Colloid Polym Sci 273:370–378 (1995)
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ORIGINAL CONTRIBUTION

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Dynamic surface tension of micellar solutions studied by the maximum bubble pressure method

3. Theory of the solutions containing micelles

Received: 2 April 1991
Accepted: 12 July 1994

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Abstract A theoretical model for the dynamic surface tension of an air bubble expanding in micellar surfactant solution is proposed. The model accounts for the effect of expansion of the bubble surface during the adsorption of surfactant molecules (monomers) and the effect of disintegration of polydisperse micelles on the surfactant diffusion. Assuming small deviations from equilibrium and constant rate of expansion analytical expression for the surface tension and the subsurface concentration of monomers as a function of time is derived. The characteristic time of micellization is computed from the experimental data for two surfactants (sodium dodecyl sulfate and nonylphenol polyglycol ether) obtained by the maximum bubble pressure method.

Key words Dynamic surface tension
– micellar surfactant solutions
– maximum bubble pressure method

Introduction

Micellar surfactant solutions are widely used in many practical processes accompanied by deformation of a single bubble or of foam bubbles. Since the surface properties of a bubble markedly change during these processes, the equilibrium between micelles and monomers (single surfactant molecules) is disturbed. The effect of micelles on the dynamic surface tension $\sigma(t)$ was studied experimentally in ref. [1] by means of the maximum bubble pressure (MBP) method. Two surfactants were investigated: sodium dodecyl sulfate (SDS) and nonylphenol polyglycol ether with 10 mol ethylene oxide, commercially known as Veranol H10. The experiment showed that for both surfactants the micelles appreciably accelerate the surface tension relaxation. In our present study, we propose a theoretical model for the adsorption and diffusion of surfactant species toward an air bubble expanding in a micellar solution which allows to calculate the dynamic surface tension $\sigma(t)$. Our treatment is based on the results of ref. [2] where we considered the simpler case of surfactant solutions without micelles.

To account for the effect of the micelles on the dynamic surface tension one should understand first the micellization kinetics in homogeneous solutions, where the surfactant concentration is uniform at each point of the solution [3–6]. Two subsequent processes of micelle relaxation, fast and slow, are observed experimentally in such systems. To explain their nature, Aniansson and Wall [5, 6] have considered the micelles as polydisperse species of mean aggregation number m and dispersion (variance) ω.

During the fast relaxation process the micelles release monomers and decrease their (average) size keeping the total micelle concentration, c_m, constant. During the slow process some of the micelles disintegrate in order to restore the equilibrium with the free monomers. Fast and slow relaxation processes results in an exponential decay of the concentration of free monomers with time t with decay constant τ_F and τ_{SL} respectively ($\tau_F \ll \tau_{SL}$). Aniansson and Wall have derived the following expressions for the time constants τ_F and τ_{SL}:

Fast relaxation process:

$$\frac{1}{\tau_F} = \frac{k_m^-}{\omega^2}\left(1 + \frac{\omega^2}{m}\theta\right), \tag{1.1}$$

where k_m^- is mean dissociation rate constant of the micelles; θ is excess concentration of monomers, aggregated in micelles

$$\theta = \frac{\bar{c} - \bar{c}_1}{\bar{c}_1} = \frac{m\bar{c}_m}{\bar{c}_1} \tag{1.2}$$

$\bar{c}_1$ is the concentration of free monomers which is equal to the critical micelle concentration (CMC); $\bar{c}$ is the total surfactant concentration, $\bar{c} = \bar{c}_1 + m\bar{c}_m$ (bar above the letter denotes equilibrium quantity). Equation (1.1) allows to calculate m and ω from experimental data, e.g., for SDS $m = 64$ and $\omega = 13$ [6].

Slow relaxation process:

$$\frac{1}{\tau_{SL}} = \frac{m}{R_M \bar{c}_1 \theta} \, \frac{1 + \frac{m_2}{m}\theta}{1 + \frac{\omega^2}{m}\theta}, \tag{1.3}$$

where $m_2 = m^2 + \omega^2$; R_M is the so-called resistance of the premicellar aggregates (rare micelles). R_M is a complicated function of θ and the temperature. For example, for SDS solution $R_M = 1.8 \times 10^5$ cm^2.s/mol at $\theta = 1$ and temperature 25 °C [6].

In view of Eqs. (1.1) and (1.3) the time constant τ_F and τ_{SL} depend on the parameters of micelle size distribution, the reaction path-way and the amount of monomers aggregated in micelles (θ). While τ_F^{-1} increases linearly with θ, τ_{SL}^{-1} can be more complicated function of θ, observed also experimentally [6].

The micellization kinetics seems rather different in nonhomogeneous solutions, where diffusion of surfactant takes place simultaneously in the solution [7]. In this case the diffusion is coupled with the micellization. If the equilibrium between the adsorption layer and the subsurface layer is perturbed, free surfactant monomers are transferred by diffusion from the bulk of solution to the interface. Since this disturbs the local equilibrium between free monomers and micelles, the micelles diffuse, too. However, it is not clear in advance which type of relaxation, fast or slow, affects the surfactant diffusion.

Recently, Feinerman and Rakita [8] published MBP-data for micellar solutions of SDS containing 0.1 M NaCl. They calculated micellization time constant τ_M using for the dynamic surface tension

$$\sigma(v) = \bar{\sigma} - \frac{R_g T_a \Gamma_\infty^2}{\bar{c}_1} \, \frac{\sqrt{\frac{\pi v}{2D_1}}}{1 + \sqrt{\frac{\pi}{2v\tau_M}}}. \tag{1.4}$$

Here, $R_g = 8.314 \times 10^7$ dyn.cm/K.mol; T_a is the absolute temperature; Γ_∞ is the saturation adsorption; $v \sim t^{-1}$ is the bubbling frequency; D_1 is the monomer diffusivity. In deriving Eq. (1.4) it is not specified to which micellization process, fast or slow, corresponds the time constant τ_M. Feinerman and Rakita have obtained two values of τ_M of the order of several seconds: $\tau_M = 12$ s at $\bar{c} = 2 \times 10^{-6}$ mol/cm^3, and $\tau_M = 3.7$ s at $\bar{c} = 4 \times 10^{-6}$ mol/cm^3 (CMC of SDS plus 0.1 M NaCl is 1.16×10^{-6} mol/cm^3). The authors have attributed τ_M to the slow relation process although their diffusion model seems too simplified to include all features of the kinetics of micellization as described in the theory of Aniansson and Wall [5, 6].

