distribution, Eq. (2.11), for c_s, and replaced the summation by integration (as an approximation).

To determine the functions $C_{\mathrm{m}}(\mathbf{r},t)$, $m(\mathbf{r},t)$ and $\sigma(\mathbf{r},t)$, we have to derive a corresponding set of equations. For this goal, we multiply Eq. (2.3) by $s^i, i=0,1,2$, and sum up for $s\geq n_{\mathrm{r}}$. Thus, with the help of Eqs. (2.12)–(2.14), we derive (Appendix A):

$$\frac{\mathrm{d}C_m}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_{m,0} = J \tag{2.15}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(mC_{\mathrm{m}}\right) + \nabla\cdot\mathbf{I}_{\mathrm{m},1} = n_r J + J_{\mathrm{m},0} \tag{2.16}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\left(m^2+\sigma^2\right)C_{\mathrm{m}}\right] + \nabla\cdot\mathbf{I}_{\mathrm{m},2} = n_r^2 J - J_{\mathrm{m},0} + 2J_{\mathrm{m},1} \tag{2.17}$$

where we have introduced the following notations:

$$\mathbf{I}_{m,i} \equiv \sum_{s\geq n_r} s^i \mathbf{I}_s \qquad (i=0,1,2,) \tag{2.18}$$

$$J \equiv J_{n_r}, \qquad J_{\mathrm{m},i} \equiv \sum_{s>n_r} s^i J_s \qquad (i=0,1) \tag{2.19}$$

Here, $\mathbf{I}_{\mathrm{m},i}$ and $J_{\mathrm{m},i}$ are the i-th moments of the diffusion and reaction fluxes, respectively; J is the reaction flux for $s=n_{\mathrm{r}}$ (at the boundary between the rare and abundant micelles, see Fig. 1). With the help of Eqs. (2.7) and (2.11), we obtain (Appendix A):

$$J_{\mathrm{m},0} = k_{\mathrm{m}}^{-} C_{\mathrm{m}} \left[\frac{c_1}{c_{1,\mathrm{eq}}} \exp\left(\frac{\sigma^2-\sigma_{\mathrm{eq}}^2}{2\sigma_{\mathrm{eq}}^4} - \frac{m-m_{\mathrm{eq}}}{\sigma_{\mathrm{eq}}^2}\right) - 1\right] \tag{2.20}$$

$$J_{\mathrm{m},1} = k_{\mathrm{m}}^{-} m C_{\mathrm{m}} \left[\frac{c_1}{c_{1,\mathrm{eq}}}\left(1 - \frac{\sigma^2-\sigma_{\mathrm{eq}}^2}{m\sigma_{\mathrm{eq}}^2}\right) \times \exp\left(\frac{\sigma^2-\sigma_{\mathrm{eq}}^2}{2\sigma_{\mathrm{eq}}^4} - \frac{m-m_{\mathrm{eq}}}{\sigma_{\mathrm{eq}}^2}\right) - 1\right] \tag{2.21}$$

As before, the subscript "eq" denotes the equilibrium value of the respective quantity. In addition, following [2] we have assumed that the dissociation rate constant of the abundant micelles is (approximately) the same, i.e., $k_s^{-}=k_{\mathrm{m}}^{-}$ for $s\geq n_{\mathrm{r}}$. Furthermore, applying the Fick's law, Eq. (2.6), and using Eqs. (2.12)–(2.14), we derive:

$$\mathbf{I}_{\mathrm{m},o} = -D_{\mathrm{m}}\nabla C_{\mathrm{m}}, \qquad \mathbf{I}_{\mathrm{m},1} = -D_{\mathrm{m}}\nabla\left(mC_{\mathrm{m}}\right) \tag{2.22}$$

$$\mathbf{I}_{\mathrm{m},2} = -D_{\mathrm{m}}\nabla\left[\left(m^2+\sigma^2\right)C_{\mathrm{m}}\right] \tag{2.23}$$

where we have assumed that the diffusivity of the abundant micelles is (approximately) the same, i.e., $D_{\mathrm{s}}=D_{\mathrm{m}}$ for $s\geq n_{\mathrm{r}}$. Thus, Eqs. (2.15)–(2.17) become a set of three equations for determining the parameters C_{m}, m, and s of the model micelle size distribution, Eq. (2.11). To close the system of equations, we need an additional relationship to determine the unknown flux J. Such a relationship is derived in the following subsection; see Eq. (2.32).

2.3. Balance equations for the monomers and oligomers

Let us multiply Eq. (2.3) by s, and sum up for $2\leq s<n_{\mathrm{r}}$. In view of Eqs. (2.2) and (2.19), we can bring the result in the form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(c_{\mathrm{o}}+c_{\mathrm{r}}\right) + \nabla\cdot\left(\mathbf{I}_{\mathrm{o}}+\mathbf{I}_{\mathrm{r}}\right) = -n_{\mathrm{r}}J - J_{\mathrm{m},0} \tag{2.24}$$

where

$$c_{\mathrm{o}} \equiv \sum_{s=1}^{n_{\mathrm{o}}} s c_s, \qquad c_{\mathrm{r}} \equiv \sum_{s=n_{\mathrm{o}}+1}^{n_{\mathrm{r}}-1} s c_s \tag{2.25}$$

c_{o} and c_{r} give the total number of monomers (per unit volume) incorporated, respectively, in oligomers and rare micelles. The diffusion fluxes in Eq. (2.24) are defined as follows:

$$\mathbf{I}_{\mathrm{o}} \equiv \sum_{s=1}^{n_{\mathrm{o}}} s\mathbf{I}_s, \qquad \mathbf{I}_{\mathrm{r}} \equiv \sum_{s=n_{\mathrm{o}}+1}^{n_{\mathrm{r}}-1} s\mathbf{I}_s \tag{2.26}$$

The theory by Aniansson and Wall [2] makes use of the following two simplifying assumptions: (i) In the *oligomer* region, Ω_{o} $(2\leq s\leq n_{\mathrm{o}})$, the characteristic time for monomer release from an aggregate, $1/k_{\mathrm{s}}^{-}$, is much shorter than the characteristic times of all other processes: convection, diffusion, "fast" and "slow" micelle relaxation processes (see Section 4). (ii) In the *rare-aggregate* region, Ω_{r} $(n_{\mathrm{o}}<s<n_{\mathrm{r}})$, the aggregate concentration is very small in comparison with the concentrations in the other two regions (Fig. 1). The latter two assumptions imply that for $2\leq s<n_{\mathrm{r}}$ the terms in the left hand side of Eq. (2.3) are negligible (in a first approximation), which leads to [2]:

$$J_2 = J_3 = \ldots = J_{n_{\mathrm{r}}} \equiv J \tag{2.27}$$

Using Eqs. (2.8) and (2.27), we succeeded to find an exact solution of the nonlinear system of algebraic equations, Eq. (2.7), for c_s $(2\leq s\leq n_{\mathrm{r}})$, see Appendix A:

$$\frac{c_s}{c_{s,\mathrm{eq}}} = \frac{c_1^s}{c_{1,\mathrm{eq}}^s} - J\sum_{i=0}^{s-2} \frac{c_1^i}{c_{1,\mathrm{eq}}^i} \frac{1}{k_{s-i}^{-} c_{s-i,\mathrm{eq}}} \qquad (s=2,\ldots,n_{\mathrm{r}}) \tag{2.28}$$

This new result leads to the following two main conclusions. In the oligomer region, Ω_{o}, where $1/k_s^{-}$ is a

small quantity, the term with J in Eq. (2.28) is negligible, and then

$$c_s/c_{s,\mathrm{eq}} = c_1^s/c_{1,\mathrm{eq}}^s \qquad (s = 2, \ldots, n_\mathrm{o}) \tag{2.29}$$

i.e., the oligomers are in quasi-equilibrium with the monomers. Substituting Eq. (2.29) into Eq. (2.25), we express the total number of surfactant molecules in the region Ω_o. (Fig. 1) as a function of c_1:

$$c_\mathrm{o} = \sum_{s=1}^{n_\mathrm{o}} s c_{s,\mathrm{eq}} \frac{c_1^s}{c_{1,\mathrm{eq}}^s} \tag{2.30}$$

Because the concentration of the rare aggregates is negligibly small, $c_\mathrm{r} \ll c_\mathrm{o}$, Eq. (2.24) reduces to a balance equation for the oligomers alone:

$$\frac{\mathrm{d}c_\mathrm{o}}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_\mathrm{o} = -n_\mathrm{r}J - J_{\mathrm{m},0} \tag{2.31}$$

To find an expression for J, we match the Gaussian distribution, Eq. (2.11), with Eq. (2.28) at the boundary between the regions of abundant and rare micelles (at $s = n_\mathrm{r}$):

$$\frac{C_\mathrm{m}}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(n_\mathrm{r}-m)^2}{2\sigma^2}\right] = c_{n_\mathrm{r},\mathrm{eq}} \frac{c_1^{n_\mathrm{r}}}{c_{1,\mathrm{eq}}^{n_\mathrm{r}}} - J\sum_{i=0}^{n_\mathrm{r}-2} \frac{c_1^i}{c_{1,\mathrm{eq}}^i} \frac{c_{n_\mathrm{r},\mathrm{eq}}}{k_{n_\mathrm{r}-i}^- c_{n_\mathrm{r}-i,\mathrm{eq}}} \tag{2.32}$$

Eq. (2.32) closes our set of equations, which is described in the next subsection. After linearization, Eq. (2.32) reduces to Eq. (3.9); see below.

2.4. Basic system of four nonlinear differential equations

Eqs. (2.15)–(2.17) form a system of four basic differential equations for determining the monomer concentration, $c_1(\mathbf{r},t)$, and the three parameters of the micelle distribution, $C_\mathrm{m}(\mathbf{r},t)$ $m(\mathbf{r},t)$, and $s(\mathbf{r},t)$. This basic system is to be considered in conjunction with the following algebraic expressions for the auxiliary variables: The reaction fluxes $J_{\mathrm{m},0}$, $J_{\mathrm{m},1}$, and J are given by Eqs. (2.20) (2.21) (2.32); the diffusion fluxes $\mathbf{I}_{\mathrm{m},0}$, $\mathbf{I}_{\mathrm{m},1}$, and $\mathbf{I}_{\mathrm{m},2}$ are defined by Eqs. (2.22) and (2.23); the concentration of surfactant in monomeric and oligomeric form, c_o, is given by Eq. (2.30).

The considered system is nonlinear, because it contains several nonlinear equations: Eqs. (2.16) (2.17) (2.20) (2.21) (2.30) (2.32). In the next section, we address the special case of small deviations from equilibrium, when all equations can be linearized.

