Micellar surfactant solutions: Dynamics of adsorption at fluid interfaces subjected to stationary expansion

Krassimir D. Danov\textsuperscript{a}, Peter A. Kralchevsky\textsuperscript{a,∗}, Kavssery P. Ananthapadmanabhan\textsuperscript{b}, Alex Lips\textsuperscript{b}

\textsuperscript{a} Laboratory of Chemical Physics and Engineering, Faculty of Chemistry, University of Sofia, 1164 Sofia, Bulgaria
\textsuperscript{b} Unilever Research & Development, Trumbull, CT 06611, USA

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Dedicated to Professor Ivan B. Ivanov (LCPE, University of Sofia) on the occasion of his 70th birthday.

Abstract

Here, we consider a micellar surfactant solution whose surface is subjected to stationary expansion. The adsorption at the fluid interface gives rise to diffusion of surfactant monomers and micelles, and to release of monomers by the micelles. To describe this process, we applied a recently derived general system of four ordinary differential equations, which are linearized for the case of small perturbations. The numerical solution of the problem reveals the existence of four distinct kinetic regimes. At the greatest expansion rates, the surfactant adsorption is affected by the fast micellar process (regime AB). At lower expansion rates, the fast process equilibrates and the adsorption occurs under diffusion control (regime BC). With the further decrease of the expansion rate, the surfactant adsorption is affected by the slow micellar process (regime CD). Finally, at the lowest expansion rates, both the fast and slow micellar processes are equilibrated, and the adsorption again occurs under diffusion control (regime DE). For each separate kinetic regime, convenient analytical expressions for the dynamic surface tension and adsorption are derived. At low micelle concentrations, “rudimentary” kinetic diagrams are observed, which are characterized by merging or disappearance of the regimes BC and CD. Usually, only one of the kinetic regimes is experimentally detected. The developed theoretical model enables one to identify which of the four regimes is observed in a given experiment, and to interpret properly the obtained data. We applied the model to process available data for the nonionic surfactant Brij 58, and for two cationic surfactants, C\textsubscript{14}TAB and C\textsubscript{16}TAB. Good agreement between theory and experiment is achieved.

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1. Introduction

The diffusion and convective transport of monomers and aggregates in surfactant solutions 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.\cite{1}, and Aniansson and Wall\cite{2}. The existence of “fast” and “slow” processes of the micellar dynamics has been established. The experimental techniques for investigation of the surfactant self-assembly have been reviewed in a recent book\cite{3}. Detailed reviews on micellar kinetics and dynamic surface tension have been published by Noskov and Grigoriev\cite{4}, and Noskov\cite{5}.

The first theoretical model of surfactant adsorption from micellar solutions was proposed by Lucassen\cite{6} in relation to the analysis of tensiometric data from experimental methods with oscillating surface area\cite{7}. 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 \(n\) (the micelle aggregation number). This nonlinear problem was linearized for the case of small perturbations, and the assumption for local quasi-equilibrium between micelles and monomers was employed\cite{6,8–10}. The nonlinear problem was solved numerically by Miller\cite{11} and analytically by Breward and Howell\cite{12}, again using the assumption for monodisperse micelles. An alternative
approach to the nonlinear problem, based on the von Karman’s method, was proposed in [13]. More realistic models for the diffusion in micellar solutions, which account for the polydispersity of the micelles and the multi-step character of the micellar process, were developed independently by Noskov [14], Johner and Joanny [15], and Dushkin et al. [16,17].

In the model [6], the assumption for a complete local dynamic equilibrium between monomers and micelles makes possible to use the equilibrium mass-action law for the micellization reaction. In such a case, the surfactant transfer corresponds to a conventional diffusion-limited adsorption characterized by an apparent diffusion coefficient, $D_A$, which depends on the micelle diffusivity, concentration and aggregation number [8,9]. $D_A$ is independent of the rate constants of the fast and slow micellar processes: $k_{B}$ and $k_{S}$. Correspondingly, if the quasi-equilibrium model [6] is applicable to a given experimental situation, then $k_{B}$ and $k_{S}$ cannot be determined from the obtained data for the dynamic surface tension or adsorption.

Later, Joos et al. [8–10,18] confirmed experimentally that in some cases the adsorption from micellar solutions can be actually described as a diffusion-limited process characterized by an apparent diffusivity, $D_A$, but the experimental data were not in agreement with the expression for $D_A$ from [6]. An alternative semiempirical expression for $D_A$ was proposed [8,9], which agrees well with the experiment, but lacks a theoretical basis. In subsequent studies, Joos et al. [10,19] established that sometimes the dynamics of adsorption from micellar solutions exhibits a completely different kinetic pattern: the interfacial relaxation is exponential, rather than inverse-square-root, as it is for the diffusion-limited kinetics. The theoretical developments [10,19,20] revealed that the exponential relaxation is influenced by the kinetics of the micellization processes, and from its analysis one could determine the rate constant of the fast process, $k_{B}$. The observation of different kinetic regimes for different surfactants and/or methods makes the physical picture rather complicated.

Recently, we proposed a theoretical model, which generalizes previous models of micellization kinetics in several aspects [21,22]. We avoided the use of the quasi-equilibrium approximation (local chemical equilibrium between micelles and monomers). The theoretical problem was reduced to a system of four nonlinear differential equations. Its solution gives the concentration of surfactant monomers, the total micelle concentration, the mean aggregation number, and the micelle polydispersity as functions of the spatial coordinates and time.

In a subsequent study [22], we applied the theoretical model from reference [21] to the case of surfactant adsorption at a quiescent interface, i.e. to the relaxation of surface tension and adsorption after a small initial perturbation. Computer modeling of the adsorption process was carried out. This analysis revealed the existence of four different relaxation regimes (stages) for a given micellar solution: Regime AB: adsorption influenced by the fast micellar process; Regime CD: diffusion-limited adsorption at equilibrated fast micellar process, but negligible slow micellar process; Regime DE: adsorption influenced by the slow micellar process; and Regime DE: diffusion-limited adsorption at equilibrated both the fast and slow micellar processes [22].

Experimentally, depending on the specific surfactant and method, one usually registers only one of the above regimes. Therefore, to interpret properly the data, one has to identify which of the four kinetic regimes is observed in the respective experiment. In particular, it was established [22] that the exponential relaxation of the surface tension, detected and investigated in references [19,20], corresponds to the regime AB.

The diffusion-limited adsorption observed in the experiments by Joos et al. [8,9], is consistent with the regime BC. On the other hand, the diffusion-limited adsorption in the study by Lucassen [6], corresponds to the regime DE.

In general, the form of the theoretical expressions, and the shape of the kinetic diagrams depend on the type of the interfacial dynamics used in a given experimental method. In this respect, at least four groups of experimental methods could be identified: (i) initial interfacial perturbation: the fast formed drop method [22,24] and the inclined plate method [10,19,25]; (ii) stationary expansion: the strip method [10,26], the overflowing cylinder (OFC) [27–31], and the Langmuir trough at constant expansion rate [10]; (iii) non-stationary expansion: the dynamic drop volume method [8,18], the maximum-bubble-pressure method [32–35], and the expanding-drop method [36,37]; and (iv) methods with oscillating surface area [6,7,38–41].

In [22] we considered the theoretical description in relation to the first group of experimental methods, those with adsorption at a quiescent interface, after an initial perturbation. Here, our aim is to apply the general theory from reference [21] to analyze the second group of methods, viz. the methods with stationary expansion of a fluid interface [10,26–31]. The paper is organized as follows.

In Section 2 we give a brief overview of the basic dynamic equations for surfactant concentrations below the critical micellization concentration (CMC) for the case of stationary interfacial expansion. In Section 3, we formulate the basic equations for micellar solutions, and their special form in the case of stationary expansion. The theory is simpler in terms of the total (integral) perturbations, which are considered in Section 4. Numerical results are presented in the form of kinetic diagrams. The four kinetic regimes, AB, BC, CD, and DE, are identified and discussed. Next, in Section 5, analytical expressions describing the dependence of adsorption on the interfacial expansion rate are derived for each of the four regimes. Section 6 is devoted to the “rudimentary” kinetic diagrams, which are observed at low micelle concentrations. Finally, in Section 7 we apply the theoretical model to fit three sets of available experimental data for dynamic surface tension and adsorption obtained by means of the strip and OFC methods. It is interesting to note that the experimental data complies with the regime BC for the considered experiments.

2. Concentrations below the CMC: basic equations

When a fluid interface is subjected to uniform expansion and/or compression, the interfacial area becomes a function of time, $A(t)$. The rate of surface dilatation, $\dot{A}(t)$, and the surface...
dilatation, \( \dot{\alpha}(t) \), are defined as follows, see e.g. [10,42]:

\[
\dot{\alpha}(t) \equiv \frac{1}{A} \frac{dA}{dt} = \frac{d\alpha(t)}{dt}, \quad \alpha(t) = \int_0^t \dot{\alpha}(t) \frac{dt}{A(0)}
\]

(2.1)

Under stationary interfacial dilatation (or compression), we have \( \dot{\alpha} = \text{const.} \). In this case, the interfacial dilatation induces surfactant diffusion and adsorption, which are described by the equations [9,10]:

\[
\frac{a}{\Gamma} \frac{d\gamma}{dt} = D_1 \frac{\partial^2 \gamma}{\partial z^2} \quad (2.2)
\]

\[
\frac{\partial c}{\partial z} = D_0 \frac{\partial^2 c}{\partial z^2} \quad (2.3)
\]

Here and hereafter, the subscripts “eq” and “p” denote equilibrium value and perturbation of the respective parameter of the system. Thus, \( c_{1,p} = c_1(z, t) - c_{1,eq} \) is the perturbation in the concentration of the surfactant monomers, \( c_1 \); as usual, \( t \) is time, and \( z \) is coordinate normal to the interface; the latter is located at \( z = 0 \). \( \Gamma \) and \( D_1 \) denote surfactant adsorption and diffusivity. Because we are dealing with a stationary process, the derivatives \( \partial c_1 / \partial t \) and \( \partial^2 \gamma / \partial t^2 \) in Eqs. (2.2) and (2.3) are missing. In addition, the convective term in Eq. (2.2) is expressed by using the approximation of van Voorst Vader et al. [43].

\[
\frac{\partial c}{\partial t} = \nu \left( \frac{\partial^2 c}{\partial z^2} \right) c \quad (2.5)
\]

Here, one of the two neighboring fluid phases is assumed to be a micellar surfactant solution. As known [2–5], the micelle size distribution exhibits three different regions (Fig. 1): (i) region of the monomers and oligomers, \( \Omega_{m} \) \((1 < n < n_{0})\); (ii) region of the rare aggregates, \( \Omega_{r} \) \((n_{0} < n < n_{s})\); and (iii) region of the abundant (typical) micelles, \( \Omega_{m} \) \((n > n_{s})\). In the region \( \Omega_{m} \), the aggregate concentration is assumed to be relatively small (Fig. 1).