The other models for the adsorption kinetics in the presence of micelles, available in literature, consider quiescent solution with constant surface area. Moreover, most of them oversimplify the micellization kinetics (for a review see ref. [7]). Bearing in mind that the diffusion of monomers can be characterized by its own time constant τ_D, one can expect that only one of the micelle relaxation processes considered above could affect the dynamic surface tension. This is that process, whose time constant (τ_F or τ_{SL}) is comparable with τ_D. The diffusion time τ_D is a measure for the speed the concentration gradients spread in the solution. That is why only a micellization process commensurable to the diffusion could be observed experimentally. Knowing the micellization time constants, taken from independent kinetic experiment, and the diffusion time constant, measured in MBP-experiment below CMC, one can conclude which micellization process could influence the dynamic surface tension.

The same idea was used independently by Noskov [9] whose approach to the adsorption kinetics from micellar solutions is quite similar to the approach used in ref. [7].

In Section 2 we derive new equations for the convective diffusion of polydisperse micelles. This equations are solved in Section 3 to obtain expressions for the dynamic surface tension and for the subsurface concentration. Using these expressions we compute in Section 4 the micellization time constant from MBP-data for SDS and Veranol H10 published in ref. [1].

Diffusion model

To account for the effect of micelles, one should postulate first the way they form. Following Aniansson and Wall we consider a step-wise reaction mechanism of formation of one s-mer A_s, an aggregate containing s monomers,

$$A_1 + A_{s-1} \underset{k_s^-}{\overset{k_s^+}{\longleftrightarrow}} A_s, \quad s = 2, 3, 4, \ldots, \tag{2.1}$$

k_s^+ and k_s^- are the rate constants of association and dissociation, respectively. Expression (2.1) describes shift in the equilibrium between the aggregates caused by any local disturbance in their bulk concentrations, e.g., due to concentration gradients in the vicinity of expanding air bubble. Based on (2.1) the convective diffusion of species is described by the following set of equations:

$$\frac{\partial c_1}{\partial t} + V\frac{\partial c_1}{\partial x} = D_1\frac{\partial^2 c_1}{\partial x^2} + 2J_2 + \sum_{s=3}^{\infty} J_s \tag{2.2a}$$

$$\frac{\partial c_s}{\partial t} + V\frac{\partial c_s}{\partial x} = D_s\frac{\partial^2 c_s}{\partial x^2} + J_s - J_{s+1}\,, \quad s = 2, 3, 4, \ldots \tag{2.2b}$$

$$J_s = k_s^+ c_1 c_{s-1} - k_s^- c_s\,, \quad s = 2, 3, 4, \ldots \tag{2.3}$$

$$\sum_{s=1}^{\infty} c_s = c \tag{2.4}$$

The bubble surface is considered as a flat interface with space variable x because the characteristic diffusion length is much smaller than the bubble radius [2]. $c_s(x, t)$ is the s-mer concentration; $V(x, t)$ is the hydrodynamic velocity; D_s is the s-mer diffusivity; $J_s(x, t)$ is the total rate of s-th elementary reaction (2.1), called reaction flux [6]. Equation (2.2a) describes the diffusion of the free monomers with source terms, containing J_s, which give the influx of monomers released by the aggregates at the s-th reaction. The source terms J_s and J_{s+1} in (2.2b) account for that s-mers produced at the s-th reaction are consumed at the $(s + 1)$-th reaction respectively. The local conservation of monomers, Eq. (2.4), shows that the total surfactant concentration $c(x, t)$ is no longer constant as accepted in the usual micellization kinetics [6]. The reason is the adsorption and diffusion of monomers creating local concentration gradients which can lead in turn to $c \neq \bar{c}$.

The boundary and initial conditions for the concentrations of species are

$$\frac{1}{A}\frac{d}{dt}(A\Gamma) = D_1\left.\frac{\partial c_1}{\partial x}\right|_{x=0} \tag{2.5a}$$

$$\left.\frac{\partial c_s}{\partial x}\right|_{x=0} = 0, \quad s = 2, 3, 4, \ldots \tag{2.5b}$$

$$c_1(0, t) = \Phi(t) \tag{2.5c}$$

$$c_s(\infty, t) = \bar{c}_s, \quad s = 1, 2, 3, \ldots \tag{2.5d}$$

$$c_s(x, 0) = \bar{c}_s, \quad s = 1, 2, 3, \ldots \tag{2.5e}$$

$$c_1(0, 0) = \Phi_0, \tag{2.5f}$$

$$\Gamma(t) = \Gamma_0 \tag{2.5g}$$

Here, $\Gamma(t)$ is the adsorption; $\Phi(t)$ is the subsurface concentration of free monomers; Γ_0 and Φ_0 are the respective initial values (if $\sigma(0)$ is equal to the surface tension of pure water, then $\Gamma_0 = 0$ and $\Phi_0 = 0$). Equation (2.5a) is the conservation of monomers on an expanding bubble surface of area $A(t)$. Equations (2.5b) state that the aggregates $(s > 2)$ do not adsorb onto the bubble surface. On the other hand, the concentrations of species far from the bubble should be equal to their equilibrium values $\bar{c}_s$ - Eqs. (2.5d).

