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

2. Theory of the solutions below CMC

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Abstract: A theoretical model for the dynamic surface tension of an air bubble expanding in surfactant solution is proposed. The model accounts for the effect of convection on the surfactant diffusion and the effect of expansion of the bubble surface during the adsorption of surfactant molecules. Assuming small deviation from equilibrium and constant rate of expansion, an analytical solution for the surface tension and the subsurface concentration as a function of time is derived. The parameters of the model are computed from experimental data for sodium dodecyl sulfate obtained by the maximum bubble pressure method.

Key words: Dynamic surface tension – maximum bubble pressure method – rate of expansion

Introduction

Our previous paper [1] deals with the dynamic surface tension of surfactant solutions studied experimentally by means of the maximum bubble pressure method (MBP-method). For this purpose air bubbles were blown with frequency v on the tip of a vertical glass capillary immersed upwards in water surfactant solution. Measuring the time t (the reversal of the bubbling frequency) and the pressure in the system, we obtained the dynamic surface tension $\sigma(t)$ of both micellar surfactant solutions and solutions without micelles. Here, we propose a theoretical model for the surfactant transfer and adsorption at concentrations below the critical micelle concentration (CMC). The model accounts for the effect of convection on the surfactant diffusion in the vicinity of the bubble and for the effect of expansion of the bubble surface during the adsorption of surfactant molecules. Our treatment aims to prove the approximations first made in the model for a much simpler system without micelles. Based on the results of this study, we will extend the model for the solutions containing micelles in our next paper [2].

The transfer of surfactant molecules to the bubble surface can be considered as a sequence of two processes [3]: diffusion from the bulk phase to the subsurface layer and adsorption onto the surface. It is proven in the literature [3–15] that for most of the usual surfactants, such as sodium dodecyl sulfate (SDS), the diffusion is much slower than the adsorption itself (diffusion controlled adsorption kinetics). There are two approaches to the diffusion controlled kinetics (for a review, see refs. [16, 17]). In the first approach the adsorption $\Gamma(t)$ is expressed through the subsurface concentration $\Phi(t)$, where Φ is the surfactant concentration in the subsurface layer. Practically, $\Phi(t)$ is an unknown function of t which can be found either i) experimentally [9, 16], or ii) by relating Γ and Φ with an adsorption isotherm of a general type, $\Gamma(\Phi)$, and then numerically solving the respective set of equations [14]. The second approach allows analytical solutions for the adsorption only if a linear relationship between Γ and Φ is assumed. This assumption is valid for dilute surfactant solutions [4, 5, 8, 16] or at small deviations from equilibrium [17]. Although the first approach is more general, the second approach is more useful for fitting experimental data and can also be generalized for micellar surfactant solutions [18].

Usually, the data obtained by the MBP-method are interpreted in the frames of the following two approximations to the adsorption kinetics:

i) Long time approximation [19, 20]

$$\sigma(t) = \bar{\sigma} + \frac{2R_g T_a \bar{\Gamma}^2}{\bar{c}} \frac{1}{\sqrt{\pi D t}} , \tag{1.1}$$

where $R_g = 8 \cdot 314 \times 10^7$ dyn·cm/mol·K is the universal gas constant, T_a is the absolute temperature, $\bar{c}$ is the equilibrium surfactant concentration, Γ is the equilibrium adsorption, and D is the surfactant diffusivity. The multiplier 2 on the righthand side of (1.1) is for anionic surfactant without added electrolyte. Recently, Garrett and Ward [20] fitted their MBP-data for SDS by Eq. (1.1). They introduced a characteristic time of diffusion,

$$\tau_D = \frac{1}{D}\left(\frac{\bar{\Gamma}}{\bar{c}}\right) , \tag{1.2}$$

which was calculated to be about 5×10^{-3} s at surfactant concentration 7×10^{-6} mol/cm^3. Eq. (1.1) is valid at $t \gg \tau_D$.

ii) Small time approximation [19, 21]

$$\sigma(t) = \sigma_0 - 2R_g T_a \bar{c} \sqrt{\frac{Dt}{\pi}} , \tag{1.3}$$

where σ_0 is the surface tension of pure water. Equation (1.3) is valid at $t \ll \tau_D$.