3. Small deviations from equilibrium

In the case of small deviations from equilibrium, the set of equations in Section 2 could be linearized and explicit analytical solutions could be obtained. In particular, one can derive expressions for the relaxation times, which characterize how rapidly a micellar solution restores its equilibrium state after an initial homogeneous bulk perturbation due to a jump in temperature, pressure or concentration (see Section 4). We will present the basic variables in the form:

$$c_1 = c_{1,\mathrm{eq}} + c_{1,\mathrm{p}}, \qquad C_\mathrm{m} = C_{\mathrm{m,eq}} + C_{\mathrm{m,p}}$$
$$m = m_\mathrm{eq} + m_\mathrm{p}, \qquad \sigma = \sigma_\mathrm{eq} + \sigma_\mathrm{p} \tag{3.1}$$

where the subscripts "eq" and "p" mark the corresponding equilibrium values and the perturbations. At equilibrium, all diffusion and reaction fluxes, $\mathbf{I}_\mathrm{s}$ and J_s, are equal to zero. Therefore, such fluxes could appear in the equations only as perturbations. For this reason, we will skip the subscript "p" for all fluxes.

Next, we substitute Eq. (3.1) in the balance equation for monomers and oligomers, Eq. (2.31), expand in series for small perturbations, and preserve only the linear terms. Introducing the auxiliary notation

$$S \equiv \sum_{s=1}^{n_\mathrm{o}} s^2 \frac{c_{s,\mathrm{eq}}}{c_{1,\mathrm{eq}}} \tag{3.2}$$

we obtain:

$$S\frac{\mathrm{d}c_{1,\mathrm{p}}}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_\mathrm{o} = -n_\mathrm{r}J - J_{\mathrm{m},0} \tag{3.3}$$

If the concentration of the monomers is much greater than that of all oligomers, then one could keep only the term with $s = 1$ in Eq. (3.2), which yields $S \approx 1$. In Appendix B, we show that the linearization of Eqs. (2.15)–(2.17) leads to the following equations for the perturbations of C_m, m and σ.

$$\frac{dC_{\mathrm{m,p}}}{\mathrm{d}t} + \nabla\cdot\mathbf{I}_{\mathrm{m},0} = J \tag{3.4}$$

$$C_{\mathrm{m,eq}}\frac{\mathrm{d}m_\mathrm{p}}{\mathrm{d}t} + \nabla\cdot\left(\mathbf{I}_{\mathrm{m},1} - m_\mathrm{eq}\mathbf{I}_{\mathrm{m},0}\right) = \left(n_\mathrm{r} - m_\mathrm{eq}\right)J + J_\mathrm{m,o} \tag{3.5}$$

$$2\sigma_\mathrm{eq}C_{\mathrm{m,eq}}\frac{\mathrm{d}\sigma_\mathrm{p}}{\mathrm{d}t} + \nabla\cdot\left[\mathbf{I}_{\mathrm{m},2} - 2m_\mathrm{eq}\mathbf{I}_{\mathrm{m},1} + \left(m_\mathrm{eq}^2 - \sigma_\mathrm{eq}^2\right)\mathbf{I}_{\mathrm{m},0}\right] = \left[\left(n_\mathrm{r} - m_\mathrm{eq}\right)^2 - \sigma_\mathrm{eq}^2\right]J - \left(2m_\mathrm{eq} + 1\right)J_{\mathrm{m},0} + 2J_{\mathrm{m},1} \tag{3.6}$$

Furthermore, substituting Eq. (3.1) into the expressions for the reaction fluxes, Eqs. (2.20) and (2.21), and linearizing, we obtain:

$$J_{\mathrm{m},0} = k_\mathrm{m}^- C_{\mathrm{m,eq}}\left(\frac{c_{1,\mathrm{p}}}{c_{1,\mathrm{eq}}} + \frac{\sigma_\mathrm{p} - \sigma_\mathrm{eq}m_\mathrm{p}}{\sigma_\mathrm{eq}^3}\right) \tag{3.7}$$

$$J_{\mathrm{m},1} = k_\mathrm{m}^- m_\mathrm{eq} C_{\mathrm{m,eq}}\left(\frac{c_{1,\mathrm{p}}}{c_{1,\mathrm{eq}}} + \frac{\sigma_\mathrm{p} - \sigma_\mathrm{eq}m_\mathrm{p}}{\sigma_\mathrm{eq}^3} - \frac{2\sigma_\mathrm{p}}{m_\mathrm{eq}\sigma_\mathrm{eq}}\right) \tag{3.8}$$

Finally, we substitute Eq. (3.1) into Eq. (2.32), and derive (Appendix B):

$$RJ = \frac{n_\mathrm{r}c_{1,\mathrm{p}}}{c_{1,\mathrm{eq}}} - \frac{C_{\mathrm{m,p}}}{C_{\mathrm{m,eq}}} + \frac{\left(m_\mathrm{eq} - n_\mathrm{r}\right)m_\mathrm{p}}{\sigma_\mathrm{eq}^2} - \frac{\left(m_\mathrm{eq} - n_\mathrm{r}\right)^2 - \sigma_\mathrm{eq}^2}{\sigma_\mathrm{eq}^2}\frac{\sigma_\mathrm{p}}{\sigma_\mathrm{eq}} \tag{3.9}$$

$$R \equiv \sum_{j=2}^{n_\mathrm{r}} \frac{1}{k_j^- c_{j,\mathrm{eq}}} \approx \sum_{j>n_\mathrm{o}}^{n_\mathrm{r}} \frac{1}{k_j^- c_{j,\mathrm{eq}}} \tag{3.10}$$

R is termed [2] resistance to "flow" through the region of the rare micellar aggregates, Ω_r (Fig. 1). In Eq. (3.10), at the last step, we have used the fact that the concentrations of the oligomers are much greater than those of the rare micelles, and therefore all terms with $2 \le j \le n_o$ could be neglected.

The linear equations obtained in this section will be used for description of the relaxation of bulk (Section 4) and interfacial perturbations [40].

4. Relaxation of a spatially uniform perturbation

4.1. Micellar relaxation times

The previous studies are using the simplifying assumption that the width of the micelle size distribution, characterized by σ , is not affected by the perturbation (σ_p=0). In such a case, the reaction fluxes J and $J_{m,0}$, see Eqs. (3.7) and (3.9), define two different characteristic times, which correspond to the known fast and slow processes of micelle relaxation [2,3,42]; see also [12,13, 28,31,32]. Physically, the fast process corresponds to variation of the mean aggregation number, m, due to exchange of monomers between the abundant micelles and the surrounding solution, at constant total micelle concentration, C_m. The slow relaxation process is related to decay or formation of abundant micelles and variation in their total number concentration, C_m.

In the present theoretical model (Section 3), we do not use the simplifying assumption σ_p=0. Instead, we derived a new equation for determining σ_p, Eq. (3.6), which contains an additional flux, $J_{m,1}$, given by Eq. (3.8). Thus, we could anticipate that a third relaxation time will appear in the theory, which characterizes the relaxation of the width of the micellar peak (see region Ω_m in Fig. 1). Below, we will see what is the magnitude of this third relaxation time and whether it is of importance for the interpretation of experimental data.

Hereafter, we consider homogeneous bulk perturbations. In such case, all diffusion and convective fluxes are equal to zero (unlike the reaction fluxes), and the perturbations depend only on time, t. If we multiply Eq. (3.4) by m_{eq}, and sum up the result with Eqs. (3.3) and (3.5), we can derive

$$Sc_{1,p} + m_{eq}C_{m,p} + m_p C_{m,eq} = 0 \tag{4.1}$$

This is the form of the surfactant conservation law in terms of perturbations. Eq. (4.1) expresses the perturbation $c_{1,p}$ as a linear combination of the perturbations $C_{m,p}$ and m_p. Consequently, $c_{1,p}$ is not an independent variable in the considered case of homogeneous perturbations. In other words, we are dealing with three independent perturbations, $C_{m,p}$, m_p and σ_p, which have to be determined from Eqs. (3.4)–(3.6). Following the standard procedure, we assume that these perturbations are proportional to $\exp(-\nu t)$, where $1/\nu$ is the characteristic relaxation time. In this way, from Eqs. (3.4)–(3.6) we obtain the following system of equations, which is applicable to homogeneous perturbations:

$$-C_{m,p}\nu = J \tag{4.2}$$

$$-C_{m,eq}m_p\nu = (n_r - m_{eq})J + J_{m,0} \tag{4.3}$$

$$-2\sigma_{eq}C_{m,eq}\sigma_p\nu = \left[(n_r - m_{eq})^2 - \sigma_{eq}^2\right]J - (2m_{eq}+1)J_{m,0} + 2J_{m,1} \tag{4.4}$$

The equations for the reaction fluxes, Eqs. (3.7)–(3.9), imply that Eqs. (4.2)–(4.4) form a linear homogeneous system for determining $C_{m,p}$, m_p and σ_p. As known, such a system has a nontrivial solution only when its determinant is equal to zero. Thus, from Eqs. (4.2)–(4.4) we obtain a cubic characteristic equation for ν, which has three real positive roots. The reciprocal values of these roots give the three characteristic relaxation times: t_c, t_m, and t_σ, which are related to the relaxations of $C_{m,p}$, m_p and σ_p, respectively (see Section 4.4 below). Correspondingly, any relaxing parameter, Y, of the micellar system could be expressed as a linear combination of three exponents:

$$Y = Y_1\exp(-t/t_c) + Y_2\exp(-t/t_m) + Y_3\exp(-t/t_\sigma) \tag{4.5}$$

where Y_1, Y_2 and Y_3 are constant amplitudes; see also Eqs. (4.34) (4.48) (4.51). To obtain explicit analytical expressions for the characteristic times t_c, t_m, and t_σ, we consider separately the slow and fast micellar relaxation processes.