The dilatation of the fluid interface gives rise to surfactant adsorption and diffusion. Both surfactant monomers and...
aggregates take part in the diffusion. The aggregates (micelles) exchange monomers between each other and with the surrounding solution (Fig. 2). This complex process can be adequately described by four functions of \( z \) and \( t \) [21]. These are the concentration of surfactant monomers, \( c_1(z,t) \), and the three parameters of the micelle distribution, \( \bar{C}_{CMC}(z,t) \), \( m(z,t) \), and \( \sigma(z,t) \), see Fig. 1. A full system of nonlinear differential equations for determining the latter four functions has been derived in [21]. For small deviations from equilibrium (small perturbations), this system of equations, expressed in terms of the perturbations, can be linearized; see Eqs. (2.4), (2.22)–(2.23) and (3.3)–(3.6) in [21]:

\[
\frac{\partial \Delta c_1}{\partial t} - \alpha_z \frac{\partial \Delta c_1}{\partial z} = D_1 \frac{\partial^2 \Delta c_1}{\partial z^2} - (m_{eq} - w_{eq}) \Delta J - \Delta J_{0} \tag{3.2}
\]

\[
\frac{\partial \Delta C_{CMC}}{\partial t} - \frac{\partial \Delta C_{CMC}}{\partial z} = D_m \frac{\partial^2 \Delta C_{CMC}}{\partial z^2} + J \tag{3.3}
\]

\[
\frac{\partial \Delta m}{\partial t} - \frac{\partial \Delta m}{\partial z} = D_m \frac{\partial^2 \Delta m}{\partial z^2} - \frac{w_{eq} \Delta m_{eq} \alpha_z J + m_{eq}}{\beta_{eq} \beta_{eq}} \Delta J_{0} \tag{3.4}
\]

\[
\frac{\partial \Delta \sigma}{\partial t} - \frac{\partial \Delta \sigma}{\partial z} = D_m \frac{\partial^2 \Delta \sigma}{\partial z^2} + \frac{(w^2 - 1) \sigma_{eq} \alpha_z \beta_{eq} \beta_{eq} \Delta J_{0}}{2 \beta_{eq} \beta_{eq}} \tag{3.5}
\]

Here we use the same notations as in reference [21]: we have set \( S = 1 \), see Eqs. (3.2) and (3.3) in [21], because the concentration of the surfactant monomers is much greater than that of the oligomers. As before, the subscripts “eq” and “\( \alpha \)” mark the equilibrium values and the perturbations of the respective variables; see the comments after Eq. (2.3). \( D_m \) is the diffusion coefficient of the micelles; \( J_{0} \), and \( J \) are reaction fluxes due, respectively, to the fast and slow micellar processes [21]:

\[
J_{0} = k_\alpha C_{CMC} \left( \frac{c_1}{c_1_{eq}} + \frac{c_2 - c_2_{eq}}{c_2_{eq}} \right) \tag{3.6}
\]

\[
J = \frac{(c_{tot} - C_{CMC})}{C_{CMC}} \left( \frac{m_{eq} C_{CMC}}{c_1_{eq}} - \frac{m_{eq} C_{CMC}}{\beta_{eq}} \right) \frac{w_{eq}}{\sigma_{eq}} \tag{3.7}
\]

Here, \( k_\alpha \) is the rate constant of monomer dissociation from the micelles; \( k_\alpha \) is the rate constant of the slow micelle relaxation process, see Eq. (4.26) in [21]. The parameter \( \beta \) in Eqs. (3.4)–(3.7) is the equilibrium concentration of surfactant in micellar form, scaled by the critical micellization concentration, CMC:

\[
\beta \equiv \left( \frac{C_{tot} - C_{CMC}}{C_{CMC}} \right) \tag{3.8}
\]

\( C_{tot} \) is the total surfactant concentration and the monomeric concentration is \( c_1_{eq} = \text{CMC} \). Another equilibrium dimensionless parameter is

\[
w \equiv \frac{(m_{eq} - n_1)}{\sigma_{eq}} > 1 \tag{3.9}
\]

where \( n_1 \) is aggregation number at the boundary between the regions of the rare aggregates and the abundant micelles at equilibrium (Fig. 1); \( \sigma_{eq} \) is the polydispersity of the equilibrium micelle size distribution. The convective terms in Eqs. (3.2)–(3.5), those containing \( \alpha_z \), are obtained by using the approximation of van Voorst Vader et al. [43], see Section 2.

In view of Eqs. (3.6) and (3.7), Eqs. (3.2)–(3.5) form a system of four linear differential equations for determining the evolution of the perturbations in the four basic parameters of the micellar system: \( c_1(z,t) \), \( C_{tot}(z,t) \), \( m(z,t) \), and \( \sigma(z,t) \) to solve this...
problem, we need boundary conditions at the interface (z = 0) and in the bulk of solution (z → ∞). Based on experimental results, it is usually accepted that the micelles do not adsorb at the fluid interface, and that only the monomers can adsorb [10,11]. These assumptions lead to the following mass balance equations at the interface:

\[ \frac{\partial C_i}{\partial t} + \alpha F_i = D_i \frac{\partial^2 C_i}{\partial z^2} \]  

at \( z = 0 \) and \( t > 0 \) \( \quad (3.10) \)

Here, \( \xi_1, \xi_2, \xi_m, \) and \( \xi_\sigma \) are the dimensionless perturbations in the concentration of surfactant monomers, \( c_{1,2,m} \), micelle concentration, \( C_m \), micelle mean aggregation number, \( m_p \), and polydispersity of the abundant micelles, \( \sigma_p \). The negative sign in Eq. (3.13) is chosen to make \( \xi_1, \xi_2, \xi_m, \) and \( \xi_\sigma \) positive by definition.

It is important to note that the convenient definitions of the dimensionless perturbations \( \xi_1, \xi_2, \xi_m, \) and \( \xi_\sigma \) are different for different dynamic problems. Here, and in references [21,22], we are using the same notation for the dimensionless perturbations of the same variables, despite some differences in the used scaling. This should not lead to any misunderstandings, because the treatment of different dynamic problems is completely independent here and in references [21,22].

Because we are dealing with a steady-state process, the perturbations, \( \xi_1, \xi_2, \xi_m, \) and \( \xi_\sigma \), are independent of time, but they are dependent on the dimensionless spatial coordinate, \( \zeta \), in other words, \( \xi_i \equiv \xi_i(\zeta), i = 1,2,m, \) in view of Eqs. (2.6), (2.8) and (3.13), the dimensionless perturbation in the subsurface concentration of monomers, \( \xi_m \approx \xi_2(\zeta = 0) \), is related to the perturbations in the surfactant adsorption, \( \Gamma_i \), and surface tension, \( \gamma \), as follows:

\[ \Gamma_m - \frac{\Gamma}{\Gamma_{eq}} = \frac{c_{1,eq} \gamma (\gamma - \gamma_{eq})}{\gamma_{eq} \Gamma_{eq}} = \xi_1,0 \]  

(3.14)

For micellar solutions, the concentration, \( c_{1,eq} \), the adsorption, \( \Gamma_{eq} \), and the adsorption length, \( b_0 \), are to be calculated at the CMC. In view of Eqs. (13.12) and (13.13), for a stationary process Eqs. (3.12)–(3.15) acquire the form:

\[-\theta \frac{\partial \xi_1}{\partial t} = \frac{\partial^2 \xi_1}{\partial \zeta^2} - \left( m_{eq} - \omega_{eq} \right) K_m \psi_1 \frac{\beta K_m}{\sigma_{eq} \psi_m} \]  

(3.15)

\[-\theta \frac{\partial \xi_m}{\partial t} = B_m \frac{\partial^2 \psi_m}{\partial \zeta^2} - K_s \frac{\omega_{eq} \psi_m}{\sigma_{eq}^2} \frac{K_m}{\sigma_{eq}} \frac{\Gamma_{eq}}{\psi_m^2} \]  

(3.16)

\[-\theta \frac{\partial \xi_m}{\partial t} = B_m \frac{\partial^2 \psi_m}{\partial \zeta^2} + K_s \frac{\omega_{eq} \psi_m}{\sigma_{eq}^2} \frac{K_m}{\sigma_{eq}} \frac{\Gamma_{eq}}{\psi_m^2} \]  

(3.17)

\[-\theta \frac{\partial \xi_\sigma}{\partial t} = B_m \frac{\partial^2 \psi_m}{\partial \zeta^2} + K_s \left( \omega^2 - 1 \right) \frac{m_{eq}}{2 \sigma_{eq}^2} \frac{\psi_m}{\sigma_{eq}} \]  

(3.18)

where \( B_m \equiv D_m / D_i \), and the reaction fluxes, \( J_{\alpha,0} \), and \( J_i \) in Eqs. (3.6)–(3.7), are also expressed in dimensionless form:

\[ \psi_m = \frac{T_m}{T_{eq} D_i K_s \sigma_{eq}} = \xi_1 - \xi_m + \frac{\xi_\sigma}{\sigma_{eq}} \]  

(3.19)

\[ \psi_\sigma = \frac{h_2^2 J}{T_{eq} D_i K_s \sigma_{eq}} = \left( m_{eq} - \omega_{eq} \xi_1 - m_{eq} \xi_\sigma \right) \psi_m + \omega_{eq} \xi_\sigma \left( \omega^2 - 1 \right) \xi_\sigma \]  

(3.20)

Eq. (3.19) shows that if \( \xi_\sigma \approx 0 \) and \( \xi_1 \approx \xi_m \), then \( \psi_m \approx 0 \), i.e. the system is equilibrated with respect to the fast micellar process, \( J_{\alpha,0} \approx 0 \). In addition, Eq. (3.20) implies that if \( \xi_\sigma \approx 0 \), and
Considering $\xi_1 \approx \xi_2 \approx \xi_{m}$, then $\psi_i \approx 0$, i.e. the system is equilibrated with respect to the slow micellar process, $J_{v} \approx 0$.