Equations (1.1) and (1.3) are particular cases of the more general equation of Ward and Tordai [3],

$$\Gamma(t) = 2\bar{c}\sqrt{\frac{Dt}{\pi}} - \sqrt{\frac{D}{\pi}} \int_0^t \frac{\Phi(\tau)}{\sqrt{t-\tau}} \mathrm{d}\tau , \tag{1.4}$$

derived originally for quiescent interface of constant area. However, when an air bubble is blown up there are two effects which can additionally influence the adsorption kinetics. The first effect is the convection caused by the advancing bubble surface in the solution. The second effect is the expansion of the adsorbed surfactant layer during the bubble growth. One possibility to account for the contribution of these two effects [21–23] is based on the mathematical approach used in polarography [24]. In this case the final expression for the adsorption is given by [22]

$$\Gamma(t) = 2\bar{c}\sqrt{\frac{3Dt}{7\pi}} - \sqrt{\frac{D}{\pi t^{4/3}}} \int_0^{\frac{3}{7}t^{7/3}} \frac{\Phi\left(\frac{3}{7}t^{7/3}\right)}{\sqrt{\frac{3}{7}t^{7/3} - \tau}} \mathrm{d}\tau \tag{1.5}$$

The integral terms in the righthand side of Eqs. (1.4) and (1.5) vanish at small times when $\Phi \approx 0$ and then these two equations resemble Eq. (1.3) at $\sigma = \sigma_0 - R_g T_a \Gamma$ [21]. Since this requirement cannot be satisfied every time, one needs an explicit time dependence of Γ (or Φ) and σ in order to fit experimental data.

In Section 2 below we derive an equation for $\sigma(t)$ by solving the respective diffusion problem at certain approximations: small deviations from equilibrium and constant rate of bubble expansion. In Section 3, we fit experimental data for SDS obtained by the MBP-method [1] and calculate the model parameters.

2. Dynamic surface tension

Let us approximate the bubble surface as in refs. [19–23] with a plane placed at $x = 0$ so that the x-axis is directed toward the bulk of solution. The diffusion of surfactant molecules is described by the following equations:

$$\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} \tag{2.1}$$

$$\frac{1}{A}\frac{\mathrm{d}}{\mathrm{d}t}(A\Gamma) = D\left.\frac{\partial c}{\partial x}\right|_{x=0} \tag{2.2}$$

$$c(0, t) = \Phi(t) \tag{2.3}$$

$$c(\infty, t) = \bar{c} \tag{2.4}$$

$$c(x, 0) = \bar{c} \tag{2.5}$$

$$c(0, 0) = \Phi_0 \tag{2.6}$$

$$\Gamma(0) = \Gamma_0 . \tag{2.7}$$

Here, $c(x, t)$ is the bulk surfactant concentration, $V(x, t)$ is the velocity of hydrodynamic flow in the solution caused by the bubble growth, $A(t)$ is the area of the bubble surface in contact with the surfactant solution, Φ_0 and Γ_0 are the initial values of the subsurface concentration and adsorption, respectively. If $\sigma(0) = \sigma_0$ (surface tension of pure water), then $\Phi_0 = 0$ and $\Gamma_0 = 0$. We solve Eqs. (2.1)–(2.7) at the following approximations:

i) Small deviations from equilibrium: $|c - \bar{c}| \ll \bar{c}$, $|\Gamma - \bar{\Gamma}| \ll \bar{\Gamma}$, $|\sigma - \bar{\sigma}| \ll \bar{\sigma}$. For typical data for the surface tension $\sigma_0 = 72$ dyn/cm and $\bar{\sigma} \sim 50$ dyn/cm, the deviation $\sigma_0 - \bar{\sigma} \sim 22$ dyn/cm is sufficiently less than the equilibrium value $\bar{\sigma}$. In this case the adsorption and the surface tension can be expanded in series

$$\Gamma(t) = \bar{\Gamma} + \frac{\mathrm{d}\bar{\Gamma}}{\mathrm{d}\bar{c}}[c(0, t) - \bar{c}] \tag{2.8a}$$

$$\sigma(t) = \bar{\sigma} + \frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}\bar{c}}[c(0, t) - \bar{c}]\,, \tag{2.8b}$$

where the derivatives are calculated at $c = \bar{c}$. The derivative

$$\delta_\mathrm{D} = \frac{\mathrm{d}\bar{\Gamma}}{\mathrm{d}\bar{c}}$$

has the meaning of a characteristic length of diffusion [15, 17, 18]. δ_D is a measure for the thickness of the subsurface layer.

ii) Hydrodynamic velocity represented as [21]

$$V(x, t) = -\dot{\alpha}(t)x\,, \tag{2.9}$$

where $\dot{\alpha}$ is the rate of expansion of the bubble surface

$$\dot{\alpha} = \frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}t}\,. \tag{2.10}$$

In our case, we will assume that $\dot{\alpha}$ is a constant throughout the bubble expansion (for comments see Section 3).