4.2. Characteristic time of the slow relaxation process

In this case, by definition $k_m^-/\nu \gg 1$. We substitute the reaction fluxes $J_{m,0}$ and $J_{m,1}$ from Eqs. (3.7) and (3.8) into Eqs. (4.3) and (4.4), and carry out the transition $k_m^- \to \infty$. This is equivalent to set each of the fluxes $J_{m,0}$ and $J_{m,1}$ equal to zero. As a result, we obtain:

$$\sigma_p = 0 \tag{4.6}$$

$$m_p = \sigma_{eq}^2 \frac{c_{1,p}}{c_{1,eq}}. \tag{4.7}$$

In other words, for the *slow* relaxation process, the perturbation in the width of the micelle size distribution is equal to zero (σ_p=0), while the perturbation in the micelle mean aggregation number is proportional to the perturbation in the monomer concentration, $m_p \propto c_{1,p}$. Substituting Eq. (4.7) into Eqs. (3.9) and (4.1), we obtain the following expressions for the reaction flux J and monomer concentration, $c_{1,p}$:

$$J = \frac{1}{R}\left(m_{eq}\frac{c_{1,p}}{c_{1,eq}} - \frac{C_{m,p}}{C_{m,eq}}\right) \tag{4.8}$$

$$\frac{c_{1,p}}{c_{1,eq}} = -\frac{m_{eq}C_{m,p}}{\sigma_{eq}^2 C_{m,eq} + Sc_{1,eq}} \tag{4.9}$$

Finally, we substitute Eq. (4.9) into Eq. (4.8), and the result —into Eq. (4.2). Thus we obtain the following expression for $v \equiv v_c$

$$v_c = \frac{1}{t_c} = \frac{1}{RC_{\mathrm{m,eq}}}\left(1 + \frac{m_{\mathrm{eq}}^2 C_{\mathrm{m,eq}}}{Sc_{1,\mathrm{eq}} + \sigma_{\mathrm{eq}}^2 C_{\mathrm{m,eq}}}\right) \tag{4.10}$$

where t_c is the relaxation time of the slow process. The latter expression coincides with the result by Aniansson and Wall [2]. At sufficiently high micellar concentrations ($C_{\mathrm{m,eq}} \gg Sc_{1,\mathrm{eq}}/\sigma_{\mathrm{eq}}^2$), Eq. (4.10) predicts a linear increase of the relaxation time, t_c, with $C_{\mathrm{m,eq}}$:

$$t_c \approx \frac{R\sigma_{\mathrm{eq}}^2}{m_{\mathrm{eq}}^2 + \sigma_{\mathrm{eq}}^2} C_{\mathrm{m,eq}} \tag{4.11}$$

4.3. Two characteristic times of the fast relaxation process

In this case, the characteristic relaxation time, $1/v$, is much smaller than t_c. Thus, carrying out the transition $1/v \to 0$ in Eq. (4.2), we obtain $C_{\mathrm{m,p}} = -J/v \to 0$. In other words, the perturbation in the total concentration of the abundant micelles is zero for the *fast* process. Setting $J/v \to 0$ also in Eqs. (4.3) and (4.4), we derive:

$$m_{\mathrm{p}} v = -\frac{J_{\mathrm{m,o}}}{C_{\mathrm{m,eq}}} \tag{4.12}$$

$$\sigma_{\mathrm{p}} v = \frac{2m_{\mathrm{eq}} + 1}{2\sigma_{\mathrm{eq}} C_{\mathrm{m,eq}}} J_{\mathrm{m},0} - \frac{1}{\sigma_{\mathrm{eq}} C_{\mathrm{m,eq}}} J_{\mathrm{m},1} \tag{4.13}$$

Further, substituting $C_{\mathrm{m,p}} \to 0$ in the mass conservation law, Eq. (4.1), we obtain:

$$c_{1,\mathrm{p}} = -C_{\mathrm{m,eq}} m_{\mathrm{p}}/S \tag{4.14}$$

Combining Eqs. (3.7) (4.12) (4.14), we derive:

$$m_{\mathrm{p}} v = k_{\mathrm{m}}^{-}\left(\frac{C_{\mathrm{m,eq}} m_{\mathrm{p}}}{Sc_{1,\mathrm{eq}}} - \frac{\sigma_{\mathrm{p}} - \sigma_{\mathrm{eq}} m_{\mathrm{p}}}{\sigma_{\mathrm{eq}}^3}\right) \tag{4.15}$$

Next, we substitute $J_{\mathrm{m},0}$ and $J_{\mathrm{m},1}$ from Eqs. (3.7) and (3.8) into Eq. (4.13), and replace $c_{1,\mathrm{p}}$ from Eq. (4.14):

$$\frac{2\sigma_{\mathrm{eq}}\sigma_{\mathrm{p}} v}{k_{\mathrm{m}}^{-}} = \frac{\sigma_{\mathrm{p}} - \sigma_{\mathrm{eq}} m_{\mathrm{p}}}{\sigma_{\mathrm{eq}}^3} + \frac{4\sigma_{\mathrm{p}}}{m_{\mathrm{eq}}\sigma_{\mathrm{eq}}} - \frac{C_{\mathrm{m,eq}} m_{\mathrm{p}}}{Sc_{1,\mathrm{eq}}} \tag{4.16}$$

Eqs. (4.15) and (4.16) form a linear homogeneous system for the perturbations m_{p} and σ_{p}. This system has a nontrivial solution only if its determinant is equal to zero. The latter requirement leads to a quadratic equation for v, whose solution is:

$$\frac{2\sigma_{\mathrm{eq}}^2}{k_{\mathrm{m}}^{-}} v_{1,2} = 3 + u + \varepsilon \pm \left[(3 + u + \varepsilon)^2 - 8(1 + u)\right]^{1/2} \tag{4.17}$$

$$u \equiv \frac{\sigma_{\mathrm{eq}}^2 C_{\mathrm{m,eq}}}{Sc_{1,\mathrm{eq}}}; \qquad \varepsilon \equiv \frac{1}{2\sigma_{\mathrm{eq}}^2}. \tag{4.18}$$

Eq. (4.18) implies that the dimensionless parameter u can vary from zero at the CMC ($C_{\mathrm{m,eq}} = 0$) up to high values, $u \gg 1$, at $C_{\mathrm{m,eq}} \gg c_{1,\mathrm{eq}}$. In addition, for most systems, we have $1/6\sigma_{\mathrm{eq}}^2 = \varepsilon/3 \ll 1$, and then Eq. (4.17) can be simplified:

$$v_1 \equiv v_{\mathrm{m}} \equiv \frac{1}{t_m} \approx \frac{k_{\mathrm{m}}^{-}}{\sigma_{\mathrm{eq}}^2}(1 + u) \tag{4.19}$$

$$v_2 \equiv v_\sigma \equiv \frac{1}{t_\sigma} \approx 2\frac{k_{\mathrm{m}}^{-}}{\sigma_{\mathrm{eq}}^2} \tag{4.20}$$

where t_m and t_σ are the two characteristic times of the fast relaxation process. One can check that the expression for t_m exactly coincides with the expression for the relaxation time of the fast process derived by Aniansson and Wall [2]. On the other hand, t_σ is a new relaxation time, which appears in our theory because we consider perturbations in the width of the micellar peak, i.e., $\sigma_{\mathrm{p}} \neq 0$. (The previous studies have used $\sigma_{\mathrm{p}} \equiv 0$ as a simplifying assumption.) Eq. (4.20) implies that t_σ is independent on the micelle concentration, $C_{\mathrm{m,eq}}$, unlike t_m.

For $0 < u \leq 1$, i.e., in the vicinity of the CMC, Eqs. (4.19) and (4.20) yield $t_m \geq t_\sigma$. Out of this relatively narrow concentration zone, we have another relation, viz.:

$$t_c > t_\sigma > t_m \qquad (u > 1) \tag{4.21}$$

In other words, the longest is the relaxation time of the slow process, t_c, which is related to the relaxation of the micelle concentration, C_{m} (see Section 4.6 for details). The shortest is the conventional relaxation time of the fast process, t_m, which is related to the relaxation of the micelle mean aggregation number, m. The relaxation time, t_σ, which is related to the relaxation of the width of the micelle peak, σ, has an intermediate value for $u > 1$.

Both t_c and t_m are accessible to experimental measurements, and have been found to affect the occurrence of processes of scientific and practical importance [3,31,32,42]. Then, Eq. (4.21) implies that the intermediate relaxation time, t_σ, should be also accessible for measurement by the experimental relaxation methods. Note that t_σ is simply related to k_{m}^{-}, see Eq. (4.20), and correspondingly, the measurement of t_σ allows one to determine k_{m}^{-}. At surfactant concentrations much above the CMC ($u \gg 1$), Eqs. (4.19) and (4.20) predict $t_\sigma \gg t_m$. In such a case, one should be able to clearly distinguish between these two relaxation times. On the other hand, at $u \approx 1$ (close to the CMC) we have $t_\sigma \approx t_m$, and it could be difficult to distinguish between them (unless they govern the relaxation of different experimental parameters; see Section 4.6).

It should be noted that Eq. (4.20) for t_σ is identical with Eq. (11) (for $n = 2$) in the paper by Wall and Aniansson [5]. However, the two equations have been obtained in quite different contexts and have different meaning. In [5], the perturbation is mathematically expressed as an infinite series of exponentials with different decay times, at *constant* σ . In contrast, here the width of the micellar peak, σ, is *variable*, and t_σ is its characteristic relaxation time. Moreover, in [5] the fast process is characterized by a single characteristic time, t_m, while here, the fast process is characterized by both t_m and t_σ . At the lower micelle concentrations ($\beta \approx 1$) t_m and t_σ are comparable by magnitude (see Section 4.5). Then the

relaxation of the monomer concentration is described by a superposition of two exponentials (rather than a single one), as discussed at the end of Section 4.5. In other words, in our case the relaxation of $c_{1,p}$ is affected by t_σ. On the other hand, τ_2 in Eq. (11) of [5] does not enter the expression for ξ_1 therein.

4.4. Exact solution and interplay of the relaxation processes

In general, we consider small perturbations in the three parameters describing the shape of the micellar peak (Fig. 1), viz. its height, position and width, characterized, respectively, by C_m, m, and σ. In Sections 4.2 and 4.3 we derived analytical expressions for the corresponding relaxation times, t_c, t_m, and t_σ, at the cost of some approximations. However, it is possible to solve the problem exactly. This will give us the exact values of the relaxation times; will allow us to check the approximated expressions and to see whether all of t_c, t_m, and t_σ influence the relaxation of each separate perturbation, $C_{m,p}$, m_p, and σ_p. For this goal, it is convenient to introduce dimensionless variables:

$$\xi_1 \equiv \frac{c_{1,p}}{c_{1,eq}}; \quad \xi_c \equiv \frac{C_{m,p}}{C_{m,eq}}; \quad \xi_m \equiv \frac{m_p}{m_{eq}}; \quad \xi_\sigma \equiv \frac{\sigma_p}{\sigma_{eq}} \tag{4.22}$$