With the help of Eqs. (3.12)-(3.13), setting $d\Gamma/dt = 0$, we obtain the dimensionless form of the boundary conditions, Eqs. (3.10) and (3.11):

$$
\frac{d\xi_1}{dx} = -\theta, \quad \frac{d\xi_2}{dx} = 0, \quad \frac{d\xi_3}{dx} = 0, \quad \frac{d\xi_4}{dx} = 0 \text{ at } \xi = 0 \tag{3.21}
$$

In the bulk of solution ($\xi \to \infty$), all perturbations vanish.

4. Results for the total perturbations

4.1. Basic equations

Under steady-state interfacial expansion, the deviation from equilibrium affects the concentrations of surfactant monomers in the bulk of solution, but only in some vicinity of the interface.

The total perturbations of $\xi_1$, $\xi_2$, $\xi_3$, and $\xi_4$ can be defined as integrals:

$$
\xi_i = \int_0^\infty \xi_i(\xi) d\xi \quad (i = 1, 2, 3),
$$

The integration of Eqs. (3.15)-(3.20) with respect to $\xi$, along with the boundary conditions, Eq. (3.21), yields:

$$
-\partial\xi_1/\partial \xi_1 - (m_{eq} - w_{eq}) \beta K_{m} m_{eq} - \beta K_{m} m_{eq} = -\theta \tag{4.2}
$$

$$
-\partial\xi_2/\partial \xi_2 + \beta K_{m} m_{eq} = 0 \tag{4.3}
$$

$$
-\partial\xi_3/\partial \xi_3 - \beta K_{m} m_{eq} = 0 \tag{4.4}
$$

$$
-\left( \frac{\theta + m_{eq}}{m_{eq}} \right) \xi_4 + K_{m} (\theta - 1) m_{eq} \frac{\partial \psi_i}{\partial \xi_4} = \frac{K_{m}}{m_{eq}} \frac{\partial \psi_i}{\partial \xi_4} \tag{4.5}
$$

where the integrated (total) reaction fluxes, $\psi_i$ and $\varphi_{m,i}$, are:

$$
\psi_{m,i} = \xi_{i} - \xi_{i0} + \frac{\xi_{i0}}{m_{eq}} \tag{4.6}
$$

$$
\psi_{i} = \left( m_{eq} - w_{eq} \right) \xi_{i} - m_{eq} \xi_{i0} + \frac{m_{eq}}{w_{eq}} \left( \psi_{m,i} - \xi_{i0} \right) \tag{4.7}
$$

In view of Eqs. (4.6)-(4.7), the Eqs. (4.2)-(4.5) form a linear inhomogeneous system of four algebraic equations for determining the four total perturbations, $\xi_1$, $\xi_2$, $\xi_3$, and $\xi_4$.

Thus system could be solved by using standard methods. We used the LU decomposition method [47].

4.2. Numerical results and discussion

Numerical results for $\xi_1(\theta)$, $\xi_2(\theta)$, $\xi_3(\theta)$, and $\xi_4(\theta)$, obtained by solving the linear system of Eqs. (4.2)-(4.5), are given in Fig. 3 for a relatively high micelle concentration, $\beta = (C_{m} / C_{MC})C_{MC} = 100$. In our computations, we assigned typical values to the following constant parameters of the system:

$$
m_{eq} = 60, \quad \sigma_{eq} = 5, \quad w = 3, \quad R_{m} = 0.2 \tag{4.8}
$$

The rate constants of the fast and slow processes, $K_{m}$ and $K_{s}$, are varied. To illustrate their influence, we obtained numerical data for the following three values: $K_{m} = 10^3$ (Fig. 3a); $K_{m} = 10^5$ (Fig. 3b), and $K_{m} = 10^6$ (Fig. 3c), at the same $K_{s} = 10^5$. The perturbation $\xi_{m}(\theta)$, which is similar for Fig. 3a-c, is shown only in Fig. 3c.

The general picture in a regular kinetic diagram, Fig. 3, is the following. At high rates of surface deformation (point A in Fig. 3) the total perturbation of the monomer concentration is $\xi_{1} \approx 1$, while the other perturbations, $\xi_{2}, \xi_{3}, \xi_{m}$, are $\approx 0$. In the limit of low deformation rates, $\theta \to 0$, all perturbations become zero. For this reason, $\xi_{2}, \xi_{3}, \xi_{m}$, and $\xi_{4}$ have extremum (sometimes a flat plateau), while $\xi_{1}$ monotonically decays with the decrease of $\theta$.

The most important feature of the relaxation curves (Fig. 3) is that $\xi_{m}(\theta)$ at a given point, denoted by B, while $\xi_{1}$, $\xi_{2}$, $\xi_{3}$, at another point, denoted by D. The surface deformation rates, corresponding to the points B and D, are denoted by $\theta_{B}$ and $\theta_{D}$, respectively.

In the regime AB, corresponding to the greatest rates of interfacial deformation ($\theta > \theta_{0}$), effects of the fast micellar process affects the micellar reaction kinetics. As shown in Section 5.2 below, for higher micelle concentrations ($\beta > 10$), the effect of the fast micellar process is predominant, while for the lower micelle concentrations ($\beta \approx 1$), the effects of the fast and slow processes become comparable.

As seen in Fig. 3, for $\theta < \theta_{0}$, we have $\xi_{m} \approx 0$ and $\xi_{1} \approx \xi_{2} \approx \xi_{3} \approx \xi_{4} \approx 0$. In view of Eq. (4.6), this means that for $\theta < \theta_{0}$ the flux of the fast micellar process, $\psi_{m,i}$, is equal to zero. In other words, for $\theta < \theta_{0}$ the monomers and micelles are equilibrated with respect to the fast micellar process. An expression for estimating $\theta_{0}$ is given by Eq. (5.40) below.

Likewise, Fig. 3 shows that for $\theta < \theta_{0}$, we have $\xi_{m} \approx 0$ and $\xi_{2} \approx \xi_{3} \approx \xi_{4} \approx 0$. In view of Eq. (4.7), this means that for $\theta < \theta_{0}$ the flux of the slow micellar process, $\psi_{s,i}$, is also equal to zero. In other words, for $\theta < \theta_{0}$ (regime DE) the monomers and micelles are equilibrated with respect to both fast and slow micellar processes. Thus, in the regime DE, the dynamics of adsorption occurs under diffusion control, see Eq. (5.46) below. An expression for estimating $\theta_{0}$ is given by Eq. (5.48).

In the regime BC (Fig. 3), the monomers and micelles are equilibrated with respect to the fast process $\xi_{m}(\theta) \approx \xi_{1}(\theta)$, but the effect of the slow process is negligible ($\xi_{s} \ll \xi_{1}$). Then, in the region BC none of the two micellar processes affects the dynamics of adsorption, and, therefore, the latter also happens under diffusion control, see Eq. (5.37) below.

In the regime CD (Fig. 3), again, the monomers and micelles are equilibrated with respect to the fast process $\xi_{m}(\theta) \approx \xi_{1}(\theta)$, however the effect of the slow process becomes considerable. In other words, in the region CD, the slow micellar process affects...
Fig. 3. Total perturbations in monomer concentration, $\xi_1$, micelle concentration, $\xi_c$, mean aggregation number, $\xi_m$, and polydispersity, $\xi_\sigma$, plotted vs. the dimensionless rate of surface expansion, $\theta$, for $\beta = 100$ and $K_m = 1000$. (a) $K_m/K_s = 10^7$; (b) $K_m/K_s = 10^6$; (c) $K_m/K_s = 10^5$; the other parameters are given by Eq. (4.8). The curves are obtained by numerical solution of the linear system, Eqs. (4.2)–(4.5). $\xi_\sigma(\theta)$ is similar for (a–c), and is shown only in (c). $\xi_m$ and $\xi_1$ merge at the point B; $\xi_c$ and $\xi_1$ merge at the point D. $\theta_B$, $\theta_C$ and $\theta_D$ are the coordinates of the respective points estimated by means of Eqs. (5.40), (5.41) and (5.48).

the dynamics of adsorption. An estimate for the position of the point C, $\theta = \theta_C$, where the effect of the slow process becomes considerable, is given by Eq. (5.41).

The presence of four distinct kinetic regimes, AB, BC, CD, and DE, is a general property of the process of adsorption from micellar solutions. In particular, such regimes are observed in the case of surfactant adsorption at a quiescent interface, reference [22], and at an interface subjected to stationary expansion (the present paper, Fig. 3). Two of these regimes, AB and CD, are affected by the micellar reaction kinetics: the rate constants $K_m$ and $K_s$ influence the adsorption kinetics, and consequently, they could be determined by analysis of data for dynamic surface tension and adsorption; see Eqs. (5.5), (5.7), (5.35) and (5.39).

In contrast, the other two regimes, BC and DE correspond to dynamics of adsorption under diffusion control. In this case, the dynamic surface tension is not affected by the micellar rate constants $K_m$ and $K_s$, it can be described as diffusion in a solution of surfactant of apparent diffusion coefficients $D_{BC}$ and $D_{DE}$. The coefficients $D_{BC}$ and $D_{DE}$ depend on the equilibrium micelle concentration, mean aggregation number and polydispersity through the parameters $\beta$, $m_{eq}$ and $\sigma_{eq}$; see Eqs. (5.38) and (5.47) below.