To further simplify Eq. (2.1), we assume that the adsorption is influenced mainly by the hydrodynamic flow in the subsurface layer of thickness δ_D, i.e., the velocity (2.9) is given by

$$V = -\dot{\alpha}\delta_\mathrm{D} = \text{const}\,. \tag{2.11}$$

Hence, Eqs. (2.1), (2.2), (2.4)–(2.6), and (2.8a) read in dimensionless variables:

$$\frac{\partial \xi}{\partial T} - a\frac{\partial \xi}{\partial X} = \frac{\partial^2 \xi}{\partial X^2} \tag{2.12}$$

$$\frac{\partial \xi}{\partial T} + a(b + \xi) = \left.\frac{\partial \xi}{\partial X}\right|_{X=0} \tag{2.13}$$

$$\xi(\infty, T) = 0 \tag{2.14}$$

$$\xi(X, 0) = 0 \tag{2.15}$$

$$\xi(0, 0) = \xi_0\,, \tag{2.16}$$

where $\xi(X, T) = (c - \bar{c})/\bar{c}$ is the relative deviation of the surfactant concentration from its equilibrium value, $\xi_0 = (\Phi_0 - \bar{c})/\bar{c}$, $a = \dot{\alpha}\tau_\mathrm{D}$, $b = \bar{\Gamma}/(\bar{c}\delta_\mathrm{D})$, $X = x/\delta_\mathrm{D}$, $T = t/\tau_\mathrm{D}$, and

$$\tau_\mathrm{D} = \frac{1}{D}\left(\frac{\mathrm{d}\bar{\Gamma}}{\mathrm{d}\bar{c}}\right)^2 \tag{2.17}$$

is the characteristic time of diffusion.

Equations (2.13)–(2.16) were solved by means of Laplace transformation to obtain the image of the subsurface concentration. After that this image was inverted (Appendix A) and the subsurface concentration $\xi(0, t)$ was related to the surface tension by Eq. (2.8b). The final result is

$$\begin{aligned}\frac{\Delta\sigma(T)}{\Delta\sigma_0} = \frac{\xi(0, T)}{\xi_0} &= \frac{1}{2G}\mathrm{e}^{-\frac{a^2T}{4}}\Bigg\{(1 + G)\mathrm{E}\Bigg[(1 + G)\frac{\sqrt{T}}{2}\Bigg] - (1 - G)\mathrm{E}\Bigg[(1 - G)\frac{\sqrt{T}}{2}\Bigg]\Bigg\} \\ &\quad + \frac{E_G}{2\Delta\sigma_0}\Bigg\{1 + \frac{1}{2}\mathrm{e}^{-\frac{a^2T}{4}}\mathrm{E}\left(\frac{a\sqrt{T}}{2}\right) \\ &\quad + \frac{1}{4G}\mathrm{e}^{-\frac{a^2T}{4}}\Bigg\{[6 - a - 3(1 + G)]\mathrm{E}\Bigg[(1 + G)\frac{\sqrt{T}}{2}\Bigg] \\ &\quad - [6 - a - 3(1 - G)]\mathrm{E}\Bigg[(1 - G)\frac{\sqrt{T}}{2}\Bigg]\Bigg\}\Bigg\}\,,\end{aligned} \tag{2.18}$$

where $\Delta\sigma = \sigma(t) - \bar{\sigma}$, $\Delta\sigma_0 = \sigma(0) - \bar{\sigma}$,

$$G = \sqrt{1 - a(6 - a)} \tag{2.19a}$$

$$E(z) = e^{z^2} \operatorname{erfc}(z) \tag{2.19b}$$

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-y^2} \, dy = 1 - \operatorname{erfc}(z) \tag{2.19c}$$

E_G is the Gibbs' elasticity given by

$$E_G = -\bar{\Gamma} \frac{d\bar{\sigma}}{d\bar{\Gamma}} .$$

Equation (2.18) represents the relaxation of the surface tension affected by the convection and the expansion of the bubble surface. Due to the approximations made, both effects are accounted for by the dimensionless parameter $a = \dot{\alpha}\tau_D$. For a quiescent interface (no convection and expansion) $a = 0$ and $G = 1$ from Eq. (2.19a). In this case (2.18) reduces to the known result [4, 15, 17].