From Eqs. (4.1) and (4.22) we express the dimensionless perturbation in the monomer concentration:

$$\xi_1 = -\frac{\beta}{S}(\xi_c + \xi_m) \tag{4.23}$$

where we have introduced the relative micelle concentration, β:

$$\beta \equiv \frac{C_{tot} - CMC}{CMC} = m_{eq}\frac{C_{m,eq}}{c_{1,eq}} \tag{4.24}$$

with C_{tot} being the total surfactant concentration. Further, from Eqs. (3.9) and (4.22) we express the reaction flux J:

$$\frac{J}{k_S^-} = \left(m_{eq} - w\sigma_{eq}\right)\xi_1 - \xi_c + w\frac{m_{eq}}{\sigma_{eq}}\xi_m - \left(w^2 - 1\right)\xi_\sigma \tag{4.25}$$

$$w \equiv \frac{m_{eq} - n_r}{\sigma_{eq}} > 1; \quad k_S^- \equiv \frac{1}{Rc_{1,eq}} \tag{4.26}$$

where the equilibrium dimensionless parameter w is proportional to the distance between the positions of the micellar peak, m_{eq}, and the boundary, n_r, between the rare aggregates and the abundant micelles (Fig. 1). The parameter k_S^-, defined by Eq. (4.26), can be interpreted as rate constant of the slow relaxation processes. Likewise, from Eqs. (3.7), (4.22) and (4.23) we obtain an expression for the reaction flux, $J_{m,0}$:

$$\frac{J_{m,0}}{k_m^- C_{m,eq}} = -\frac{\beta}{S}\xi_c - \left(\frac{m_{eq}}{\sigma_{eq}^2} + \frac{\beta}{S}\right)\xi_m + \frac{1}{\sigma_{eq}^2}\xi_\sigma \tag{4.27}$$

Finally, from Eqs. (3.8), (4.22) and (4.23) we obtain:

$$\frac{J_{m,1}}{k_m^- m_{eq} C_{m,eq}} = -\frac{\beta}{S}\xi_c - \left(\frac{m_{eq}}{\sigma_{eq}^2} + \frac{\beta}{S}\right)\xi_m + \left(\frac{1}{\sigma_{eq}^2} - \frac{2}{m_{eq}}\right)\xi_\sigma \tag{4.28}$$

The substitution of Eqs. (4.27) and (4.28) into Eqs. (4.2)–(4.4), after some transformations, leads to a linear homogeneous system of equations:

$$\sum_{j=c,m\sigma}\left(a_{ij} - \lambda\delta_{ij}\right)\xi_j = 0, \qquad i = c, m, \sigma \tag{4.29}$$

where $\lambda \equiv -v/k_m^-$ is a dimensionless parameter; δ_{ij} is the Kronecker symbol; a_{ij} is a matrix, whose elements are given in Appendix C. The system (4.29) has a nontrivial solution only if its determinant is equal to zero, which leads to:

$$\lambda^3 - I_1\lambda^2 + I_2\lambda - I_3 = 0 \tag{4.30}$$

where the three invariants of the matrix (a_{ij}) are

$$\begin{aligned} I_1 &= a_{cc} + a_{mm} + a_{\sigma\sigma};\\ I_2 &= a_{cc}a_{mm} - a_{cm}a_{mc} + a_{mm}a_{\sigma\sigma} - a_{m\sigma}a_{\sigma m} + a_{cc}a_{\sigma\sigma} - a_{c\sigma}a_{\sigma c};\\ I_3 &= det\left(a_{ij}\right) \end{aligned} \tag{4.31}$$

Note that a_{ij}, I_1, I_2, and I_3 depend on the following dimensionless parameters of the system:

$$m_{eq},\ \sigma_{eq},\ w,\ \beta,\ S, \text{ and } \theta \equiv k_S^-/k_m^- \tag{4.32}$$

Consequently, the same is true for the three roots of Eq. (4.30), which determine the three characteristic relaxation times of the system:

$$\lambda_j \equiv -\frac{1}{\tau_j} \equiv -\frac{1}{k_m^- t_j}; \quad j = c, m, \sigma \tag{4.33}$$

Solving Eq. (4.30), we determine the three eigenvalues, λ_c, λ_m, and λ_s. In general, the matrix a_{ij} is non-symmetric, but nevertheless, for physically reasonable values of the system's parameters, all three eigenvalues are real and negative, see Section 4.5. The next step is to determine the three eigenvectors, $\mathbf{f}^{(c)}$, $\mathbf{f}^{(m)}$, and $\mathbf{f}^{(s)}$, from Eq. (4.29). The components, $f_i^{(j)}$, of the latter three vectors could be determined by means of a standard software, using the matrix elements, a_{ij}, as input parameters; see Appendix C. Further, the relaxation of an arbitrary perturbation, in either C_m, m, or σ, can be expressed in the general form [43]:

$$\xi_i = \sum_{j=c,m,\sigma} X_j f_i^{(j)} \exp\left(-\tau/\tau_j\right), \quad i = c, m, \sigma \tag{4.34}$$

where $\tau = k_m^- t$ is the dimensionless time. The constants X_j have to be determined from the initial conditions, at $\tau = 0$. It is useful to consider the following three normalized independent modes:

$$\xi_c(0) = 1; \quad \xi_m(0) = 0; \quad \xi_\sigma(0) = 0: \quad \text{mode}(1,0,0) \tag{4.35}$$

$$\xi_c(0) = 0; \quad \xi_m(0) = 1; \quad \xi_\sigma(0) = 0: \quad \text{mode}(0,1,0) \tag{4.36}$$

$$\xi_c(0) = 0; \quad \xi_m(0) = 0; \quad \xi_\sigma(0) = 1: \quad \text{mode}(0,0,1) \tag{4.37}$$

For each mode, we substituted the respective initial condition into Eq. (4.34), and determined the respective values

of the constants X_j. In Appendix C it is explained how one could determine the coefficients to Eq. (4.37) $X_j^{(c)}$ corresponding to Eq. (4.35), $X_j^{(m)}$ corresponding to Eq. (4.36), and $X_j^{(\sigma)}$ corresponding to Eq. (4.37). Then, the evolution of each of C_m, m, and σ corresponding to the boundary conditions, Eqs. (4.35)–(4.37), is given by the respective version of Eq. (4.34):

$$\xi_i^{(k)} = \sum_{j=c,m,\sigma} X_j^{(k)} f_i^{(j)} \exp\left(-\tau/\tau_j\right), \; i,k = c,m,\sigma \tag{4.38}$$

$\xi_i^{(k)}(t)$ expresses the evolution of the parameter . $\xi_i (i=c,m,\sigma)$, which is due to the relaxation of an initial perturbation, $\xi_k(0)=1$, in the parameter k $(k=c,m,\sigma)$. In general, an initial perturbation in one of the parameters, for example C_m, engenders variation also in the other two parameters, m and σ. This fact is important for the interpretation of experimental data, and is illustrated in Section 4.5, where graphs of $\xi_i^{(k)}(t)$ are given for all i, $k=c,m,\sigma$.

Finally, let us consider an arbitrary perturbation, corresponding to the initial condition:

$$\xi_c(0) = A_c;\; \xi_m(0) = A_m;\; \xi_\sigma(0) = A_\sigma \tag{4.39}$$

Then, we can calculate the evolution of each parameter, $\xi_c(t)$, $\xi_m(t)$, and $\xi_\sigma(t)$, due to the relaxation of the considered initial perturbation:

$$\xi_i(t) = \sum_{k=c,m,\sigma} A_k \xi_i^{(k)}(t),\; i = c,m,\sigma \tag{4.40}$$

Here $\xi_i^{(k)}$ is defined by Eq. (4.38). This completes the solution of our problem.

Because we are dealing with small perturbations, the amplitudes in Eq. (4.40) must be small, $A_k \ll 1$, while the characteristic functions $\xi_i^{(k)}(t)$ could be of the order of 1, see Figs. 2 – 4. Note also, that simple and accurate asymptotic expressions for $\xi_c(t)$, $\xi_m(t)$ and $\xi_\sigma(t)$ can be derived in the case when $t_c \gg t_m$, t_σ; see Eqs. (4.46) (4.48) (4.51).

4.5. Numerical results and discussion

To obtain numerical results, we have to assign physically reasonable values to the system's parameters, specified by Eq. (4.32). We used the following values:

$$m_{eq} = 60;\; \sigma_{eq} = 5;\; w = 3;\; S = 1.1,\; \theta = 10^{-7} \tag{4.41}$$

In particular, $w=3$ means that the concentration of the rare aggregates is $\approx 0.001\; c_m$; this follows from Eq. (2.11), where $(s-m)^2/\sigma^2$ should be replaced by w^2. The value $S=1.1$ means that the oligomers give a contribution of 10% to the sum in Eq. (3.2); if the monomers were completely predominant, then we would have $S=1$. To determine $\theta \equiv k_S^-/k_m^-$, we varied this ratio until we found a value, for which the theoretical predictions were similar to what we know from the experiment [3]. We carried out calculations at two values $\beta=1$ and 100, corresponding to surfactant concentrations $2\times$CMC, and well above the CMC; see Eq. (4.24).

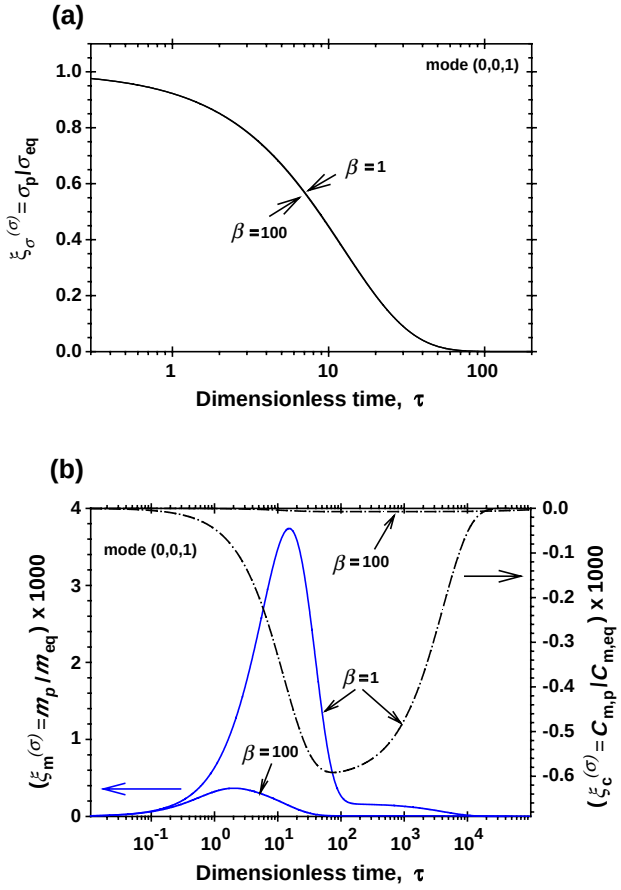

Fig. 2. Plots of $\xi_i^{(\sigma)}$ $(i=\sigma,\; m,\; c)$ versus the dimensionless time, $\tau = k_m^- t$: evolution of a micellar system after an initial perturbation in the micelle polydispersity, σ. The deviations from equilibrium of the micelle concentration, aggregation number, and polydispersity are, respectively, $C_{m,p}$, m_p and σ_p. The curves are calculated for two dimensionless micelle concentrations: $\beta=1$ and 100; the other parameters are given by Eq. (4.41). (a) Diagonal term $\xi_\sigma^{(\sigma)}$; (b) Cross terms $\xi_m^{(\sigma)}$and $\xi_c^{(\sigma)}$.