It should be also noted that in addition to the regular kinetic diagrams (Fig. 3 and Section 5) one could sometimes observe rudimentary kinetic diagrams (Section 6), characterized by merging or disappearance of the regimes BC and CD.

5. Regular kinetic diagrams: numerical results and analytical expressions

5.1. Numerical results for the subsurface concentration and adsorption

The parameters, which are measured in the experiment, are the interfacial tension $\gamma$ [26], and the adsorption $\Gamma$ [27–31]. For small deviations from equilibrium, which are typical for surfactant concentrations above the CMC, the perturbations in $\gamma$ and $\Gamma$ are directly related to the perturbation in the subsurface concentration of monomers, $\xi_{11} = \xi_1(\zeta = 0)$, see Eq. (3.14). For this reason, in Section 5 we will focus our attention on the calculation of $\xi_{11}(\theta)$ and on the investigation of its behavior.

In Section 4, we calculated $\xi_{11}(\theta)$ by solving the linear system of algebraic Eqs. (4.2)–(4.5). The problem for calculation of $\xi_{11}(\theta)$ is more complicated, because we have to solve a linear
Regime AB}

The regime AB takes place for sufficiently great rates of surface deformation, i.e. for \( \theta > \theta_s \), see Eq. (5.40). In this regime, \( \xi \gg \beta K_{\text{tr}} \). The equations are plotted in Fig. 4, where the perturbations \( \xi (\theta, \beta) \), \( \xi (\theta, \beta) \), and \( \xi (\theta, \beta) \) are shown. For all of them, the subscript “0” indicates that they are proportional to the perturbations in the surface tension and adsorption, see Eq. (3.14). The curves obtained by numerical solution of the general system of equations in the Appendix A \( \theta_0, \theta_1, \) and \( \theta_2 \) are estimated by means of Eqs. (5.40), (5.41) and (5.48).

For this goal, we used a second-order difference scheme that is described in Appendix A. Illustrative numerical results are plotted in Fig. 4, where the perturbations \( \xi (\theta, \beta) \), \( \xi (\theta, \beta) \), and \( \xi (\theta, \beta) \) are shown. For all of them, the subscript “0” indicates that they are proportional to the perturbations in the surface tension and adsorption, see Eq. (3.14). The curves obtained by numerical solution of the general system of equations in the Appendix A \( \theta_0, \theta_1, \) and \( \theta_2 \) are estimated by means of Eqs. (5.40), (5.41) and (5.48).

The kinetic diagram for the subsurface perturbations in Fig. 4 has the same structure as that for the total perturbations in Fig. 3. Regimes AB, BC, CD, and DE can be identified in the same way as in Section 4. The situation with the point D is similar. Below, we consider separately in Section 5.3. Thus, in view of Eqs. (5.3) and (5.18), the solution of Eq. (5.4), along with the boundary condition, Eq. (3.21), is:

\[
\hat{\xi}_1 = \hat{f}(0.5 + \beta K_{\text{AB}}) (\theta / 2)^{1/2}
\]

(5.5)

where \( \hat{f} \) is the known gamma function, \( \hat{f}(x + 1) = x \hat{f}(x) \) [49, 50]. Using the fact that \( \hat{f}(0.5) = \pi^{1/2} \) and \( \hat{f}(1) = 1 \), we obtain the asymptotic form of Eq. (5.5) for small \( \beta K_{\text{AB}} \):

\[
\hat{\xi}_1 = \frac{\theta}{\sqrt{2} \pi} (\beta K_{\text{AB}})^{1/2} \quad (a_{\beta \text{AB}} \ll 1)
\]

(5.6)

Eq. (5.6) is equivalent to Eq. (2.7) that describes diffusion-limited adsorption for concentrations below the CMC; see also Eqs. (3.12) and (3.14). In other words, for \( a_{\beta \text{AB}} \ll 1 \) the effect of the micelles on the adsorption kinetics is negligible.

In the other limiting case, \( a_{\beta \text{AB}} \gg 1 \), the asymptotics of Eq. (5.6) is given by Eq. (5.22), i.e. we have:

\[
\hat{\xi}_1 = \frac{\theta}{\sqrt{2} \pi} (\beta K_{\text{AB}})^{1/2} \quad (a_{\beta \text{AB}} \gg 1, \text{regime AB})
\]

(5.7)

For \( K_{\text{AB}} \gg \theta \), Eq. (5.7) gives \( \hat{\xi}_1 \propto \theta \), which essentially differs from the square-root dependence in Eq. (5.6).

In general, Eq. (5.5), and its asymptotic form, Eq. (5.7), which characterize the dependence \( \hat{\xi}_1 (\theta) \) in the regime AB, contain the reaction constant \( K_{\text{AB}} \), which accounts for the effect of the micelles on the adsorption kinetics. We can express \( K_{\text{AB}} \) in the form

\[
K_{\text{AB}} = (1 + R_s) \frac{K_m}{m_{eq}}
\]

(5.8)

where the parameter \( R_s \) characterizes the relative importance of the slow micellar process in comparison with the fast one. For the parameter values in Eq. (4.8), we obtain:

\[
R_s = 1.215 \times 10^{-3} \frac{K_s}{K_m}
\]

(5.9)

Thus, for \( K_s / K_m \geq 10^3 \) and \( \beta = 100 \) (Figs. 3 and 4), Eq. (5.9) yields \( R_s \ll 1 \), and the contribution of the slow process is negligible; then \( R_s \) could be neglected in Eq. (5.8), and the adsorption kinetics is influenced only by the fast micellar process. In contrast, for \( K_s / K_m \ll 10^3 \) and \( \beta = 1 \) (low micelle concentration, see
To solve Eq. (5.10), we introduce a new function, \( \tilde{f}(y) \), as follows:

\[
f(y) = \exp \left( \frac{\gamma_0^2}{2} \right) \tilde{f}(y)
\]

The substitution of Eq. (5.12) into Eq. (5.10) yields the Weber differential equation [51]:

\[
\frac{d^2 \tilde{f}}{dy^2} + \left( \frac{\gamma_0^2}{2} + \frac{1}{2} + 2a \right) \tilde{f} = 0
\]

(5.13)

Because \( \tilde{f}(y) \to 0 \) for \( y \to \infty \), the solution of Eq. (5.13) can be expressed in terms of the known Whittaker function, \( U \), see chapter 19 in reference [49]:

\[
\tilde{f}(y) = XU(b, y), \quad b = 0.5 + 2a
\]

(5.14)

where \( X \) is unknown constant. In view of Eq. (5.12), the substitution of Eq. (5.14) into the boundary condition, Eq. (5.11), yields:

\[
\frac{df}{dy}\bigg|_{y=0} = \frac{d\tilde{f}}{dy}\bigg|_{y=0} = XU(b, 0) = -1
\]

(5.15)

where the prime denotes first derivative with respect to \( y \). Combining Eqs. (5.12), (5.14) and (5.15), we obtain:

\[
f(0) = \frac{U(b, 0)}{U'(b, 0)}
\]

(5.16)

Eq. (19.3.5) in [49] gives exact expressions for the functions entering Eq. (5.16):

\[
U(b, 0) = \frac{\sqrt{\pi}}{2^{2b+1/4} \Gamma(3/4 + b/2)}
\]

(5.17)

Finally, we substitute Eq. (5.17) into Eq. (5.16), and take into account that \( b = 0.5 + 2a \). As a result, we obtain:

\[
f(0, a) = \frac{1}{\sqrt{2}} \frac{\Gamma(0.5 + a)}{\Gamma(1 + a)}
\]

(5.18)

Because \( \Gamma(0.5) = \pi^{1/2} \) and \( \Gamma(1) = 1 \), the asymptotics of Eq. (5.18) for small \( a \) is:

\[
f(0, a) = (\pi/2)^{1/2} \quad \text{for} \quad a \ll 1
\]

(5.19)

To find the asymptotic of \( f(0,a) \) for large \( a \), we will use Eq. (6.1.40) in [49]

\[
\ln P(z) = \left( z - \frac{1}{2} \right) \ln z - z + \frac{1}{2} \ln(2\pi) + O(1/z)
\]

(5.20)

(1/\(z \ll 1 \)). With the help of the latter expression, one could prove that

\[
\ln \frac{P(z)}{P(z + 0.5)} = -\frac{1}{2} \ln z + O \left( \frac{1}{z \ln z} \right)
\]

(5.21)

Substituting \( z = 0.5 + a \) in the latter expression, and using Eq. (5.18), we derive the asymptotics of \( f(0,a) \):

\[
f(0, a) \approx \frac{1}{\sqrt{2\pi a + 1}} \quad \text{for} \quad a \gg 1
\]

(5.22)
5.4. Region BCDE

By definition, for \( \theta < \theta_0 \) we have \( \xi_1 \approx \xi_m \) and \( \xi_2 \approx 0 \), see Figs. 3 and 4. Physically, this means that the surfactant monomers and micelles are equilibrated with respect to the fast process. Therefore, we could simplify the general mass-transport problem, Eqs. (3.15)–(3.18). For this goal, we multiply Eq. (3.17) by \( \sigma \partial^2 \beta / m_{eq} \) and sum it up with Eq. (3.15). The result reads:

\[
-\partial \frac{d}{dx}(\xi + u\phi_m) = \frac{d^2}{dx^2}(\xi + u\phi_m) - m_{eq}K_\beta \varphi_s \]

\[
u \approx \frac{\sigma^2 \xi}{m_{eq}}
\]

The boundary condition for Eq. (5.23) requires a special derivation. For this purpose, let us consider a small cylinder of height, \( \nu \), and basis parallel to the interface. The integration of Eq. (5.23) for \( 0 < \xi < \infty \) along with the boundary conditions \( \partial \xi / \partial \xi = -\theta \) and \( \partial \phi_m / \partial \zeta = 0 \) at \( \zeta = 0 \) (see Eq. (3.21)), yields:

\[
\int_0^\nu d\xi = \frac{\sigma^2 \nu (\xi + u\phi_m) + m_{eq}K_\beta \varphi_s}{\zeta = \nu + \theta}
\]