Since the mathematical problem formulated above cannot be solved analytically in its general form, we simplify the set of differential equations (2.2) by taking into account the contribution of fluxes J_s during the micelle relaxation. Following the procedure developed in ref. [7], we substantially reduce the number of equations. Assuming small deviations from equilibrium the relative concentrations of s-mers, $\xi_s(x, t)$, obey the conditions

$$|\xi_s| = \left|\frac{c_s - \bar{c}_s}{\bar{c}_s}\right| \ll 1, \quad s = 1, 2, 3, \ldots\,,$$

so that the fluxes (2.3) become

$$J_s = k_s^- \bar{c}_s(\xi_1 + \xi_{s-1} - \xi_s), \quad s = 2, 3, 4, \ldots \tag{2.6}$$

Three large groups of s-mers which determine the behavior of the micellar system as a whole can be distinguished: oligomers $(s = 1\,, 3, \ldots, s_1)$, premicellar aggregates $(s = s_1 + 1, s_1 + 2, s_1 + 3, \ldots, s_2)$ and abundant micelles $(s = s_2 + 1, s_2 + 2, s_2 + 3, \ldots, s_3;\ s_3 \to \infty)$. The fluxes J_s in the oligomer and micelle regions, important during the fast relaxation process, are scaled by the characteristic flux $J_F = \bar{c}_1/\tau_F$. The fluxes in the premicellar region, important during the slow relaxation process, are scaled by $J_{SL} = \bar{c}_1/\tau_{SL}$. When the diffusion is affected by the slow relaxation process $(\tau_D \sim \tau_{SL})$, the fluxes in the regions of oligomers and of micelles are neglected. In the opposite case of diffusion influenced by the fast relaxation process $(\tau_D \sim \tau_F)$ the respective fluxes in the premicellar region are disregarded. Hence, the number of source terms is greatly decreased which allows to sum up the respective diffusion equations for s-mers introducing average quantities describing the cooperative behavior of the species.

Finally, we obtain two pairs of diffusion equations for the free monomers and the micelles valid for diffusion affected either by the slow relaxation process or by the fast process:

1) $\tau_D \sim \tau_{SL}$. In this case,

$$\frac{\partial \xi_1}{\partial t} + V\frac{\partial \xi_1}{\partial x} = D_1^* \frac{\partial^2 \xi_1}{\partial x^2} - \frac{m}{R_M \bar{c}_1} \frac{1}{1 + \frac{\omega^2}{m}\theta}(m\xi_1 - \xi_m) \tag{2.7a}$$

$$\frac{\partial \xi_m}{\partial t} + V\frac{\partial \xi_m}{\partial x} = D_m \frac{\partial^2 \xi_m}{\partial x^2} - \frac{m}{R_M \bar{c}_1 \theta}(m\xi_1 - \xi_m)\,. \tag{2.7b}$$

Here, $\xi_m(x, t)$ is relative deviation of the total micelle concentration from equilibrium

$$\xi_m = \frac{1}{\bar{c}_m} \sum_{s_2+1}^{s_3} c_s \xi_s = \frac{c_m - \bar{c}_m}{\bar{c}_m}\,,$$

where

$$c_m = \sum_{s_2+1}^{s_3} c_s\,.$$

D_m is the mean diffusivity of micelles if all the abundant micelles are supposed to be of approximately equal diffusivities (i.e., $D_s \cong D_m$). D_1^* is an effective diffusivity of the free monomers defined by [7]

$$D_1^* = D_1 \frac{1 + \frac{D_m}{D_1}\frac{\omega^2}{m}\theta}{1 + \frac{\omega^2}{m}\theta}\,. \tag{2.8}$$

D_1^* accounts for the polydispersity of micelles and is equal to D_1 for monodisperse micelles, where $\omega = 0$, or below CMC, where $\theta = 0$. Equation (2.8) differs from the respective equation of Joos and Van Hunsel [10], which reads in our notations,

$$D_1^* = D_1(1 + m\theta)\left(1 + \frac{D_m}{D_1} m\theta\right). \tag{2.9}$$

Equation (2.9) is derived for monodisperse micelles ($\omega = 0$) assuming a local equilibrium between monomers and micelles, i.e., zero reaction flux (see also ref. [11]). This assumption is valid only if the micellization is much faster than the diffusion, which is not the case $\tau_D \sim \tau_{SL}$ considered by us.

2) $\tau_D \sim \tau_F$. The final diffusion equations read

$$\frac{\partial \xi_1}{\partial t} + V\frac{\partial \xi_1}{\partial x} = D_1 \frac{\partial^2 \xi_1}{\partial x^2} - \frac{k_m^-}{m}\theta\left(\xi_1 - \frac{1}{\omega^2}\zeta_m\right) \tag{2.10a}$$

$$\frac{\partial \zeta_m}{\partial t} + V\frac{\partial \zeta_m}{\partial x} = D_m \frac{\partial^2 \zeta_m}{\partial x^2} + k_m^-\left(\xi_1 - \frac{1}{\omega^2}\zeta_m\right), \tag{2.10b}$$

where $\zeta_m(x, t)$ is relative deviation of the total amount of monomers aggregated in micelles

$$\zeta_m = \frac{1}{\bar{c}_m} \sum_{s_2+1}^{s_3} s\bar{c}_s \xi_s\,.$$

Equation (2.10b) is a counterpart of Eq. (2.7b) for the case $\tau_D \sim \tau_F$, since the total micelle concentration remains constant ($\xi_m = 0$) as during the fast process in homogeneous solutions [5, 6]. However, the micelles belonging to each s-mer fraction can diffuse which leads to variation of ζ_m. An appropriate boundary condition for ζ_m can be derived from Eqs. (2.5b, d, e).

To further simplify Eqs. (2.5), (2.7) and (2.10), we expand in series the adsorption and the surface tension

$$\Gamma(t) = \bar{\Gamma} + \frac{d\bar{\Gamma}}{d\bar{c}_1}\bar{c}_1 \xi_1(0, t) \tag{2.11a}$$

$$\sigma(t) = \bar{\sigma} + \frac{d\bar{\sigma}}{d\bar{c}_1}\bar{c}_1 \xi_1(0, t)\,. \tag{2.11b}$$

In view of (2.11a) it is appropriate to scale the space variable x by the characteristic diffusion length

$$\delta_D = \frac{d\bar{\Gamma}}{d\bar{c}_1} \tag{2.12a}$$

while time t is scaled by the diffusion time

$$\tau_D = \frac{1}{D_1}\left(\frac{d\bar{\Gamma}}{d\bar{c}_1}\right)^2. \tag{2.12b}$$

The convective terms are scaled by an appropriate characteristic velocity to make them of the same order as the diffusion terms. Here, we use the velocity profile proposed in ref. [2]

$$V = -\dot{\alpha}x \cong -\dot{\alpha}\delta_D\,, \tag{2.13}$$

where

$$\dot{\alpha} = \frac{1}{A}\frac{dA}{dt} \approx \text{const}$$

is the rate of bubble expansion. As motivated in ref. [2] $\dot{\alpha}$ can be considered constant throughout the bubble growth.