Next, we calculated the matrix elements a_{ij}, using equations from Appendix C, and the invariants I_1, I_2, and I_3, given by Eq. (4.31). Further, we solved Eq. (4.30) numerically, and with the help of Eq. (4.33) we determined the exact values of the three dimensionless relaxation times, τ_c, τ_m, and τ_σ. In Table 1, they are compared with the output of the respective approximated expressions, as follows. The characteristic time of the slow process, τ_c, was calculated from Eqs. (4.10) and (4.11), which have been transformed in the following dimensionless form:

$$\frac{1}{\tau_c} = \frac{m_{eq}\theta}{\beta}\left(1 + \frac{m_{eq}\beta}{S + \sigma_{eq}^2\beta/m_{eq}}\right) \tag{4.42}$$

$$\tau_c \approx \frac{\beta\sigma_{eq}^2}{\left(m_{eq}^2 + \sigma_{eq}^2\right)m_{eq}\theta} \quad (\beta \gg 1) \tag{4.43}$$

See also Eqs. (4.24) and (4.26). Note that Eq. (4.42) is more accurate expression for τ_c, while Eq. (4.43) is its simplified version for $\beta \gg 1$. Furthermore, the relaxation times

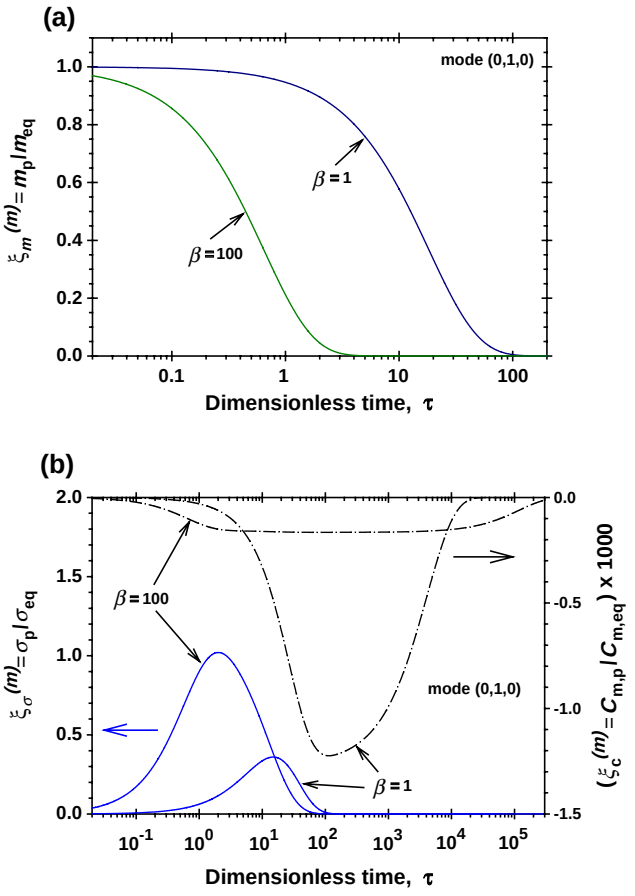

Fig. 3. Plots of $\xi_i^{(m)}(i=m,\sigma,c)$ versus the dimensionless time, $\tau=k_{\mathrm{m}}^{-}t$: evolution of a micellar system after an initial perturbation in the micelle mean aggregation number, m. The deviations from equilibrium of the micelle concentration, aggregation number, and polydispersity are, respectively, $C_{\mathrm{m,p}}$, m_{p} and σ_{p}. The curves are calculated for two dimensionless micelle concentrations: $\beta=1$ and 100; the other parameters are given by Eq. (4.41). (a) Diagonal term $\xi_m^{(m)}$ (b) Cross terms $\xi_\sigma^{(m)}$ and $\xi_c^{(m)}$.

of the mean micelle aggregation number and polydispersity, τ_m and τ_σ, were calculated from the dimensionless forms of Eqs. (4.17)–(4.19):

$$\frac{2\sigma_{\mathrm{eq}}^2}{\tau_{m,\sigma}} = 3+u+\varepsilon \pm \left[(3+u+\varepsilon)^2 - 8(1+u)\right]^{1/2} \tag{4.44}$$

$$\frac{1}{\tau_m} \approx \frac{1}{\sigma_{\mathrm{eq}}^2}(1+u); \quad \frac{1}{\tau_\sigma} \approx \frac{2}{\sigma_{\mathrm{eq}}^2} \tag{4.45}$$

where $u=(\beta\sigma_{\mathrm{eq}}^2)/(Sm_{\mathrm{eq}})$, and $\varepsilon=(2\sigma_{\mathrm{eq}}^2)^{-1}$. Note that Eq. (4.44) is more accurate expression for τ_m and τ_σ, while Eq. (4.45) is its simplified version for $\varepsilon \ll 3$.

The results in Table 1 indicate that the approximate Eqs. (4.42)–(4.45) give the values of the relaxation times very accurately, except Eq. (4.43) at $\beta=1$ (where the latter equation is out of the range of its validity). In particular, Eq. (4.45) enables one to identify which of the roots of Eq. (4.44), or of the exact Eq. (4.30), corresponds to τ_m and τ_σ. As expected, both the exact and approximate solutions imply that τ_σ is practically independent of the surfactant concentration, characterized by β. On the other hand, when the surfactant concentration rises, τ_c increases, while τ_m decreases.

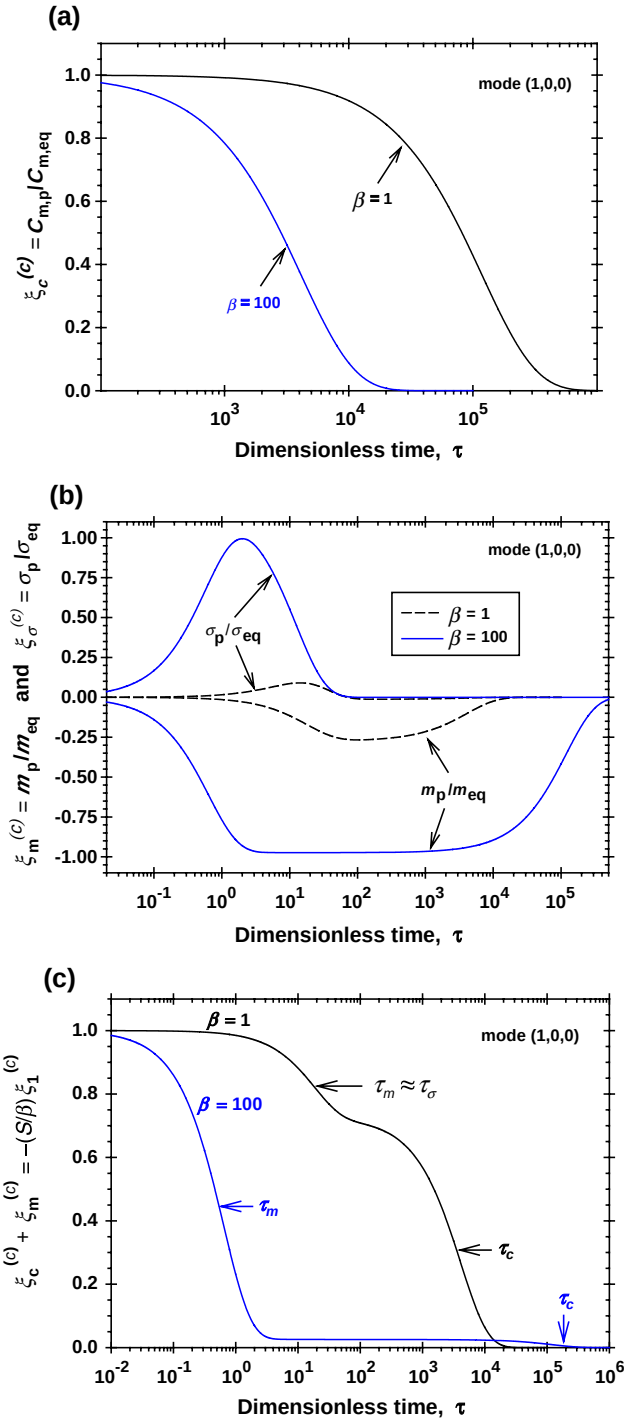

Fig. 4. Plot of $\xi_i^{(c)}(i=c,m,\sigma)$ versus the dimensionless time, $\tau=k_{\mathrm{m}}^{-}t$: evolution of a micellar system after an initial perturbation in the total micelle concentration, C_{m}. The deviations from equilibrium of the micelle concentration, aggregation number, and polydispersity are, respectively, $C_{\mathrm{m,p}}$, m_{p} and σ_{p}. The curves are calculated for two dimensionless micelle concentrations: $\beta=1$ and 100; the other parameters are given by Eq. (4.41). (a) Diagonal term $\xi_c^{(c)}$ (b) Cross terms $\xi_m^{(c)}$ and $\xi_\sigma^{(c)}$; (c) $\xi_c^{(c)}+\xi_m^{(c)}=-(S/\beta)\xi_1^{(c)}$.

Table 1
Calculated values of the micellar relaxation times

Dimensionless relax. time	Exact, Eq. (4.30)	More accurate expressions, Eqs. (4.42) and (4.44)	Simplified expressions, Eqs. (4.43) and (4.45)
$\beta=1$			
τ_c	4.12×10^{3}	4.11×10^{3}	1.15×10^{3}
τ_m	1.87×10^{1}	1.87×10^{1}	1.81×10^{1}
τ_σ	1.21×10^{1}	1.21×10^{1}	1.25×10^{1}
$\beta=100$			
τ_c	1.18×10^{5}	1.18×10^{5}	1.15×10^{5}
τ_m	6.43×10^{-1}	6.43×10^{-1}	6.43×10^{-1}
τ_σ	1.25×10^{1}	1.25×10^{1}	1.25×10^{1}

Next, let us imagine an initial perturbation in the polydispersity, σ, at fixed micelleconcentration and aggregation number. Such a perturbation is described by Eq. (4.37). Determining $f_i^{(j)}$ and $X_j^{(\sigma)}$, as explained in Appendix C, we applied Eq. (4.38) to calculate the time dependencies of the height, position and width of the micellar peak, described by the functions $\xi_c^{(\sigma)}(t)$, $\xi_m^{(\sigma)}(t)$, and $\xi_\sigma^{(\sigma)}(t)$.