Next, in Eq. (5.25) we make the transition \( L \rightarrow 0 \) and use the relationship \( \xi_m \approx \xi_1 \), which is fulfilled in the whole region BCD. Thus, we obtain the boundary condition in the form:

\[
(1 + u\phi_m \frac{d\xi_1}{d\xi}) = -\theta \quad \text{at} \quad \zeta = 0
\]

In view of Eq. (3.20) for \( \varphi_s \), the substitution \( \xi_m \approx 0 \) and \( \xi_1 \approx \xi_m \) in Eqs. (5.23) and (3.16) yields:

\[
-(1 + u\phi_m \frac{d\xi_1}{d\xi}) = \left(1 + u\phi_m \frac{d^2\xi_1}{d\xi^2} - m_{eq}K_\beta (\xi_1 - \xi_2)\right)
\]

\[
-(1 + u\phi_m \frac{d\xi_1}{d\xi}) = B_n \frac{d^2\xi_1}{d\xi^2} + \frac{m_{eq}K_\beta}{\bar{\beta}} (\xi_1 - \xi_2)
\]

(5.27)

The simplified model, based on Eqs. (5.26)–(5.28), is applicable for \( \theta < \theta_0 \) or \( \xi_1 \approx \xi_2 \). Indeed, the derivation of Eq. (5.26) ensures that the monomers and micelles are equilibrated with respect to the fast micellar process. However, in the close vicinity of the interface (\( \xi = 0 \)), we have a slight difference between \( \xi_1 (\zeta) \) and \( \xi_m (\zeta) \). This difference is due to the different boundary conditions: \( \partial \xi_1 / \partial \zeta = 0 \) versus \( \partial \phi_m / \partial \zeta = 0 \); i.e., the monomers adsorb (nonzero diffusion flux), but the micelles do not adsorb; see Eq. (5.21).

On the other hand, the simplified model based on Eqs. (5.26)–(5.28) presumes quasi-equilibrium with respect to the fast process, that is \( \xi_m (\zeta) \approx \xi_1 (\zeta) \). In such case, \( \xi_m (\zeta) \) is no longer independent variable. Then, at the interface we can impose only one boundary condition, for \( \xi_1 (\zeta) \), and as noted by Joos et al. [9], this must be the condition for the total interfacial mass balance of surfactant. Indeed, the derivation of Eq. (5.26) ensures that the flux of surfactant molecules at the interface must be the same for the “real” system, described by Eqs. (3.15)–(3.21), and for the simplified quasi-equilibrium model, described by Eqs. (5.26)–(5.28). This requirement ensures that the monomer distributions in the “real” and “model” systems coincide in the bulk. As seen in Fig. 6b, in the bulk we really have \( \xi_m (\zeta) \approx \xi_1 (\zeta) \). However, close to the interface we have a small difference (about...
4% between \( \xi_{\text{EE}}(\xi) \) and \( \xi_{\text{E}}(\xi) \) due to the different boundary conditions.

In conclusion, the correct values of \( \xi_{\text{E}} \) are given by the full model, Eqs. (3.15)–(3.21), see also the Appendix A. The simpler model, Eqs. (5.26)–(5.28), which assumes that \( \xi_{\text{EE}}(\xi) \equiv \xi_{\text{E}}(\xi) \) for every \( \xi \) (Fig. 6b), leads to a small difference between \( \xi_{\text{EE}}(\xi) \) and \( \xi_{\text{E}}(\xi) \) in the close vicinity of the interface. This is the “price” we pay to work with a simpler model. This difference is the greatest for the subsurface concentrations, \( \xi_{\text{EE}} \) and \( \xi_{\text{E}}(\xi) \) at \( \xi = 0 \). It disappears for the smaller values of \( \theta \), as seen in Fig. 4, or for greater distances from the interface (Fig. 6).

5.5. The regimes BC and CD

The mathematical problem could be further simplified for the region BCD, where \( \xi_e \ll \xi_0 \), see Figs. 3 and 4. Neglecting the term with \( \xi_e \) in Eq. (5.27), we obtain:

\[
-(1 + u\beta)\frac{d^2\xi_e}{d\xi^2} = (1 + u\beta K_{\text{D}})\frac{d^2\xi_0}{d\xi^2} - m_2^2 \xi_e \xi_{\text{eq}}
\]

(5.29)

Using the substitutions

\[
\xi_e = f(\sqrt{2}(1 + u\beta(1 + u\beta K_{\text{D}})))^{-1/2}
\]

(5.30)

\[
\xi_0 = \xi/\sqrt{2}(1 + u\beta(1 + u\beta K_{\text{D}}))^{1/2}
\]

(5.31)

\[
K_{\text{BD}} = \frac{m_2^2 K_{\text{D}}(1 + u\beta)}{2}
\]

(5.32)

we represent Eq. (5.29) and the boundary condition (5.26) in the form:

\[
\frac{d^2f}{d\xi^2} - \frac{d\xi}{d\xi} - 2a_{\text{BD}}f = 0
\]

(5.33)

\[
\frac{d\xi}{d\xi} = -1 \quad \text{at} \quad \theta = 0
\]

(5.34)

Eqs. (5.33) and (5.34) define a boundary problem, which is equivalent to the PFOR model in Section 5.3. Correspondingly, the solution of this boundary problem is given by Eq. (5.18) with 

\( a = a_{\text{BD}} \). Thus, in view of Eq. (5.30), we obtain:

\[
\xi_{\text{E},0} = [(1 + u\beta(1 + u\beta K_{\text{D}}))]^{-1/2} \left[ \frac{0.5 + a_{\text{BD}}}{1 + a_{\text{BD}}} \right]^{1/2} \left( \frac{\theta}{2} \right)^{1/2}
\]

(5.35)

Using Eq. (5.19), we derive the asymptotics of Eq. (5.35) for small \( a_{\text{BD}} \):

\[
\xi_{\text{E},0} = [(1 + u\beta(1 + u\beta K_{\text{D}}))]^{-1/2} \left( \frac{\pi a_{\text{BD}}}{2D_{\text{BD}}} \right)^{1/2} \quad (\text{regime BC})
\]

(5.36)

With the help of Eqs. (3.12) and (3.14), Eq. (5.36) can be expressed in the form of Eq. (2.7):

\[
\eta_{\text{AB}} = \frac{\eta_{\text{AD}}}{\eta_{\text{CD}}} = \left( \frac{\pi a_{\text{BD}}}{2D_{\text{BD}}} \right)^{1/2} \quad (\text{regime BC})
\]

(5.37)

\( D_{\text{BC}} \equiv D_1(1 + u\beta) \left( 1 + u\beta \frac{D_{\text{D}}}{D_{\text{BC}}} \right) \)

(5.38)

Here, \( D_{\text{BC}} \) is an apparent diffusion coefficient. The analogy between Eqs. (2.7) and (5.37) implies that in the regime BC we are dealing with diffusion-limited adsorption. In this regime, the fast micellar process is equilibrated, while the slow micellar process is negligible. For this reason, the rate constants of the two processes, \( K_{\text{C}} \) and \( K_{\text{S}} \), do not appear in Eq. (5.37). The apparent diffusivity, \( D_{\text{BC}} \), accounts for the presence of micelles through the parameters \( \beta, u \) and \( D_{\text{D}} \); see Eq. (5.24) and (5.38).

Note that Eq. (5.37) is specific for the considered type of dynamics (adsorption at fluid interfaces subjected to stationary expansion), while Eq. (5.38) for \( D_{\text{BC}} \) seems to be universal: it is valid also for other types of interfacial dynamics in regime BC. For example, the same expression for \( D_{\text{BC}} \) was derived in [22], for adsorption relaxation at a quiescent interface. Comparing experimental data with a simpler model of monodisperse micelles, Joos and van Hunsel [8] obtained a semiempirical expression for \( D_{\text{D}} \), which is equivalent to Eq. (5.38) with \( \beta = 1 \). Experimentally, such quadratic dependence of \( D_{\text{D}} \) on the micelle concentration, \( \beta \), has been established for the nonionic surfactant Brij 58 by means of the dynamic drop-volume method [8], and by means of the strip method [9]. The regime BC has been detected also for the surfactant Triton X-100 by means of the maximum-bubble-pressure method [52] for the long times. This regime has been also observed in measurements of dynamic surface tension (or adsorption) for other types of surfactants and experimental methods; see Section 7.

In contrast with the “diffusion-limited” regime BC, in the regime CD the adsorption dynamics is affected by the micellar kinetics through the slow micellar process. In general the regime CD is characterized by Eq. (5.35) for \( a_{\text{BD}} \leq 1 \). Note that \( a_{\text{BD}} \propto K_s \), where, as usual, \( K_s \) is the dimensionless rate constant of the slow micellar process; see Eq. (5.32). In particular, the asymptotic form of Eq. (5.35) for \( a_{\text{BD}} \gg 1 \) is:

\[
\xi_{\text{E},0} = [(1 + \beta\alpha(1 + \beta\alpha K_s))]^{-1/2} \left( \frac{\theta}{K_s + \theta} \right)^{1/2} \quad (\text{regime CD})
\]

(5.39)

see also Eqs. (5.22) and (5.32). As expected, Eq. (5.39) shows that \( \xi_{\text{E},0} \) depends on the rate constant of the slow process, \( K_s \), through \( K_{\text{BD}} \), and consequently, \( K_s \) could be determined from experimental data for \( \xi_{\text{E},0}(\theta, \beta) \) in the regime CD; see also Eq. (3.14).

The boundary between the regimes AB and BC, \( \theta = \theta_{\text{BC}} \), can be defined as the intersection point of the dependencies \( \xi_{\text{E},0}(\theta, \beta) \) in the regime CD, see also Eq. (3.14).