Finally, we assume that the total surfactant concentration remains constant

$$c(x, t) \cong \bar{c} \tag{2.14}$$

which is equivalent to the assumption $D_1 \cong D_m$, i.e. the micelles and the free monomers are of equal rate of diffusion. In view of Eqs. (2.13) and (2.14) both (2.7a) and (2.10a) reduce to one and the same equation

$$\frac{\partial \xi_1}{\partial t} - \dot{\alpha}\delta_D \frac{\partial \xi_1}{\partial x} = D_1 \frac{\partial^2 \xi_1}{\partial x^2} - \frac{1}{\tau_M}\xi_1\,, \tag{2.15}$$

where τ_M is either τ_F or τ_{SL}. Equation (2.15) can be postulated directly, if the micellization kinetics is considered as a reaction of pseudo-first order. Such an equation has already been used (without convective term) by Rillaerts and Joos [12] to find an expression for $\Gamma(t)$ (see below Eq. (B.1)). We reveal the meaning of the coefficient $1/\tau_M$ in Eq. (2.15) which is the (reverse) micellization time constant given by (1.1) or (1.3) rather than the demicellization rate constant [12].

In the next section we solve Eq. (2.15) to obtain the dynamic surface tension of the solution.

Dynamic surface tension

Based on Section 2, we can write Eqs. (2.15) and (2.5) in a dimensionless form

$$\frac{\partial \xi_1}{\partial T} - a\frac{\partial \xi_1}{\partial X} = \frac{\partial^2 \xi_1}{\partial X^2} - \mathrm{Da}\,\xi_1 \tag{3.1a}$$

$$\frac{\partial \xi_1}{\partial T} + a(b + \xi_1) = \left.\frac{\partial \xi_1}{\partial X}\right|_{x=0} \tag{3.1b}$$

$$\xi_1(\infty, T) = 0 \tag{3.1c}$$

$$\xi_1(0,0) = \xi_{10}\,, \tag{3.1d}$$

where $X = x/\delta_D$, $T = t/\tau_D$, $a = \dot{\alpha}\tau_D$, $b = \bar{\Gamma}/\bar{c}_1\delta_D$; $\xi_{10} = (\Phi_0 - \bar{c}_1)/\bar{c}_1$; $\mathrm{Da} = \tau_D/\tau_M$ is the Damköhler number giving the ratio between the diffusion term and the micellization source term in Eq. (2.15).

The mathematical problem described by Eqs. (3.1) is solved by means of Laplace transformation to obtain the respective image of free monomers concentration. After that, this image is inverted in Appendix A to finally yield

$$\begin{aligned}\frac{\Delta\sigma(T)}{\Delta\sigma_0} &= \frac{\xi_1(0,T)}{\xi_{10}}\\ &= \frac{1}{2G}\mathrm{e}^{-\frac{(a^2+4\mathrm{Da})T}{4}}\left\{(1+G)\mathrm{E}\left[(1+G)\frac{\sqrt{T}}{2}\right]\right.\\ &\quad\left.-(1-G)\mathrm{E}\left[(1-G)\frac{\sqrt{T}}{2}\right]\right\}\\ &\quad+\frac{E_G}{2\Delta\sigma_0}\,\frac{a}{2a^2-\mathrm{Da}}\left\{3a-\sqrt{(a^2+4\mathrm{Da})}\right.\\ &\quad\times\left\{1-\mathrm{e}^{-\frac{(a^2+4\mathrm{Da})T}{4}}\,\mathrm{E}\left[\frac{\sqrt{(a^2+4\mathrm{Da})T}}{2}\right]\right\}\\ &\quad+\frac{1}{2G}\mathrm{e}^{-\frac{(a^2+4\mathrm{Da})T}{4}}\left\{(1-G-3a)(1+G)\right.\\ &\quad\times\mathrm{E}\left[(1+G)\frac{\sqrt{T}}{2}\right]-(1+G-3a)(1-G)\\ &\quad\left.\left.\times\mathrm{E}\left[(1-G)\frac{\sqrt{T}}{2}\right]\right\}\right\}.\end{aligned} \tag{3.2}$$

Here, $\Delta\sigma = \sigma(T) - \bar{\sigma}$, $\Delta\sigma_0 = \sigma(0) - \bar{\sigma}$,

$$G = \sqrt{1 - a(6-a) + 4\mathrm{Da}} \tag{3.3a}$$

$$\mathrm{E}(z) = e^{z^2}\operatorname{erfc}(z) \tag{3.3b}$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{y^2}\,dy = 1 - \operatorname{erfc}(z)\,. \tag{3.3c}$$

E_G is the Gibbs elasticity, $E_G = -\,d\bar{\sigma}/d(\ln\bar{\Gamma})$. Equation (3.2) represents the dynamic surface tension affected by the convection and the expansion of bubble surface which are accounted for by the dimensionless parameter $a = \dot{\alpha}\tau_D$. The other parameter, $\mathrm{Da} = \tau_D/\tau_M$, accounts for the effect of micellization kinetics on the diffusion of monomers. Depending on the magnitude of a and Da there are special cases of Eq. (3.2):

i) If the surfactant concentration is below CMC, i.e., no micelles are present in the solution, the limit $\tau_M \to \infty$ ($\mathrm{Da} = 0$) should be carried out in (3.2) to give Eq. (2.18) from ref. [2] at $G = \sqrt{1 - a(6-a)}$.