Fig. 2a shows the calculated dependence $\xi_\sigma^{(\sigma)}(t)$. The curves corresponding to $\beta=1$ and 100 coincide, which indicates that $\xi_\sigma^{(\sigma)}(t)$ is insensitive to the micelle concentration. The inflexion point of the curve $\xi_\sigma^{(\sigma)}(t)$ corresponds to $\tau\approx\tau_\sigma$: compare Table 1 and Fig. 2a. Hence, the decay of $\xi_\sigma^{(\sigma)}$ at long times is determined by τ_σ.

Fig. 2b shows the cross terms, $\xi_c^{(\sigma)}(t)$ and $\xi_m^{(\sigma)}(t)$, which are the dimensionless variations of C_m and m, induced by the initial perturbation of σ. It is important to note that both $\xi_c^{(\sigma)}$ and $\xi_m^{(\sigma)}$ are very small. For this reason, we have plotted them multiplied by 1000. In addition, we have $\xi_c^{(\sigma)}<0$, but $\xi_c^{(\sigma)}>0$, which means that an initial increase in σ engenders a small decrease in C_m, and a small increase in m. By definition, we have $\xi_c^{(\sigma)}(0)=\xi_m^{(\sigma)}(0)=0$ at the initial moment. In addition, these quantities should decay for $t\to\infty$. For this reason, the respective time dependencies exhibit maxima or minima. For the same reason, all cross terms plotted in Figs. 3b and 4b exhibit maxima or minima.

In summary, an initial perturbation in the micelle polydispersity, σ, induces a relaxation of σ with characteristic time τ_σ, but it does not perturb noticeably the micelle concentration, C_m, and the mean aggregation number, m (Fig. 2).

Fig. 3a shows the calculated dependence $\xi_m^{(m)}(t)$. The curves corresponding to $\beta=1$ and 100 are rather different, which indicates that $\xi_m^{(m)}(t)$ is sensitive to the micelle concentration. The inflexion points of the curves $\xi_m^{(m)}(t)$ correspond to the values of t_m for the respective β: compare Table 1 and Fig. 3a. Hence, the decay of $\xi_m^{(m)}$ at long times is determined by t_m.

Fig. 3b shows $\xi_c^{(m)}(t)$ and $\xi_\sigma^{(m)}(t)$, which are the dimensionless variations of C_m and σ, induced by the initial perturbation of m. It is important to note that $\xi_c^{(m)}$ is very small, and for this reason it is plotted multiplied by 1000. In contrast, $\xi_\sigma^{(m)}$ is not small at all; close to its maximum it can be of the order of 1. (Despite the fact that here we are working with small perturbations, the characteristic functions $\xi_i^{(m)}$ could be of the order of 1; see the paragraph after Eq. (4.40).) In addition, we have $\xi_c^{(m)}<0$, but $\xi_\sigma^{(m)}>0$, which means that an initial increase in m engenders a small decrease in C_m, and a considerable increase in σ.

In summary, an initial perturbation in the micelle mean aggregation number, m, induces a relaxation of m with characteristic time τ_m, and a significant perturbation of σ, but it does not affect considerably the micelle concentration, C_m.

Finally, Fig. 4a shows the calculated dependence $\xi_c^{(c)}(t)$. The curves corresponding to $\beta=1$ and 100 are rather different, which indicates that $\xi_c^{(c)}(t)$ is sensitive to the micelle concentration. The inflexion points of the curves $\xi_c^{(c)}(t)$ correspond to the values of τ_c for the respective β: compare Table 1 and Fig. 4a. Hence, the decay of $\xi_c^{(c)}$ at long times is determined by τ_c.

Fig. 4b shows the cross terms, $\xi_m^{(c)}(t)$. and $\xi_\sigma^{(c)}(t)$, which are the dimensionless variations of m and σ, induced by the initial perturbation of C_m. It is important to note that both $\xi_m^{(c)}$ and $\xi_\sigma^{(c)}$ are considerable, especially at the higher micelle concentration ($\beta=100$). As in the previous cases, $\xi_\sigma^{(c)}$ decays for $\tau\gg\tau_\sigma$ (see the values of the relaxation times in Table 1). On the other hand, $\xi_m^{(c)}$ decays for $\tau\gg\tau_c$, which means that in the considered case τ_c (rather than τ_m) characterizes the decay of $\xi_m^{(c)}$ at the long times. In addition, we have $\xi_m^{(c)}<0$, but $\xi_\sigma^{(c)}>0$, which means that an initial increase in C_m engenders decrease in m, and increase in σ.

Thus, an initial perturbation in the micelle concentration, C_m, induces a relaxation of C_m with characteristic time τ_c, and considerable perturbations of m and σ. What concerns the perturbation in the monomer concentration, ξ_1, in accordance with Eq. (4.23) we have: $\xi_1=-(\beta/S)(\xi_c+\xi_m)$. To illustrate the relaxation of $\xi_1^{(c)}$, in Fig. 4c we have plotted $\xi_c^{(c)}+\xi_m^{(c)}$ vs. the dimensionless time, t, for two different values of β. At the higher micelle concentration, $\beta=100$, we observe a conventional relaxation curve, with two characteristic relaxation times: fast, τ_m, and slow, τ_c. In Fig. 4c, τ_m and τ_c correspond to the inflection points of the kinetic curves, and are denoted by arrows. For the considered numerical example, the values of τ_m, τ_c and τ_s can be found in Table 1.

The curve for $\beta=1$ in Fig. 4c deserves a special discussion. In this case, the two dimensionless fast relaxation times are close to each other: $\tau_m=18.7$ and $\tau_\sigma=12.1$; see Table 1. Hence, in this time interval (around $\tau\approx\tau_m\approx\tau_\sigma$), the dependence $\xi_1^{(c)}(\tau)$ must be fitted with a superposition of two exponents, those with $j=m$, s in Eq. (4.38), or with the full theory from Section 4.4. In contrast, if one fits $\xi_1^{(c)}(\tau)$ in the same time interval with a single exponent, one will obtain an apparent dimensionless fast relaxation time, τ^*, which is typically greater than τ_m and τ_σ. If the determined τ^* is (incorrectly!) identified with τ_m, one will find that the relaxation time of the fast process does not comply with Eq. (4.19) at the lower micelle concentrations, where the plot of the apparent $1/\tau_m$ vs. u will deviate from a straight line. Such deviations have been really observed; see Figs. 9 and 10 in [3]. The present model could give a possible explanation.

Finally, it should be noted that relaxation curves, like that with $\beta=1$ in Fig. 4c, can be theoretically described by the exact solution of the linear system in Section 4.4. The approximate expressions derived in Section 4.6 (for $\tau_m \ll \tau_\sigma \ll \tau_c$) are not applicable for low micelle concentrations, where τ_m and τ_s have the same order of magnitude.

4.6. Analytical expressions for the micellar evolution

Experimentally, either of the parameters C_m, m, and σ, or all of them, could be measured as functions of time. To interpret the obtained data one could apply the theory described in Section 4.4. However, it is possible to derive much simpler asymptotic expressions for the typical case of not-too-low micelle concentrations, when the three characteristic micellar times markedly differ from each other, viz. $\tau_c \gg \tau_\sigma \gg \tau_m$.

The latter relation is fulfilled for the numerical data with $\beta=100$ given in Table 1 and Figs. 2–4. In these figures, one sees that initial perturbations in m and σ cannot produce significant perturbations in C_m. In other words, the cross terms $\xi_c^{(m)}$ and $\xi_c^{(\sigma)}$ are small. The same is true for $\xi_m^{(\sigma)}$, see Fig. 2b.

Now, let us consider a general initial perturbation in C_m, m, and σ, with perturbation amplitudes A_c, A_m, and A_σ. Having in mind that $\xi_c^{(m)}$, $\xi_c^{(\sigma)} \ll 1$, from Eqs. (4.38)–(4.40) it follows:

$$\xi_c(t) \approx A_c \exp(-t/t_c) \quad (t_c \gg t_\sigma \gg t_m) \tag{4.46}$$

In other words, the relaxation of the micelle concentration, C_m, is determined solely by t_c. (As before, the relation between the dimensional time, t, and the dimensionless time, τ, is $\tau = k_m^- t$; see also Eq. (4.33)). Eq. (4.46) implies that the relaxation time of the slow process, t_c, can be directly determined from data for the relaxation of C_m.

On the other hand, as seen in Fig. 4, an initial perturbation in C_m induces also a significant long-time perturbation, $\xi_c^{(c)}$ in the micelle mean aggregation number, m, while the perturbation induced in σ, $\xi_\sigma^{(c)}$, decays much faster. Then, for $m_{eq} \gg 1$ the last term in Eq. (4.27) is negligible, and setting the left-hand side equal to zero (for the slow process) we obtain:

$$\xi_m^{(c)} \approx \frac{-\sigma_{eq}^2 \beta}{S m_{eq} + \sigma_{eq}^2 \beta} \xi_c \approx -\frac{\tau_m \beta}{S m_{eq}} \xi_c \tag{4.47}$$

see Eq. (4.45) for τ_m. Then, from Eqs. (4.38–4.40) (4.46) and (4.47), we obtain:

$$\xi_m(t) \approx -A_c \frac{\tau_m \beta}{S m_{eq}} \exp(-t/t_c) + \left(A_m + A_c \frac{\tau_m \beta}{S m_{eq}}\right) \exp(-t/t_m) \tag{4.48}$$

$(t_c \gg t_\sigma \gg t_m)$. Note that the initial condition, $\xi_m(0)=A_m$ is fulfilled. Eq. (4.48) implies that the relaxation of the micelle mean mass aggregation number, m, after a general initial perturbation, involves two relaxation processes, characterized by relaxation times t_c and t_m. Despite the fact that σ is also perturbed, $\exp(-t/t_\sigma)$ does not enter Eq. (4.48).