For \( \beta \to 0 \) (very low micelle concentrations), the denominator in Eq. (5.40) could become zero and this equation may not give physically meaningful values for \( \theta_{\text{BC}} \). This reflects the fact that at low micelle concentrations the point \( B \) cannot be defined (rudimentary kinetic diagram, see Section 6).
We could define the boundary between the regimes BC and CD, \( \theta = \theta_c \), as a point situated between the zones of validity of the asymptotic Eqs. (5.36) and (5.39). An appropriate definition of \( \theta_c \) could be obtained if we postulate that at \( \theta = \theta_c \), the relative deviation of the asymptotic Eq. (5.36) from the exact Eq. (5.35) is 25%. This definition yields:

\[
\theta_c = 1.853 K_{BD} = 1.853 m_{cm} K_{d}(1 + \mu)\theta^{-1}
\]  

(5.41)

The positions of the points \( \theta_0 \) and \( \theta_c \) in Figs. 3 and 4 (shown by vertical dashed lines) are determined from Eqs. (5.40) and (5.41). Note that smaller values of \( K \) lead to wider region BC: compare Fig. 3a-c.

### 5.6. Regime DE

By definition, for \( \theta < \theta_c \), we have \( \xi_c \approx \xi_1 \approx \xi_m \) and \( \xi_2 = 0 \), see Fig. 3. Physically, this means that the surfactant monomers and micelles are equilibrated with respect to both the fast and slow micellar processes. Consequently, we could simplify the general mass-transport problem, Eqs. (3.15)-(3.18). For this goal, we multiply Eq. (3.16) by \( \hat{m}_{cm} \) and sum it up with Eq. (5.23). The result reads:

\[
-\theta \frac{d}{d\xi}(\xi_1 + \mu \delta_0^{1/2} + \hat{m}_{cm} \xi_2) = \frac{d^2}{d\xi^2}(\xi_1 + \mu \delta_0^{1/2} + \hat{m}_{cm} \xi_2)
\]

(5.42)

The boundary condition for Eq. (5.42) can be derived in analogy with the derivation of Eq. (5.26). For this purpose, we first consider a small cylinder of height, \( L \), and bases parallel to the surface.

\[
\frac{d}{d\xi}(\xi_1 + \mu \delta_0^{1/2} + \hat{m}_{cm} \xi_2) \bigg|_{\xi = 0} = 0
\]

(5.43)

Next, in Eq. (5.43) we make the transition \( L \to 0 \) and use the relationship \( \xi_2 = \xi_1 \), which is fulfilled in the region DE. Thus, we obtain the boundary condition in the form:

\[
(1 + (m_{cm} + \mu)\beta B_{\alpha} \frac{d^2}{d\xi^2}) = 0 \quad \text{at} \quad \xi = 0
\]

(5.44)

The substitution \( \xi_c \approx \xi_1 \approx \xi_m \) in Eq. (5.42) yields:

\[
[-(1 + (m_{cm} + \mu)\beta B_{\alpha} \frac{d}{d\xi}] = [1 + (m_{cm} + \mu)\beta B_{\alpha} \frac{d^2}{d\xi^2}]
\]

(5.45)

Mathematically, the boundary problem, Eqs. (5.44) and (5.45) is analogous to the boundary problem for concentrations below the CMC, Eqs. (2.2) and (2.3), and it can be solved in a similar way. Thus, in view of Eqs. (3.12) and (3.14), an analogue of Eq. (2.7) can be derived for the regime DE:

\[
\frac{D_{DE} - \Gamma}{D_{DE}} = \rho_{DE} = \left( \frac{\pi \delta_0^{1/2}}{2D_{DE}} \right)^{1/2} = \left( \frac{\pi \delta_0^{1/2}}{2D_{DE}} \right)^{1/2}
\]

(5.46)

\[
D_{DE} \equiv D_{a}(1 + (m_{cm} + \mu)\beta B_{\alpha} D_{cm})/D_{a}
\]

(5.47)

Here, \( D_{DE} \) is an apparent diffusion coefficient. The analogy between Eqs. (2.7) and (5.46) implies that in the regime DE we are dealing with diffusion-limited adsorption. Because in this regime the fast and slow micellar processes are equilibrated, the rate constants of these two processes, \( K_u \) and \( K_c \), do not appear in Eqs. (5.46). The latter describes adsorption under purely diffusion control. The apparent diffusivity, \( D_{DE} \), accounts for the presence of micelles through the parameters \( m_{cm}, \beta, \mu \), and \( D_{cm} \); see Eq. (5.47).

Note that Eq. (5.46) is specific for the considered type of adsorption dynamics (at fluid interfaces subjected to stationary expansion), while Eq. (5.47) for \( D_{DE} \) seems to be universal: it is valid also for other types of interfacial dynamics in regime DE. For example, the same expression for \( D_{DE} \) was derived in [22] for adsorption relaxation at a quiescent interface.

As a rule, \( m_{cm} \gg \mu \), see Eq. (5.24). Then, we can neglect \( \mu \) in Eq. (5.47). The resulting expression for \( D_{DE} \) is identical to that obtained by Lucassen [6] in the framework of a simplified model assuming the presence of monodisperse micelles of aggregation number \( m_{cm} \). In [6], it was reported that this expression agrees well with experimental data for the adsorption of nonionic surfactants at interfaces of oscillating area. Because \( m_{cm} \gg \mu \), the dependence \( D_{DE}(\beta) \), predicted by Eq. (5.47), is much stronger than the dependence \( D_{DE}(\beta) \), predicted by Eq. (5.38). (As usual, \( \beta = (C_{cm} - \text{CMC})/\text{CMC} \) is the dimensionless micelle concentration.) The latter fact enables one to easily distinguish between the regimes BC and DE, both of them corresponding to diffusion-limited adsorption: \( \Gamma_{DE} - \Gamma \approx \theta^{1/2} \); compare Eqs. (5.37) and (5.46). For example, Joos et al. [8,9,18] established a considerable disagreement between their experimental data and the Lucassen’s expression for the apparent diffusivity. The reason is that the data by Joos et al. correspond to the regime BC, while the Lucassen’s expression, i.e. Eq. (5.47) with \( \mu = 0 \), is derived for the regime DE. (The two regimes have not been distinguished at that time.)

Because the point D is defined as boundary between the regions CD and DE, the boundary point \( \theta_0 \) could be determined as the intersection point of the curves \( \xi_1, \beta(\theta) \) defined by Eqs. (5.39) and (5.46). Setting equal the right-hand sides of the latter two equations, one obtains:

\[
\theta_c = K_{BD} \left( \frac{2D_{DE}}{D_{DE}} - 1 \right)^{-1}
\]

(5.48)

where the apparent diffusion coefficients \( D_{BC} \) and \( D_{DE} \) are defined by Eqs. (5.38) and (5.47). Eq. (5.32) relates \( K_{BD} \) to the rate constant of the slow micellar process, \( K_c \). In Figs. 3 and 4, the vertical dashed lines for \( \theta_0 \) are drawn by means of Eq. (5.48).
5.7. Compound asymptotic expression for the whole region ABCDE

Regular kinetic diagrams with clearly distinguished regimes AB, CD, DE and DE are observed when \( \beta \gg 1 \) and

\[
\beta K_m \gg (m_{eq} - \omega_0 m_{eq})^2 m_{eq} \quad \text{(5.49)}
\]

see the right-hand side of Eq. (5.2). In this case, the values of \( \theta \) corresponding to the separate regimes differ by order of magnitude, see Figs. 3 and 4. For this reason, one could obtain a corresponding to the separate regimes differ by order of magnitude, see Figs. 3 and 4. For this reason, one could obtain a compound analytical expression for \( \xi_n \) by merely summing up Eq. (5.5) for the regime AB, Eq. (5.35) for the region BCD, and Eq. (5.46) for the regime DE. The resulting expression reads:

\[
\xi_{1,0}(\theta) = \frac{\theta^{3/2}}{2} \left[ \frac{\Gamma(0.5 + a_{AB})}{\Gamma(1 + a_{AB})} \right] + \frac{D_{AB}^{1/2} \Gamma(0.5 + a_{AB})}{D_{eq}^{1/2} \Gamma(1 + a_{AB})} \left( \frac{\pi D_{AB}}{w_{eq}} \right)^{1/2} \left( \frac{\pi D_{AB}}{w_{eq}} \right) \quad \text{(5.50)}
\]

In view of Eqs. (5.2), (5.4), (5.32) and (5.49), \( a_{AB} \) and \( a_{BD} \) could be expressed in the form:

\[
a_{AB} = \frac{K_{m,AB}}{2m_{eq} \theta}, \quad a_{BD} = \frac{K_{m,BD}}{2m_{eq} + m_{eq} \theta} \quad \text{(5.51)}
\]

In view of Eq. (3.14) and (5.50) determines also the dependencies of the surface tension and adsorption on the expansion rate: \( \gamma = \gamma(\theta) \) and \( \theta = \theta(\theta) \). We recall that in Eq. (5.50) \( \Gamma \) denotes the known gamma function (Euler integral of the second kind) [49,50].

In Fig. 7, predictions of the approximate Eq. (5.50) (the dashed lines), are compared against the exact numerical solution described in the Appendix A (the continuous lines). As seen in Fig. 7, the dashed and continuous lines practically coincide. In other words, the approximate analytical expression, Eq. (5.50), is in excellent agreement with the exact numerical solution. We recall that Eq. (5.50) is applicable only in the case of regular kinetic diagrams, for which the relation (5.49) is satisfied.

6. Rudimentary kinetic diagrams

The rudimentary kinetic diagrams are characterized by merging or disappearance of the regimes BC and CD when the conditions: (a) \( \beta \gg 1 \) and (b) \( \beta K_m \gg (m_{eq} - \omega_0 m_{eq})^2 m_{eq} \), are violated; see Eq. (5.49). As a rule, this happens at low micelle concentrations. Below, we consider separately two typical cases.