ii) When a quiescent liquid and nonexpanding surface is considered ($a = 0$) Eq. (3.2) transforms into

$$\begin{aligned}\frac{\Delta\sigma(T)}{\Delta\sigma_0} = \frac{\xi_1(0,T)}{\xi_{10}} = \frac{1}{2G}e^{-\mathrm{Da}T}&\left\{(1+G)\mathrm{E}\left[(1+G)\frac{\sqrt{T}}{2}\right]\right.\\ &\left.-(1-G)\mathrm{E}\left[(1-G)\frac{\sqrt{T}}{2}\right]\right\}\end{aligned} \tag{3.4}$$

derived first in ref. [7] at $G = \sqrt{1 + 4\mathrm{Da}}$.

iii) There is a peculiar point in Eq. (3.2) at $1 - a(6-a) + 4\mathrm{Da} = 0$. This case, together with the case of negative values of the quantity under the radical sign in (3.3a), can be treated as in Appendix A of ref. [2].

An alternative procedure for deriving Eq. (3.2) by means of a model subsurface concentration is proposed in Appendix B.

Results and discussion

To check the applicability of our theory, we process experimental data for the dynamic surface tension of micellar surfactant solutions measured in ref. [1]. The expansion rate $\dot{\alpha}$ was not measured in our experiment, however, as shown in ref. [2], a seems always close to zero. Since the initial value of the surface tension $\sigma(0)$ is not exactly known, we first transform the data for $\sigma(t)$ into data for the subsurface concentration $\Phi(t)$ – see Fig. 1. Bearing in mind that $\sigma(0)$ should be close to the surface tension of pure water one can expect that $\Phi_0 \approx 0$. Hence, it follows from Eq. (3.4) that the subsurface concentration of free monomers is given by

$$\frac{\Phi(t)}{\bar{c}_1} = 1 - \frac{1}{2G} e^{-\mathrm{Da}\frac{t}{\tau_D}} \left\{ (1+G)\mathrm{E}\left[\frac{1+G}{2}\sqrt{\frac{t}{\tau_D}}\right] - (1-G)\mathrm{E}\left[\frac{1-G}{2}\sqrt{\frac{t}{\tau_D}}\right] \right\} \qquad (4.1)$$

Special case of (4.1) is Eq. (3.2) from ref. [2] for solution without micelles ($\mathrm{Da} = 0$, $G = 1$).

Below we apply Eq. (4.1) to fit two series of experimental data for solutions of SDS and of Veranol H10.

SDS solutions

There are two unknown parameters in Eq. (4.1): τ_D and Da, i.e. τ_M. Fortunately, the diffusion time τ_D is constant above CMC, because the concentration of free monomers does not change ($\bar{c}_1 = \mathrm{CMC}$). That is why we chose for SDS the value $\tau_D = 8.1 \times 10^{-3}$ s obtained at concentration $\bar{c}_1 = 8 \times 10^{-6}$ mol/cm^3 [2]. Hence, there is only one adjustable parameter, τ_M, which was obtained by fitting experimental points using the numerical method described in ref. [2].

Figure 1 compares the experimental data for micellar solutions of SDS with the theoretical fits drawn by Eq. (4.1) (solid lines). It is seen that the micelles enhance substantially the relaxation of the surface tension in comparison with the case without micelles (dashed line). The coincidence between theory and experiment looks fairly good for the lowest surfactant concentration 1.2×10^{-5} mol/cm^3 (empty circles) and satisfactory for concentration 1.6×10^{-5} mol/cm^3 (solid circles). At the same time, the theoretical curves deviate from the experimental data for the other two concentrations (2.4×10^{-5} and 3.2×10^{-5} mol/cm^3) represented by empty and solid boxes. This discrepancy can be explained primarily by very fast relaxation of surface tension at so high surfactant concentrations which cannot be followed adequately due to experimental uncertainty at high bubbling frequencies. This results in only a few experimental points being suitable for theoretical treatment (each point in Fig. 1 corresponds to a single frequency ν).

Nevertheless, the computed values of τ_M for different surfactant concentration listed in Table 1 seem quite reasonable. All of them are in the millisecond region in similarity with the diffusion time τ_D. The same values of τ_M are plotted as squares in Fig. 2 versus the excess surfactant concentration θ defined by Eq. (1.2). With increasing of the micellar concentration $\bar{c}_m$, i.e., θ, the reverse time constant τ_M^{-1} increases since the micellization time τ_M, computed by us, decreases. This means that the micellization kinetics becomes faster. Our results for τ_M are compared in Fig. 2

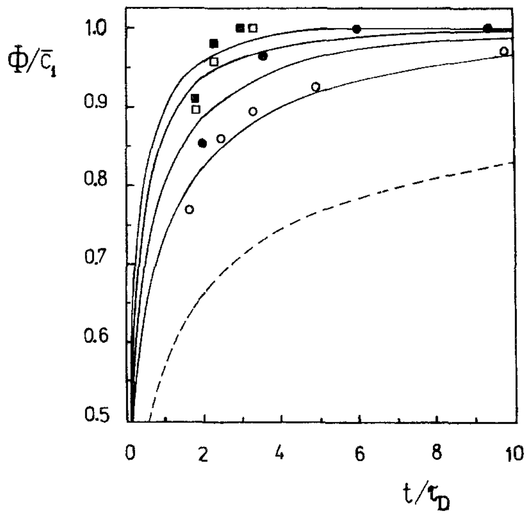
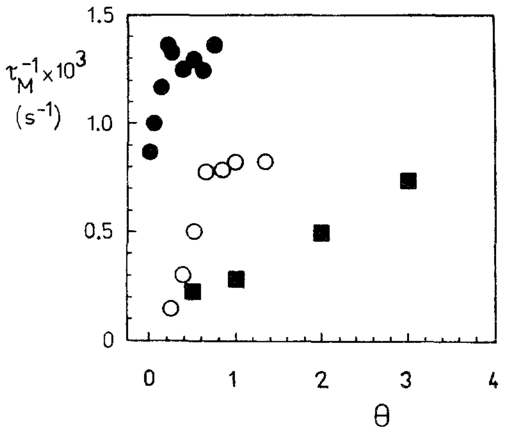