The variation of m, ξ_m, induces a variation $\xi_\sigma^{(m)}$ in σ. In view of Eqs. (3.6) and (4.4), for uniform perturbations we have:

$$2\sigma_{eq}^2 C_{m,eq} \frac{\partial \xi_\sigma}{\partial t} = \left[(n_r - m_{eq})^2 - \sigma_{eq}^2\right] J - (2m_{eq}+1) J_{m,0} + 2J_{m,1} \tag{4.49}$$

For $t_c \gg t_m \gg t_\sigma$, the term with J in the latter equation is negligible. Furthermore, in Eqs. (4.27) and (4.28) the terms with ξ_c are annihilated by the first term of ξ_m in Eq. (4.48), but the last term in ξ_m remains. Thus, Eq. (4.49) is reduced to a first order inhomogeneous differential equation for ξ_σ, whose solution gives the effect, $\Delta\xi_\sigma$, of the perturbations in C_m and m on ξ_σ:

$$\Delta\xi_\sigma = \left(A_m + A_c \frac{\tau_m \beta}{S m_{eq}}\right) \frac{m_{eq} t_\sigma}{2(t_m - t_\sigma)\sigma_{eq}^2} \exp(-t/t_m) \tag{4.50}$$

Finally, from Eqs. (4.38–4.40), we obtain:

$$\xi_\sigma(t) \approx A_\sigma \exp(-t/t_\sigma) + \left(A_m + A_c \frac{\tau_m \beta}{S m_{eq}}\right) \times \frac{m_{eq}}{2\sigma_{eq}^2} \frac{t_\sigma}{t_m - t_\sigma} [\exp(-t/t_m) - \exp(-t/t_\sigma)] \tag{4.51}$$

$(t_c \gg t_\sigma \gg t_m)$. Note that the initial condition, $\xi_\sigma(0)=A_\sigma$ is satisfied. One sees that the relaxation of the width of the micelle peak, described by $\xi_\sigma(t)$, is determined by the two characteristic relaxation times of the fast process, t_m and t_σ. Despite the fact that C_m is also perturbed, $\exp(-t/t_c)$ does not enter Eq. (4.51). The presence of the three perturbation amplitudes, A_c, A_m, and A_σ, in Eq. (4.51) implies that initial perturbations in either C_m, m, or σ, can produce a variation of σ. This result is also in agreement with Figs. 2 3 and 4. The developed theoretical model predicts that, in general, the relaxation of the micelle polydispersity, σ, will exhibit two characteristic relaxation times, t_m and t_σ, which could be determined by fitting the experimental dependence. $\xi_\sigma(t)$ with the help of Eq. (4.51). Further, from either t_m or t_σ one can calculate the demicellization rate constant, k_m^-, see Eqs. (4.19) and (4.20). The coincidence of the values of k_m^- obtained from t_m and t_σ could be a criterion for the adequacy of the proposed model.

It is important to note that Eqs. (4.46) (4.48) (4.51), along with the initial condition, Eqs. (4.35)–(4.37), reproduce perfectly the exact curves for $\xi_\sigma^{(\sigma)}$, $\xi_m^{(m)}$, $\xi_\sigma^{(m)}$, $\xi_c^{(c)}$, $\xi_m^{(c)}$, and $\xi_\sigma^{(c)}$ in Figs. 2-4 for $\beta=100$. The negligible cross terms ($\xi_c^{(\sigma)}, \xi_m^{(\sigma)}, \xi_c^{(m)} \ll 1$), which are shown multiplied by 1000 in Figs. 2 and 3, cannot be reproduced by the above approximate equations. In addition, as mentioned at the end of Section 4.5, at low micelle concentrations we have $t_\sigma \approx t_m$, and one of the presumptions used to derive Eqs. (4.46) (4.48) (4.51) is violated. In the latter case, one should use the exact solution of the linear system in Section 4.4 to calculate $\xi_c(t)$, $\xi_m(t)$ and $\xi_\sigma(t)$.

Having determined $\xi_c(t)$ and $\xi_m(t)$, one could easily calculate the perturbation in the monomer concentration, $1 = -(\beta/S)(\xi_c + \xi_m)$, see Eq. (4.23).

4.7. Discussion on the limitations of the present theoretical model

The basic assumption of the model by Aniansson and Wall [2], is the stepwise kinetic scheme of micelle association and dissociation, Eq. (2.1), which is used also in the present paper. Deviations from this kinetic scheme could happen for long cylindrical (rodlike, wormlike) micelles, which could split to smaller aggregates, of aggregation number greater than $s=1$; see e.g., [44]. Hence, Eq. (2.1) can be used for not-too-large micelles (spherical and elongated), for which such splitting is not observed.

Another assumption in [2], which is used here, is the approximation of the micellar peak with a Gaussian curve; see Eq. (2.11) and Fig. 1. In fact, every peak could be approximated with a Gaussian curve, unless it is markedly asymmetric. Such asymmetric distribution is typical for the giant cylindrical micelles [45,46], which are out of the scope of the present study, as discussed above. In principle, asymmetry in the micellar peak could appear also upon large deviations from equilibrium. However, the agreement of the theory by Aniansson and Wall [2] with the experiment [3,47] indicates that the micellar peak is sufficiently symmetric and can be adequately described by a Gaussian curve for a wide class of dynamic processes.

5. Summary and conclusions

The model proposed here represents a generalization of previous models in the following three aspects. First, we do not use the simplifying assumption that the width of the micellar peak is constant during the transport process. Second, we avoid the use of the quasi-equilibrium approximation, which presumes that the micelles are in local chemical equilibrium with the monomers. Third, we reduced the initial set, containing tens of equations, to a system containing only four *nonlinear* differential equations, Eqs. (2.15–2.17).

The solution of the latter system gives the following parameters: (i) the concentration of surfactant monomers, $c_1(\mathbf{r},t)$; (ii) the total number concentration of surfactant micelles, $C_{\mathrm{m}}(\mathbf{r},t)$; (iii) the micelle mean aggregation number, $m(\mathbf{r},t)$, and (iv) the halfwidth of the micellar peak, $\sigma(\mathbf{r},t)$. The general set of four equations could be applied to solve various problems, like the relaxation problem in the case of a spatially uniform perturbation (due to jumps in pressure temperature or concentration), or the problem about the kinetics of adsorption from micellar solutions, and the respective dynamic surface tension.

To derive the basic system of four differential equations (Section 2) we imposed the natural requirement that the model Gaussian curve (describing the micellar size distribution) must be equivalent to the real micellar peak with respect to the total micelle concentration, mean micelle aggregation number, and micelle polydispersity, i.e., with respect to the position, height and width of the micellar peak (Fig. 1). In the case of small deviations from equilibrium, all equations can be linearized. The respective linear system, Eqs. (3.3)–(3.6), is derived in Section 3.

In Section 4 we apply the derived system of equations to describe the relaxation of small uniform bulk perturbations. The theoretical analysis implies that the relaxation of the three basic parameters, the micelle concentration, C_{m}, the mean aggregation number, m, and the polydispersity, σ, are characterized by three distinct relaxation times: t_c, t_m, and t_σ, see Eqs. (4.10), (4.19) and (4.20). The first two of them, t_c and t_m, coincide with the conventional slow and fast micellar relaxation times [2,42]. The third relaxation time, t_σ, is close to t_m for low micelle concentrations, but at high micelle concentrations we have $t_c > t_\sigma > t_m$. The interplay of the three relaxation processes is illustrated in Figs. 2–4. Asymptotic analytical expressions, viz. Eqs. (4.46) (4.48) (4.51), are derived for the typical case $t_c \gg t_\sigma \gg t_m$. These asymptotic equations indicate that the relaxation of C_{m} is affected by t_c alone; the relaxation of m is affected by both t_c and t_m, while the relaxation of m is affected by t_σ and t_m. This result is in agreement with previous experimental studies, which are based on measurements of c_1, C_{m} and m, and establish the existence of two relaxation times: t_c and t_m. In addition, the developed model (Section 4.4) describes also the case of low micelle concentrations ($\beta \approx 1$), where t_σ and t_m have the same order of magnitude, and where the third relaxation time, t_σ, should be taken into account when interpreting experimental data; see Fig. 4c and the related text.

Our analysis indicates that if the relaxation time of micelle polydispersity, t_σ , is measured, one could independently determine the demicellization rate constant, k_{m}^{-}, by using Eq. (4.20). Moreover, it turns out that the existence of a third relaxation time, t_σ, has an essential impact on the kinetics of adsorption from micellar solutions. Qualitatively, this is understandable, because the broadening or narrowing of the micellar peak must be accompanied by uptake or release of surfactant monomers. The respective quantitative analysis of the adsorption dynamics demands additional theoretical work, which is reported in the second part of this study [40].

Finally, it is worthwhile noting that simple, but accurate analytical expressions are available for calculation of the three relaxation times, Eqs. (4.42)–(4.45); see Table 1, and for describing the evolution of a micellar system: Eqs. (4.46) (4.48) (4.51); see Figs. 2–4.

Acknowledgement

This work was supported by Unilever Research and Development, Trumbull, CT.

Appendix A. Derivation of some equations in Section 2

Using the Gaussian distribution, Eq. (2.11), and replacing the sum with integral, we derive:

$$\sum_{s=n_{\mathrm{r}}}^{\infty} c_s = \frac{C_{\mathrm{m}}}{\sqrt{2\pi}\sigma} \sum_{s=n_{\mathrm{r}}}^{\infty} \exp\left[-\frac{(s-m)^2}{2\sigma^2}\right] \approx \frac{C_{\mathrm{m}}}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} \exp\left(-\frac{s^2}{2\sigma^2}\right) \times \mathrm{d}s = C_{\mathrm{m}} \tag{A.1}$$

Likewise, we obtain Eq. (2.13):

$$\sum_{s=n_r}^{\infty} sc_s = \frac{C_m}{\sqrt{2\pi}\sigma}\sum_{s=n_r}^{\infty}(s-m)\exp\left[-\frac{(s-m)^2}{2\sigma^2}\right] + \frac{mC_m}{\sqrt{2\pi}\sigma}\sum_{s=n_r}^{\infty}\exp\left[-\frac{(s-m)^2}{2\sigma^2}\right] \approx mC_m \tag{A.2}$$

To derive Eq. (2.14), we are using the substitution $y=s-m$:

$$\sum_{s=n_r}^{\infty} s^2c_s \approx \frac{C_m}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty}(y+m)^2\exp\left(-\frac{y^2}{2\sigma^2}\right)dy = \frac{C_m}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty}y^2\exp\left(-\frac{y^2}{2\sigma^2}\right)dy + m^2C_m = \left(\sigma^2+m^2\right)C_m \tag{A.3}$$

Using the assumption for equal dissociation rates, $k_s^- = k_m^-$ for $s \geq n_r$, from Eqs. (2.7) (2.8) (2.12) (2.19), we obtain:

$$J_{m,0} = \sum_{s>n_r}\left(k_s^+c_1c_{s-1} - k_m^-c_s\right) = k_m^-\sum_{s>n_r}\left(\frac{c_{s,eq}}{c_{1,eq}c_{s-1,eq}}c_1c_{s-1} - c_s\right) \approx k_m^-\left(\frac{c_1}{c_{1,eq}}\sum_{s>n_r}\frac{c_{s,eq}}{c_{s-1,eq}}c_{s-1} - C_m\right) \tag{A.4}$$

Further, the three concentrations appearing under the sign of the latter sum are substituted from Eq. (2.11):

$$\sum_{s>n_r}\frac{c_{s,eq}}{c_{s-1,eq}}c_{s-1} = \frac{C_m}{\sqrt{2\pi}\sigma}\sum_{s>n_r}\exp\left[-\frac{\left(s-m_{eq}\right)^2}{2\sigma_{eq}^2} + \frac{\left(s-1-m_{eq}\right)^2}{2\sigma_{eq}^2} - \frac{(s-1-m)^2}{2\sigma^2}\right] \tag{A.5}$$