6.1. Conditions (a) and (b) are both violated

In this case, the points B and C merge with the point D. In other words, the regimes BC and CD are missing. As illustration, in Fig. 8a we have plotted the total perturbations \( \xi_1(\theta), \xi_2(\theta), \xi_3(\theta) \), \( \xi_4(\theta) \), and \( \xi_5(\theta) \), calculated as described in Section 4. The parameter values used in these computations are \( \beta = 1, K_m = 1, K_{eq}/K_m = 10^3 \); the other parameters are given by Eq. (4.8). For these parameter values we have:

\[
\beta K_m \approx (m_{eq} - \omega_0 m_{eq})^2 m_{eq} \quad \text{(6.1)}
\]

Because \( \beta = 1 \), both the conditions (a) and (b) are violated; see the beginning of Section 6. In Fig. 8a one sees that the curves...
and continuous lines are, respectively, the predictions of Eqs. (5.50) and (6.2), and of the exact numerical solution in the Appendix A.

Fig. 9. $K_m/K_s = 10^3$: rudimentary kinetic diagrams at a low micelle concentration, $\beta = 1$. The other parameter values are given by Eq. (4.8) and $K_m = 1$. (a) Plot of $\xi_1, \xi_2, \xi_{12}$ vs. $\theta$; (b) Plot of $\xi_1, \xi_2, \xi_{12}$ vs. $\Gamma$. The latter fact suggests trying an analytical formula for $\xi_1, \xi_2, \xi_{12}$, corresponding to the regions AB and DE.

To the right of the point D we have $\xi_1, \xi_2, \xi_{12} \approx 0$ and $\xi_{12}^m = 0$. In view of Eq. (4.6), this means that the flux of the fast micellar process, $\phi_{12}^f$, is equal to zero, and the monomers and micelles are equilibrated with respect to the fast micellar process. In addition, on the left of the point D the flux of the slow micellar process, $\phi_{12}^s$, is also equal to zero (see Eq. (4.7)), and the monomers and micelles are equilibrated with respect to both the fast and slow micellar process. Then, the dynamics of adsorption occurs under diffusion control.

6.2. Only the condition $\beta \ll 1$ is violated

In this case, the regime CD (interfacial dynamics affected by the slow micellar process) is present. As an illustration, in Figs. 9a and 10a we have plotted the total perturbations $\xi_1, \xi_2, \xi_{12}^m, \xi_{12}^s$, and $\xi_{12}^t$, calculated as described in Section 4. The parameter values are the same as in Fig. 8a, except the ratio $K_m/K_s$, which is equal to $10^6$ and $10^7$ for Figs. 9 and 10, respectively. For these parameter values, the relation (5.49) is satisfied. Hence, only the condition $\beta \ll 1$ is violated.

In Figs. 9b and 10b, the exact numerical solution described in the Appendix A (continuous line) is compared with the predictions of the approximated Eq. (5.50) (the dash-dotted line) and Eq. (6.2) (the dashed line). One sees that in some regions of $\theta$-values, Eqs. (5.50) and (6.2) are close to the exact solution for $\xi_1, \xi_2, \xi_{12}$, but in other regions there is a considerable difference. For this reason, in the considered case of rudimentary kinetic diagrams it is preferable to use the exact numerical solution.
7. Comparison of theory and experiment

To compare our model with the experiment, and to illustrate its applicability, here we present fits of experimental data published by other authors.

7.1. Dynamic surface tension of Brij 58 measured by the strip method

The dynamic surface tension, \( \gamma \), of the nonionic surfactant polyoxyethylene-20 hexadecyl ether (Brij 58) has been measured by Li et al. [9] by means of the strip method. It has been established by other authors.

\( \gamma \) is determined by Li et al. [9] by means of the strip method. It has been established that for each given surfactant concentration the experimental data satisfies the relationship \( \gamma = \gamma_{eq} \propto u^{1/2} \), where \( u \) is the surface expansion rate, see Eq. (2.1). In other words, the data indicate adsorption under diffusion control. In addition, Li et al. [9] have established that the apparent diffusivity of the surfactant solution, determined from their data, agrees with an expression equivalent to our Eq. (5.38) with \( a = 1 \). This finding implies that this set of experimental data corresponds to dynamics of adsorption in the regime BC. Consequently, the data could be interpreted by using the analytical expressions for the regime BC derived in Section 5.5. Combining Eqs. (3.14) and (5.37), we obtain:

\[
\gamma = \gamma_{eq} = \Gamma_{eq} \equiv \frac{\pi a}{2 D u} \left( \frac{\pi a}{2 D u} \right)^{1/2}
\]  

(7.1)

From equilibrium surface-tension data for aqueous solutions of Brij 58 it is known that CMC = 1.0 \times 10^{-4} \text{ mol/cm}^2 and \( \Gamma_{eq} = 2.70 \times 10^{-3} \text{ mol/cm}^2 \text{ (at CMC)} \) [9]. Then, from the slope of the experimental plot \( \gamma - \gamma_{eq} \) versus \( u^{-1/2} \) for a fixed micellar concentration, \( \beta \), one can determine the apparent diffusivity of the surfactant solution, \( D_{uc}(\beta) \). On the other hand, Eq. (5.38) yields:

\[
D_{uc}(\beta) \equiv D_1 (1 + a \beta)(1 + u B_m \beta)
\]  

(7.2)

Here, as usual, \( \beta = (C_{sat} - \text{CMC})/\text{CMC}; B_m = D_m/D_1 \) is the ratio of the diffusivities of the micelles and monomers. For Brij 58 the value \( D_1 = 5 \times 10^{-6} \text{ cm}^2/\text{s} \) was used [9].

The points in Fig. 11 represent the data for \( D_{uc}(\beta) \) versus \( \beta \) from reference [9]. We fitted these data with parabola, \( D_{uc}(\beta) \), in accordance with Eq. (7.2). The best fit yields \( B_m = 0.243 \) and \( a = 1.06 \). The latter values are close to those in [9] where \( a = 1 \) is presumed, and \( B_m = 0.25 \) is obtained. From our value of \( u = \sigma_{eq}/m_{eq} \) and the micellar aggregation number, \( m_{eq} = 70 \) for Brij 58 [53], we calculate the polydispersity of the micelles: \( \sigma_{eq} = 8.6 \).

The fit of the experimental data in Fig. 11 is very good, and the obtained values of the parameters \( B_m \) and \( \sigma_{eq} \) are reasonable. This confirms that the adsorption kinetics in this experiment corresponds to the regime BC. We recall that in this regime, the rate constants of the fast and slow micellar processes, \( K_m \) and \( K_c \), do not affect the surfactant adsorption kinetics, and cannot be determined from the fit of the data.

7.2. Dynamic adsorption of C14TAB and C16TAB by the overflowing cylinder method

The overflowing cylinder method allows one to measure directly dynamic adsorption, \( \Gamma(\alpha) \), by ellipsometry [27,30,31], or by neutron reflection [28]. Sets of such experimental data for aqueous solutions of the cationic surfactants tetradecyl- and hexadecyl-trimethylammonium bromide (C14TAB and C16TAB) have been published in reference [12]; see also [31].

The solutions contain 100 mM electrolyte, NaBr, which suppresses the electrostatic effects. As demonstrated below, it turns out that these data agree well with the kinetic regime BC, like the data for Brij 58 in Section 7.1.

The data in [12] give \( \Gamma \) for various couples of values \( (\alpha, \beta) \). However, a systematic dependence \( \Gamma(\alpha) \) at fixed \( \beta \) is not available. For this reason, the approach for data interpretation from Section 7.1 cannot be applied. Instead, we will use the following modified approach. Eqs. (5.37) and (5.38) can be represented in the form:

\[
\Gamma = \Gamma_{eq} - \Gamma_{eq}^{a_{T}a_{T}} Y^{1/2}
\]  

(7.3)

\[
Y \equiv \frac{\pi a}{2(1 + a \beta)(1 + u B_m \beta)}
\]  

(7.4)

where \( \Gamma_{eq}^{a_{T}a_{T}} = h \beta \) is the characteristic diffusion time of the surfactant monomers. We plotted the experimental data for \( \Gamma \) versus \( Y \) in accordance with Eqs. (7.3) and (7.4). The parameters \( u \) and \( B_m \) were varied until the best fit of the data by linear regression was achieved (Fig. 12). The intercept of this linear regression, corresponding to \( Y = 0 \) (i.e. \( a = 0 \)), gives the equilibrium adsorption at CMC, \( \Gamma_{eq}^{a_{T}a_{T}} \).

Fig. 12a shows the fit of the data for C14TAB from reference [12], plotted as \( \Gamma \) versus \( Y \); see Eq. (7.3). The best fit corresponds to \( B_m = 0.232 \) and \( u = \sigma_{eq}/m_{eq} = 1.2 \). The aggregation number of the C14TAB micelles is reported to be \( m_{eq} = 80 \), in the absence of added electrolyte [53]. Assuming that the addition
of 100 mM NaBr does not change $\eta_{eq}$ from $u = 1.2$ we determine that the polydispersity of the $C_{14}$TAB micelles is $\sigma_{eq} = 9.8$. The obtained values of $B_{ag}$ and $\sigma_{eq}$ are reasonable, and the data in Fig. 12a comply well with a straight line, whose intercept gives a realistic value for $I_{eq}$. This agreement between theory and experiment confirms that, in the considered case, the kinetic regime is BC.

Fig. 12b is similar to 12a, but this time the surfactant is $C_{16}$TAB. The best fit corresponds to $B_{ag} = D_{ag}/D_{1} = 0.180$ and $u = \sigma_{ag}^{2}/m_{ag} = 0.26$. The obtained smaller value of $B_{ag}$ for $C_{16}$TAB (in comparison with $C_{14}$TAB) seems reasonable, because $C_{16}$TAB exhibits a tendency to form larger elongated micelles [54, 55]. For a surfactant with hexadecyl chain, the aggregation number of the minimum spherical micelle is about 100 [31, 55]. The addition of electrolyte is known to increase the aggregation number of the micelles of ionic surfactants as for $100 \text{mM} C_{16}$TAB and $C_{14}$TAB published in reference [12].