Fig. 1 Subsurface concentration $\Phi(t)$ of micellar SDS solutions with different surfactant concentration in mol/cm^3: 1.2×10^{-5} (○); 1.6×10^{-5} (●); 2.4×10^{-5} (□); 3.2×10^{-5} (■). Data are measured by the MBP-method at 25 °C [1]. The solid lines are drawn by Eq. (4.1), while the dashed line corresponds to the case below CMC [2] ($\tau_D = 8.1 \times 10^{-3}$ s)

Table 1 Parameters of micellar SDS solutions

$\bar{c} \times 10^5$ (mol/cm^3)	θ	$\tau_M \times 10^3$ (s)	Da
1.2	0.5	4.5	1.82
1.6	1.0	3.6	2.26
2.4	2.0	2.1	3.96
3.2	3.0	1.1	7.11

Fig. 2 Concentration dependence of the reverse relaxation time of micellization τ_M^{-1} of SDS solutions computed from the data in Fig. 1 (■). The experimental data of other authors are obtained by means of the p-jump method at 25 °C in ref. [3] (○) and ref. [4] (●), respectively



with experimental data of other authors for the slow relaxation time τ_{SL} [3, 4]. These data are measured by p-jump relation method at the same temperature (25 °C).

One can conclude from the results in Fig. 2 that the values of τ_M obtained by the MBP-method, a sort of surface stress relaxation experiment, are of the same order of magnitude as the values of τ_{SL}, obtained by the p-jump method which is a bulk relaxation technique. In the former method the concentration of species in the solution, except with time, varies also with the distance from the air/water interface thus creating concentration gradients which can affect in turn the micellization kinetics. In the latter method the concentration remains one and the same at any point of the solution varying only with time. The different way the micellization kinetics is influenced by the surfactant concentration can explain the difference in the values of τ_M obtained by the MBP-method and the values of τ_{SL} measured by other bulk relaxation methods. Besides, even values of τ_M measured by one and the same chemical relaxation technique, e.g. p-jump, can differ appreciably. The slow relaxation time, τ_{SL}, can exhibit a complicated concentration dependence (cf. (1.3)) because the resistance of the premicelle region, R_M, is also a function of θ. As seen from Fig. 2 τ_M, obtained in MBP-experiment, increases with θ in a similar way as τ_{SL} measured by p-jump technique. At the same time, the magnitude of τ_M differs appreciably from the characteristic time of fast relaxation τ_F which lays for SDS in the microsecond region ($\tau_F^{-1} \sim 10^5$–$10^6\ \mathrm{s}^{-1}$ [6]).

The lack of exact coincidence between τ_M and τ_{SL} can be due also to the approximations made in our theory. For example, disregarding of convection and expansion of the bubble surface can lead to smaller diffusion time τ_D than in the case of immobile surface. Hence, the values of τ_M can be smaller than the expected ones, i.e., τ_M^{-1} will be larger. On the other hand, the diffusivities of micelles and free monomers are not equal as accepted in our model. For SDS they are $D_1 = 5.7 \times 10^{-6}\ \mathrm{cm}^2/\mathrm{s}$ and $D_m \cong 10^{-6}\ \mathrm{cm}^2/\mathrm{s}$ [13]. Finally, the disregard of the surface tension gradient along the bubble surface (effect of Marangoni) can also influence the calculated values of τ_M, like that of τ_M (for comments see ref. [2]).

Nevertheless, one can conclude that the diffusion in SDS solutions is most probably affected by the slow relaxation process of micellization.

Veranol H10 solutions

The MBP-data for the dynamic surface tension of Veranol H10 solutions [1] are processed in the same way as the data for SDS. We obtained first diffusion time constant $\tau_D = 14.66$ s at concentration $\bar{c}_1 = 3.16 \times 10^{-8}\ \mathrm{mol/cm}^3$ (close to CMC which is about $5 \times 10^{-8}\ \mathrm{mol/cm}^3$). Figure 3 shows the reverse micellization time τ_M^{-1} vs the excess concentration of micelles θ. The values of τ_M at concentrations 10^{-7} and $10^{-6}\ \mathrm{mol/cm}^3$ are calculated by means of Eq. (4.1). The other two values, at concentrations 3.16×10^{-6} and $10^{-5}\ \mathrm{mol/cm}^3$, are computed by the approximate equation

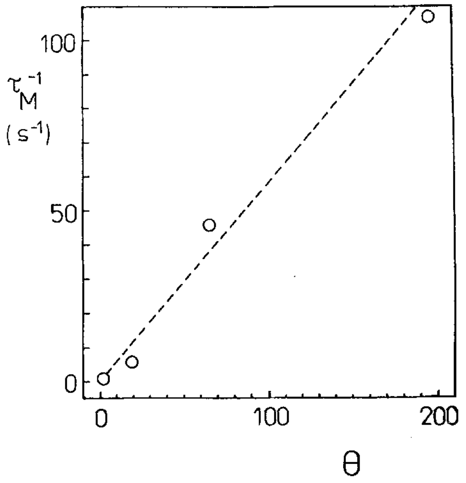


Fig. 3 Concentration dependence of the reverse relaxation time of micellization τ_M^{-1} of Veranol H10 solutions computed from the data measured by the MBP-method at 25 °C [1] ($\tau_D = 14.66$ s). Dashed line is drawn as a guide for the eye

$$\frac{\Phi(t)}{\bar{c}_1} = 1 - \mathrm{e}^{-\mathrm{Da}\frac{t}{t_D}} \tag{4.2}$$

Equation (4.2) is applicable at large Damköhler numbers (Da $\gg$ 1) [7] and reflects a change in the way the monomers have been transported to the bubble surface. At the smaller surfactant concentrations the monomers (and the micelles) can diffuse to supply the bubble surface with material. At the higher concentrations, however, the amount of micelles becomes so large that they can exchange monomers directly with the surface adsorption layer. As seen from Fig. 3, τ_M^{-1} is an almost linear function of θ following the general trend to increase (τ_M to decrease) with increasing the concentration of micelles. Since τ_M for Veranol H10 varies in a fairly large limits (from 0.005 to 1 s) it is not clear which of the relaxation processes (fast or slow) affects the dynamic surface tension. Besides, data for the micellization kinetics of this surfactant are not available from an independent bulk experiment.