Next, we substitute $n=s-1-m$, and bring the latter sum into the form:

$$\frac{C_m}{\sqrt{2\pi}\sigma}\exp\left(\frac{\sigma^2-\sigma_{eq}^2}{2\sigma_{eq}^4} - \frac{m-m_{eq}}{\sigma_{eq}^2}\right) \times \sum_{n=-\infty}^{\infty}\exp\left[-\frac{1}{2\sigma^2}\left(n+\frac{\sigma^2}{\sigma_{eq}^2}\right)^2\right] \approx C_m\exp\left(\frac{\sigma^2-\sigma_{eq}^2}{2\sigma_{eq}^4} - \frac{m-m_{eq}}{\sigma_{eq}^2}\right) \tag{A.6}$$

Substituting the latter result into Eq. (A.4), we obtain Eq. (2.20). In analogy with Eq. (A.4), using Eqs. (2.7) (2.8) (2.13) (2.19), we derive:

$$J_{m,1} = \sum_{s>n_r}s\left(k_s^+c_1c_{s-1} - k_m^-c_s\right) \approx k_m^-\left(\frac{c_1}{c_{1,eq}}\sum_{s>n_r}^{\infty}s\frac{c_{s,eq}}{c_{s-1,eq}}c_{s-1} - mC_m\right) \tag{A.7}$$

Again, the three concentrations appearing under the sign of the latter sum are substituted from Eq. (2.11), and $n=s-1-m$ is introduced. Thus, we obtain a counterpart of Eq. (A.6):

$$\sum_{s>n_r}^{\infty}s\frac{c_{s,eq}}{c_{s-1,eq}}c_{s-1} \approx \frac{C_m}{\sqrt{2\pi}\sigma}\exp\left(\frac{\sigma^2-\sigma_{eq}^2}{2\sigma_{eq}^4} - \frac{m-m_{eq}}{\sigma_{eq}^2}\right)\sum_{n=-\infty}^{\infty}(n+m+1) \times \exp\left[-\frac{1}{2\sigma^2}\left(n+\frac{\sigma^2}{\sigma_{eq}^2}\right)^2\right] \approx C_m\left(m-\frac{\sigma^2-\sigma_{eq}^2}{\sigma_{eq}^2}\right) \times \exp\left(\frac{\sigma^2-\sigma_{eq}^2}{2\sigma_{eq}^4} - \frac{m-m_{eq}}{\sigma_{eq}^2}\right) \tag{A.8}$$

Substituting the latter result into Eq. (A.7), we arrive at Eq. (2.21). To derive Eq. (2.28), we will use a proof by mathematical induction. For $s=2$, Eq. (2.28) reduces to:

$$\frac{c_2}{c_{2,eq}} = \frac{c_1^2}{c_{1,eq}^2} - \frac{J}{k_2^-c_{2,eq}} \tag{A.9}$$

which is equivalent to

$$J = k_2^-c_{2,eq}\frac{c_1^2}{c_{1,eq}^2} - k_2^-c_2 = k_2^+c_1^2 - k_2^-c_2 \tag{A.10}$$

At the last step we applied Eq. (2.8). In view of Eq. (2.7), Eq. (A.10) is satisfied, because it is a special case of Eq. (2.7) for $s=2$. Next, assuming that Eq. (2.28) is valid for $s=2, 3, \ldots, n-1$, our aim is to prove that Eq. (2.28) is valid also for $s=n$ ($n \leq n_r$). From Eqs. (2.7) (2.8) (2.27), for $s=n$, we obtain:

$$\frac{c_n}{c_{n,eq}} = \frac{k_n^+c_1c_{n-1}}{k_n^-c_{n,eq}} - \frac{J}{k_n^-c_{n,eq}} = \frac{c_1c_{n-1}}{c_{1,eq}c_{n-1,eq}} - \frac{J}{k_n^-c_{n,eq}} \tag{A.11}$$

In the latter equation, we substitute $c_{n-1}/c_{n-1,eq}$ from Eq. (2.28) for $s=n-1$. As a result, we obtain:

$$\frac{c_n}{c_{n,eq}} = \frac{c_1^n}{c_{1,eq}^n} - J\frac{c_1}{c_{1,eq}}\sum_{i=0}^{n-3}\frac{c_1^i}{c_{1,eq}^i}\frac{1}{k_{n-1-i}^-c_{n-1-i,eq}} - \frac{J}{k_n^-c_{n,eq}} = \frac{c_1^n}{c_{1,eq}^n} - J\sum_{j=1}^{n-2}\frac{c_1^j}{c_{1,eq}^j}\frac{1}{k_{n-j}^-c_{n-j,eq}} - \frac{J}{k_n^-c_{n,eq}} = \frac{c_1^n}{c_{1,eq}^n} - J\sum_{j=0}^{n-2}\frac{c_1^j}{c_{1,eq}^j}\frac{1}{k_{n-j}^-c_{n-j,eq}} \tag{A.12}$$

where we have substituted $j=i+1$. Hence, Eq. (2.28) is valid for all values of s, for which Eq. (2.27) holds, i.e., for $2 \leq s \leq n_r$.

Appendix B. Derivation of some equations in Section 3

Using Eq. (3.1), we obtain the linearized version of Eq. (2.16) in the form:

$$C_{m,eq}\frac{dm_p}{dt} + m_{eq}\frac{dC_{m,p}}{dt} + \nabla\cdot\mathbf{I}_{m,1} = n_rJ + J_{m,0} \tag{B.1}$$

Next, we multiply Eq. (3.4) by m_{eq} and subtract the result from Eq. (B.1). Thus we obtain Eq. (3.5). Furthermore, substituting Eq. (3.1) into Eq. (2.17), and expanding in series for small perturbations, we get:

$$\left(m_{eq}^2+\sigma_{eq}^2\right)\frac{dC_{m,p}}{dt}+2m_{eq}C_{m,eq}\frac{dm_p}{dt}+2\sigma_{eq}C_{m,eq}\frac{d\sigma_p}{dt}+\nabla\cdot\mathbf{I}_{m,1}=n_r^2J-J_{m,0}+2J_{m,1} \quad (B.2)$$

To eliminate the perturbations $C_{m,p}$ and m_p, we multiply Eq. (3.4) by $m_{eq}^2+\sigma_{eq}^2$ and Eq. (3.5) by $2m_{eq}$, and subtract the results from Eq. (B.2). In this way we derive Eq. (3.6).

Setting $s=n_r$ into Eq. (2.11), we obtain:

$$c_{n_r,eq}=\frac{C_{m,eq}}{\sqrt{2\pi}\sigma_{eq}}\exp\left[-\frac{\left(n_r-m_{eq}\right)^2}{2\sigma_{eq}^2}\right] \quad (B.3)$$

A substitution of Eq. (B.3) into the right-hand side of Eq. (2.32), after some transformations, yields:

$$\frac{C_m\sigma_{eq}}{\sigma C_{m,eq}}\exp\left[\frac{\left(n_r-m_{eq}\right)^2}{2\sigma_{eq}^2}-\frac{\left(n_r-m\right)^2}{2\sigma^2}\right]\approx 1+\frac{n_rc_{1,p}}{c_{1,eq}}-RJ \quad (B.4)$$

where we have introduced the notation:

$$R\equiv\sum_{i=0}^{n_r-2}\frac{1}{k_{n_r-i}^-c_{n_r-i,eq}}=\sum_{j=2}^{n_r}\frac{1}{k_j^-c_{j,eq}} \quad (B.5)$$

At the last step, we made the replacement $j=n_r-i$. We recall that J represents a perturbation, and for this reason the equilibrium value of the sum in Eq. (2.32) has been taken. Finally, in Eq. (B.4) we expand in series for $m\to m_{eq}$ and $\sigma\to\sigma_{eq}$. As a result, we obtain Eq. (3.9).

Appendix C. Matrix elements in Section 4

The relaxation of a uniform perturbation of a micellar solution is described by the linear system of Eq. (4.29). All elements of the matrix a_{ij} can be expressed in terms of the system parameters given in Eq. (4.32). It is convenient to introduce the following auxiliary parameters:

$$y\equiv m_{eq}\frac{\theta}{\beta};z\equiv\frac{m_{eq}}{\sigma_{eq}};Q\equiv\left(m_{eq}-w\sigma_{eq}\right)\frac{\beta}{S};\tau_m\equiv\frac{Sm_{eq}\sigma_{eq}^2}{Sm_{eq}+\sigma_{eq}^2\beta} \quad (C.1)$$

In fact, τ_m represents the dimensionless relaxation time of the micelle mean aggregation number, m; see Eq. (4.45). Then, the matrix elements are expressed as follows:

$$a_{cc}=-(Q+1)y;a_{cm}=(wz-Q)y \quad (C.2)$$

$$a_{c\sigma}=-\left(w^2-1\right)y;a_{mc}=-\frac{w}{z}a_{cc}-\frac{\beta}{Sm_{eq}} \quad (C.3)$$

$$a_{mm}=-\frac{w}{z}a_{cm}-\frac{1}{\tau_m} \quad (C.4)$$

$$a_{m\sigma}=-\frac{w}{z}a_{c\sigma}+\frac{1}{\sigma_{eq}^2m_{eq}} \quad (C.5)$$

$$a_{\sigma c}=\frac{a_{c\sigma}}{2}(Q+1)+\frac{\beta}{2\sigma_{eq}^2S} \quad (C.6)$$

$$a_{\sigma m}=\frac{a_{cm}}{2}\left(w^2-1\right)+\frac{z}{2\sigma_{eq}\tau_m} \quad (C.7)$$

$$a_{\sigma\sigma}=-\frac{y}{2}\left(w^2-1\right)^2-\frac{1+4\sigma_{eq}^2}{2\sigma_{eq}^4} \quad (C.8)$$

To determine the three dimensionless characteristic relaxation times, one should substitute Eqs. (C.2) (C.3) (C.4) (C.5) (C.6) (C.7) (C.8) into Eq. (4.31), and then to solve the cubic equation, Eq. (4.30).

Alternatively, because this is a standard problem for determining the eigenvalues, λ_c, λ_m, and λ_σ, and eigenvectors, $\mathbf{f}^{(c)}$, $\mathbf{f}^{(m)}$, and $\mathbf{f}^{(\sigma)}$, of the matrix a_{ij}, one could use some available program package. For example, the program "Mathematica 5.0" provides a module "Eigensystem" for the calculation of the eigenvalues and the components of the eigenvectors, $f_i^{(j)}$. Another module, 'LinearSolve", could be applied to calculate the coefficients $X_i^{(k)}$, which appear in Eq. (4.38). This, in principle, solves the problem.

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