The obtained values of $m_{eq}$ are reasonable, and the data in Fig. 12b comply well with a straight line, whose intercept gives $\Gamma_{eq} = 0.56$; in other words, $\xi_{1,1D}$ is not so small, but nevertheless the linearized theory could be applied (the data agree with a straight line). This could be explained with the fact that the perturbation $\xi$ decays very fast with the distance from the interface, inside the micellar solution.

The above two criteria for validity of the linearized theory are applicable when the surfactant transfer takes place under the regime BC; see Eq. (5.37). When the kinetic regime is different, analogous criteria can be obtained from the requirement of the experimental data to agree with the kinetic equation of the respective regime. Thus, for the regime AB this is Eq. (5.5), or its asymptotic forms, Eqs. (5.6) and (5.7). For the regime CD this is Eq. (5.39), and for the regime DE this is Eq. (5.46). Note that mathematically Eqs. (5.7) and (5.39) are similar, and one could identify whether the regime is BC or DE from the coefficients $D_{ag}$ and $D_{bc}$ determined from the fit. In general, it is expected that $D_{bc} << D_{ag}$, see Eqs. (5.38) and (5.47).

8. Summary and conclusions

Here, we consider a micellar surfactant solution whose surface is subjected to stationary expansion. The adsorption at the fluid interface gives rise to diffusion of surfactant monomers and micelles, and to release of monomers by the micelles. To describe this process, we applied a recently derived general system of four ordinary differential equations, which are linearized for the case of small perturbations, see Eqs. (3.15)-(3.18). The
numerical solution of this problem reveals the existence of four distinct kinetic regimes (Fig. 3). At the greatest expansion rates, the surfactant adsorption is affected by the fast micellar process (regime AB, Section 5.2). At lower expansion rates, the fast process equilibrates and the adsorption occurs under diffusion control (regime BC, Section 5.5). With the further decrease of the expansion rate, the surfactant adsorption is affected by the slow micellar process (regime CD, Eq. (5.39)). Finally, at the lowest expansion rates, both the fast and slow micellar processes are observed, which are characterized by merging or disappearance of the regimes BC and CD (Section 6). Usually, only one regime is observed in a given experiment, and to interpret experimental data, the developed theoretical model enables one to identify which of the four kinetic regimes is dominant and to assess the values of the various parameters (Fig. 11 and 12), which implies that the kinetic regime is BC in the considered specific cases.

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Appendix A. Numerical procedure for solution of the boundary problem (3.15)–(3.21)

At the first step, we introduce a convenient new scaling of the normal coordinate, $\zeta$ and of the perturbations, $\xi_1$, $\xi_2$, $\xi_3$, and $\xi_4$, as follows:

$$\zeta = \xi^{i} \xi^{1/2}, \quad \xi_i = \xi^{i} \xi^{1/2} \quad (i = 1, c, m, \sigma) \quad (A.1)$$

The substitution of Eq. (A.1) into Eqs. (3.15)–(3.18), yields:

$$-\frac{d^2\xi_1}{d\zeta^2} = \frac{d^2\xi_1}{d\zeta^2} + (m_{aq} - \omega_{aq}) \frac{K_1}{K_{nl}} \xi_1 - \frac{\beta}{m_{aq}} \xi_1$$ \quad (A.2)

$$-\frac{d^2\xi_2}{d\zeta^2} = B_{\theta} \frac{d^2\xi_2}{d\zeta^2} + \frac{K_2}{\beta K_{nl}} \xi_2$$ \quad (A.3)

$$-\frac{d^2\xi_3}{d\zeta^2} = B_{\sigma} \frac{d^2\xi_3}{d\zeta^2} + \frac{K_3}{K_{nl}} \frac{\omega_{aq}}{K_{nl}} \xi_3 - \frac{1}{\sigma_{eq}} \frac{\xi_4}{\sigma_{eq}}$$ \quad (A.4)

$$-\frac{d^2\xi_4}{d\zeta^2} = B_{\mu} \frac{d^2\xi_4}{d\zeta^2} + \frac{K_4}{K_{nl}} \left(\omega - 1\right) \frac{m_{aq}}{2\beta} \xi_4 - \frac{1}{2\sigma_{eq}} \frac{\xi_4}{\sigma_{eq}}$$ \quad (A.5)

where $\theta = \theta/K_{nl}$ and the rescaled fluxes, $\tilde{\psi}_1$ and $\tilde{\psi}_2$, are defined by expressions analogous to Eqs. (3.19)–(3.20):

$$\tilde{\psi}_1 = \tilde{\psi}_1 - \tilde{\psi}_1 + \frac{\xi_1}{\sigma_{eq}}$$ \quad (A.6)

$$\tilde{\psi}_2 = (m_{aq} - \omega_{aq}) \tilde{\psi}_1 - m_{aq} \tilde{\psi}_2 + \omega_{aq} \tilde{\psi}_1 - (\omega - 1) \tilde{\psi}_2$$ \quad (A.7)

The boundary condition (3.21) is transformed in a universal form, which does not contain $\theta$:

$$\frac{d\xi_1}{d\zeta} = -1, \quad \frac{d\xi_2}{d\zeta} = 0, \quad \frac{d\xi_3}{d\zeta} = 0, \quad \frac{d\xi_4}{d\zeta} = 0 \text{ at } \zeta = 0 \quad (A.8)$$

To solve numerically the boundary problem (A.2)–(A.8), one has to specify the values of the following input parameters: (i) parameters related to the equilibrium micellar solution: $\beta$, $m_{aq}$, $\sigma_{aq}$, and $\omega$; (ii) diffusion and kinetic parameters: $B_{\theta}$ and $K_{nl}/K_{nl}$; and (iii) the dimensionless interfacial expansion rate, $\theta$. It is important to note that the boundary problem (A.2)–(A.8) does not contain the characteristic diffusion time, $\tau_{eq} = \hbar^2/D_{\mu}$. In particular, we have $K_{nl}/K_{nl} = \xi_{eq}/\xi_{eq}$, and $\theta = \theta/K_{nl}$, see Eq. (4.1). Moreover, to solve this dimensionless boundary problem, we have to introduce the absolute value of $m_{aq}$ or $K_{nl}$.

The solution of this problem yields the dependencies $\tilde{\xi}_3(\theta)$ and $\tilde{\xi}_4(\theta)$. To obtain the kinetic diagrams of $\xi_3(\theta)$ and $\xi_4(\theta)$, like those in Figs. 3, 4 and 7–10, one has to specify the value of $K_{nl}$. Because, these diagrams are given in double-logarithmic scale, it is convenient to present the relations between the two types of variables in the form:

$$\log \theta = \log \tilde{\theta} + \log K_{nl} \quad (A.9)$$

$$\log \xi_3 = \log (\xi_3(\theta) b^{1/2}) + \frac{1}{2} \log K_{nl} \quad (A.10)$$

(A.10)

$(i = 1, c, m, \sigma)$. In addition, $\tilde{\xi}_3(\theta) = \xi_3(\theta)$, see Eqs. (4.1) and (A.1). Note that log $K_{nl}$ enters Eqs. (A.9) and (A.10) as an additive term. Consequently, the variation of $K_{nl}$ implies only a simple translation of the curves $\xi_3(\theta)$ and $\xi_4(\theta)$ (in Figs. 3, 4 and 7–10), without changes in their shape. In the case of $\xi_3(\theta)$, the translation is only along the horizontal axis.

As mentioned in Section 3, the interfacial expansion creates a perturbation in the bulk of solution. Under steady-state conditions, the penetration depth of this perturbation depends on the rate of surface expansion, $\theta$. However, in terms of the new variables, defined by Eq. (A.1), $\theta$ disappears from the boundary conditions; compare Eqs. (3.21) and (A.8). For this reason, in terms of $\xi_3$, the penetration depth of the perturbation is universal and decays as $\exp(-\xi_3^2/2)$. Consequently, the width of the integration domain, $0 \leq \xi_3 \leq \xi_{eq}$, determined by $\xi_{eq}$, can be fitted in a universal manner, irrespective of the specific value of $\theta$.

In our computations, we chose $\xi_{eq} = 7$. Indeed, for $\xi_{eq} = 7$ we have $\exp(-\xi_3^2/2) = 2.3 \times 10^{-11}$, and consequently, all perturbations are practically zero for depth $\xi > 7$. 
To solve the boundary problem (A.2)–(A.8), we divided the numerical domain, [0, ξN], on N equal intervals of endpoints ξ0, ξ1, ..., ξN, with step Δξ = ξN/N. We used a second order difference scheme [47]; the first and second derivatives in the bulk are computed as follows:

\[
\frac{d^2f}{d\xi^2} = \frac{f(\xi + \Delta\xi) - 2f(\xi) + f(\xi - \Delta\xi)}{(\Delta\xi)^2} = \frac{f(\xi + \Delta\xi) - f(\xi - \Delta\xi)}{(2\Delta\xi)} \tag{A.11}
\]

In the boundary condition (A.8), the second order forward difference scheme is used for the first derivative [47]:

\[
\frac{df}{d\xi} = \frac{-3f(\xi) + 4f(\xi + \Delta\xi) - f(\xi + 2\Delta\xi)}{(2\Delta\xi)} \tag{A.12}
\]

With the help of Eqs. (A.11) and (A.12), the boundary problem (A.2)–(A.8) is reduced to a linear system of equations, which is solved using the generalized Thomas algorithm [47].

The values of functions in the discrete nodes 0, 1, 2, ..., N are ordered as \(\xi_0, \xi_1, \xi_2, ..., \xi_N\), \(\xi_{\text{d}}(\xi_0), \xi_{\text{d}}(\xi_1), \xi_{\text{d}}(\xi_2), ..., \xi_{\text{d}}(\xi_N)\), etc. This procedure reduces the considered system of equations to a system with eight upper and lower diagonals, which is obtained using the generalized Thomas algorithm [47].

Our calculations have been carried out at \(N = 400\,000\), which gives a very high accuracy of the obtained numerical results: the error in the numerical scheme is of order \((\Delta\xi)^2 = 3.06 \times 10^{-10}\).

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