Qualitatively, Veranol H10 exhibits slower mass transfer than SDS. However, diffusion and micellization of Veranol H10 seems faster than in the case of another nonionic surfactant Brij 58. Recently, we obtained in independent experiment [14] $\tau_M = 18.9$ s and $\tau_M = 5.9$ s at two different rates of expansion of an oil drop in Brij 58 solution of concentration 7.5×10^{-9} mol/cm^3 (CMC is 3.16×10^{-6} mol/cm^3). The diffusion time constant in this case is $\tau_D = 180$ s.

One can conclude from the theoretical fits of the dynamic surface tension of micellar SDS and Veranol H10 that the MBP-method may serve as a sensitive tool for direct observation of the micellization kinetics in the solution.

Acknowledgements The authors are indebted to Prof. I. B. Ivanov for encouragement of the investigations. The financial support of the Bulgarian Ministry of Science and Education is acknowledged.

Appendix A

Solving Eqs. (3.1) we obtain the Laplace image of subsurface concentration

$$\frac{\hat{\xi}_1(0,p)}{\xi_{10}} = \frac{1}{p + \sqrt{p + \frac{a^2}{4} + \mathrm{Da} + \frac{3a}{2}}} + \frac{aE_G}{\Delta\sigma_0} \frac{1}{p\left(p + \sqrt{p + \frac{a^2}{4} + \mathrm{Da} + \frac{3a}{2}}\right)}, \qquad \text{(A.1)}$$

where p is parameter of transformation. To invert the image (A.1), we replace p by a new parameter, $q = p + a^2/4 + \mathrm{Da}$, so that

$$\frac{\hat{\xi}_1(0,p)}{\xi_{10}} = \frac{1}{q + \sqrt{q} + K} + \frac{aE_G}{\Delta\sigma_0} \frac{1}{\left(q - \frac{a^2}{4}\right)(q + \sqrt{q} + K)}, \qquad \text{(A.2)}$$

where $K = a(6-a)/4 - \mathrm{Da}$. The first term on the right-hand side of (A.2) can be expressed as

$$\frac{1}{q + \sqrt{q} + K} = \frac{1}{\beta - \gamma}\left(\frac{1}{\beta + \sqrt{q}} - \frac{1}{\gamma + \sqrt{q}}\right), \qquad \text{(A.3)}$$

where $\beta = (1 - G)/2$, $\gamma = (1 + G)/2$ and $G = \sqrt{1 - 4K}$. The second term in (A.2) can be expanded as

$$\frac{1}{\left(q - \frac{a^2}{4}\right)(q + \sqrt{q} + K)} = \frac{1}{a^2}\frac{1}{\frac{a}{2} + \sqrt{q}} - \frac{1}{2a^2}\frac{1}{\frac{a}{2} - \sqrt{q}} + \frac{1 - \beta - \frac{3a}{2}}{(2a^2 - \mathrm{Da})(\beta - \gamma)}\frac{1}{\beta + \sqrt{q}} + \frac{1 - \gamma - \frac{3a}{2}}{(2a^2 - \mathrm{Da})(\beta - \gamma)}\frac{1}{\gamma + \sqrt{q}}. \qquad \text{(A.4)}$$

Finally, we insert (A.3) and (A.4) into (A.2) and invert it to its original (3.2).

Appendix B

Here, we aim to derive Eq. (3.4) by using a model profile for the subsurface concentration $\Phi(t)$. Starting point is the equation for the adsorption $\Gamma(t)$ derived in ref. [12] if the micellization kinetics is described by Eq. (2.15) at $\dot{\alpha} = 0$

$$\Gamma(t) = \bar{c}_1 \sqrt{D_1 \tau_M}\left[\left(\frac{1}{2} + \frac{t}{\tau_M}\right)\mathrm{erf}\left(\sqrt{\frac{t}{\tau_M}}\right) + e^{-\frac{t}{\tau_M}}\sqrt{\frac{t}{\pi\tau_M}}\right] - \sqrt{\frac{D_1}{\tau_M}}\left[\int_0^t \Phi(\tau)\,\mathrm{erf}\left(\sqrt{\frac{t-\tau}{\tau_M}}\right)d\tau + \sqrt{\frac{\tau_M}{\pi}}\int_0^t e^{-\frac{t-\tau}{\tau_M}}\frac{\Phi(\tau)\,d\tau}{\sqrt{t-\tau}}\right]. \qquad \text{(B.1)}$$

To obtain an explicit time dependence of Γ one should know $\Phi(t)$. Based on Eq. (4.1), we propose that

$$\Phi(t) = \bar{c}_1\left\{1 - e^{-\frac{t}{\tau_M}}\left[b_1 \mathrm{E}(\sqrt{\chi_1 t}) - b_2 \mathrm{E}(\sqrt{\chi_2 t})\right]\right\}, \qquad \text{(B.2)}$$

where the constants $b_j = b_j(\tau_D, \tau_M)$ and $\chi_j = \chi_j(\tau_D, \tau_M)$ ($j = 1, 2$) will be determined thereafter.

Let us combine (B.1) and (B.2) and calculate respective integrals:

$$\int_0^t \mathrm{erf}\left(\sqrt{\frac{t-\tau}{\tau_M}}\right)d\tau = \left(t - \frac{\tau_M}{2}\right)\mathrm{erf}\left(\sqrt{\frac{t}{\tau_M}}\right) + e^{-\frac{t}{\tau_M}}\sqrt{\frac{\tau_M t}{\pi}} \qquad \text{(B.3)}$$

$$\int_0^t \mathrm{e}^{-\frac{t-\tau}{\tau_M}}\frac{d\tau}{\sqrt{t-\tau}} = \sqrt{\pi\tau_M}\,\mathrm{erf}\left(\sqrt{\frac{t}{\tau_M}}\right) \qquad \text{(B.4)}$$

$$I(t) = \int_0^t \frac{\mathrm{E}\left(\sqrt{\frac{\tau}{\tau_M}}\right)d\tau}{\sqrt{t-\tau}} = \sqrt{\pi\tau_M}\left[1 - \mathrm{E}\left(\sqrt{\frac{\mathrm{t}}{\tau_M}}\right)\right] \qquad \text{(B.5)}$$

$$I_j(t) = \int_0^t \frac{\mathrm{E}(\sqrt{\chi_j \tau})\,d\tau}{\sqrt{t-\tau}} = \sqrt{\frac{\pi}{\chi_j}}\left[1 - \mathrm{E}(\sqrt{\chi_j t})\right], \quad j = 1, 2 \qquad \text{(B.6)}$$

$$\int_0^t e^{-\frac{\tau}{\tau_M}}\,\mathrm{erf}\left(\sqrt{\frac{t-\tau}{\tau_M}}\right)\mathrm{E}(\sqrt{\chi_j \tau})\,d\tau = \frac{\tau_M}{1 - \tau_M \chi_j}\left\{\mathrm{erf}\left(\sqrt{\frac{t}{\tau_M}}\right) + e^{-\frac{t}{\tau_M}}\left[\sqrt{\frac{\chi_j}{\pi}}\,I(t) - \frac{1}{\sqrt{\pi\tau_M}}\,I_j(t)\right]\right\}, \quad j = 1, 2 \qquad \text{(B.7)}$$

In view of (B.3)–(B.7) the equation for the adsorption becomes

$$\frac{\Gamma(t)}{\bar{\Gamma}} = \frac{1}{\sqrt{\mathrm{Da}}}\left(-\frac{b_1\sqrt{\tau_M\chi_1}}{1-\tau_M\chi_1} + \frac{b_2\sqrt{\tau_M\chi_2}}{1-\tau_M\chi_2}\right)$$
$$+\frac{1}{\sqrt{\mathrm{Da}}}\left(\frac{b_1}{1-\tau_M\chi_1} - \frac{b_2}{1-\tau_M\chi_2}\right)\mathrm{erf}\left(\sqrt{\frac{t}{\tau_M}}\right)$$
$$-\frac{1}{\sqrt{\mathrm{Da}}}\left[-\frac{b_1\sqrt{\tau_M\chi_1}}{1-\tau_M\chi_1}\mathrm{E}(\sqrt{\chi_1 t})\right.$$
$$\left.+\frac{b_2\sqrt{\tau_M\chi_2}}{1-\tau_M\chi_2}\mathrm{E}(\sqrt{\chi_2 t})\right]e^{-\frac{t}{\tau_M}} \tag{B.8}$$

To define the parameter Da in (B.8), we introduce a new diffusion time

$$\tau_D = \frac{1}{D_1}\left(\frac{\bar{\Gamma}}{\bar{c}_1}\right)^2 \tag{B.9}$$

(cf. Eq. (2.12b)) and a new diffusion length $\delta_D = \bar{\Gamma}/\bar{c}_1$ instead of (2.12a).

It is seen that (B.8) obeys the initial condition $\Gamma(0) = 0$ because $\mathrm{erf}(0) = 0$ and $\mathrm{E}(0) = 1$. To calculate constants χ_j we use that the coefficients at the functions $\mathrm{E}(\sqrt{\chi_j t})$ in (B.8) must be equal to b_j, i.e.,

$$\frac{\sqrt{\tau_M\chi_j}}{1-\tau_M\tau_j} = -\sqrt{\mathrm{Da}}, \quad j = 1,\ 2\,. \tag{B.10}$$

Solving Eq. (B.10), we obtain the following expression

$$\tau_M\chi_j = \frac{(1 \pm G)^2}{4\mathrm{Da}}, \qquad G = \sqrt{1+4\mathrm{Da}}\,, \tag{B.11}$$

where sign " + " in (B.11) refers to $j = 1$ and sign " − " is for $j = 2$.

The other two constants, b_1 and b_2, should be chosen in a way to satisfy the final equilibrium condition, $\Gamma(\infty) = \bar{\Gamma}$ at $\mathrm{erf}(\infty) = 1$ and $\mathrm{E}(\infty) = 0$. Therefore, the coefficient at the error function in Eq. (B.8) must be equal to zero

$$\frac{b_1}{1-\tau_M\chi_1} - \frac{b_2}{1-\tau_M\chi_2} = 0\,, \tag{B.12a}$$

whereas the constant term should be unity

$$-\frac{b_1\sqrt{\tau_M\chi_1}}{1-\tau_M\chi_1} + \frac{b_2\sqrt{\tau_M\chi_2}}{1-\tau_M\chi_2} = \sqrt{\mathrm{Da}}\,. \tag{B.12b}$$

The solutions of Eqs. (B.12) are

$$b_j = \sqrt{\mathrm{Da}}\,\frac{1-\tau_M\chi_j}{\sqrt{\tau_M\chi_2}-\sqrt{\tau_M\chi_1}}\,, \quad j = 1, 2 \tag{B.13}$$

Combining (B.11) and (B.13), we obtain

$$b_j = \frac{1 \pm G}{2G}\,, \quad j = 1, 2\,, \tag{B.14}$$

where again " + " is for $j = 1$ and " − "" for $j = 2$.

Finally, by introducing (B.11) and (B.14) into (B.8) the adsorption becomes

$$\frac{\Gamma(T)}{\bar{\Gamma}} = 1 - \frac{1}{2G}e^{-\mathrm{Da}T}\left\{(1+G)\mathrm{E}\left[(1+G)\frac{\sqrt{T}}{2}\right]\right.$$
$$\left.-(1-G)\mathrm{E}\left[(1-G)\frac{\sqrt{T}}{2}\right]\right\} \tag{B.15}$$

which, in view of (2.11), allows to write for the surface tension Eq. (3.4).

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