$$\frac{\Delta\sigma(T)}{\Delta\sigma_0} = \mathrm{E}(\sqrt{T}) . \tag{2.20}$$

The righthand side of Eq. (2.20) can be expanded in series to give [5]

$$\mathrm{E}(\sqrt{T}) \approx \frac{1}{\sqrt{\pi T}} \quad \text{at } T \gg 1 (t \gg \tau_D)$$

$$\mathrm{E}(\sqrt{T}) \approx 1 - 2\sqrt{\frac{T}{\pi}} \quad \text{at } T \ll 1 (t \ll \tau_D) .$$

Hence, Eqs. (1.1) and (1.3) are particular cases of (2.20).

An alternative approach to derive Eq. (2.20) from Eq. (1.4) by means of a model subsurface concentration is given in Appendix B.

3. Discussion

An essential point of our treatment is the constancy of the rate of expansion of the bubble surface $\dot{\alpha}$. The bubble area A increases with time during the two stages of bubble growth [19]: i) formation of a hemispherical bubble and ii) transition to a spherical bubble (after that the bubble escapes from the capillary tip). As accepted in literature, important for the dynamic surface tension is only the first stage since at the end of this stage the pressure inside the bubble reaches its maximum value equal to the capillary pressure. Hence, the surface tension $\sigma(t)$ corresponds exactly to the end of the first stage, while the duration of the second stage is accounted for in the dead-time correction of the actual time. The bubble surface can be expressed as

$$A(t) = 2\pi R^2 \left[1 \mp \sqrt{1 - \left(\frac{R_c}{R}\right)^2} \right] , \tag{3.1}$$

where R_c is the capillary radius (minus refers to the first stage, plus refers to the second stage of bubble growth). Since the bubble radius $R(t)$ is not known in our experiment [1] the exact time dependence of A (and $\dot{\alpha}$) cannot be found. In the same situation different approximations for $\dot{\alpha}$ are used in the literature: $\dot{\alpha} = 2/(3t)$ [21] or $\dot{\alpha} = 0.1/t$ [25, 26]. In contrast to them, we assumed that the rate of expansion $\dot{\alpha}$ is simply constant.

An idea for the validity of this assumption is given in Fig. 1 which is a typical plot of the bubble area as a function of time obtained recently in independent MBP-experiment [27]. In this case the bubble radius R was measured as a function of time from video record and the bubble area $A(t)$ was calculated using Eq. (3.1). The solid line is the best fit of the data for individual bubbles of different life time $1/\nu$. The bubble area A increases at the beginning of the bubble growth while after that A does not change appreciably. The final increase of the bubble area beyond $2\pi R_c^2$ is not important for the dynamic surface tension since

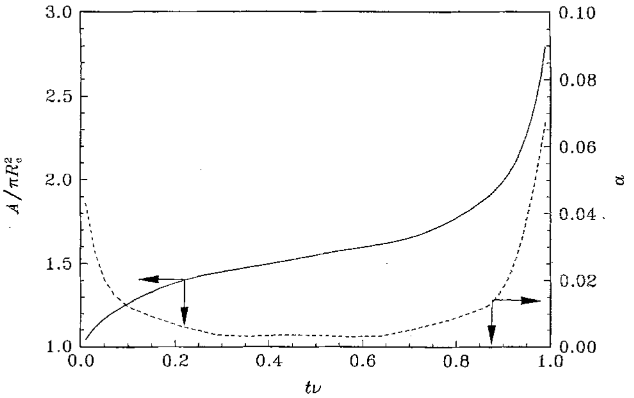

Fig. 1. Typical time dependence of the area of a single bubble expanding in SDS solution with electrolyte sodium chloride below CMC [27] (ν - bubbling frequency). The rate of expansion $a = \dot{\alpha}\tau_D$ remains nearly constant during the intermediate stage of bubble growth

this stage corresponds to the dead-time correction. From the numerical fit of the area (polynomial of ninth order), we calculated $\dot{\alpha}$ by using Eq. (2.10). Except at the beginning (and at the end) of bubble growth the rate of expansion (dashed line) remains almost constant, which supports the assumption made in Section 2.

The effect of the rate of expansion on the dynamic surface tension is illustrated in Figs. 2 and 3. The computations are carried out at $E_G/(2\Delta\sigma_0) = 1$ which is close to the values observed experimentally. The numerical procedure at different values of a is described in Appendix A.

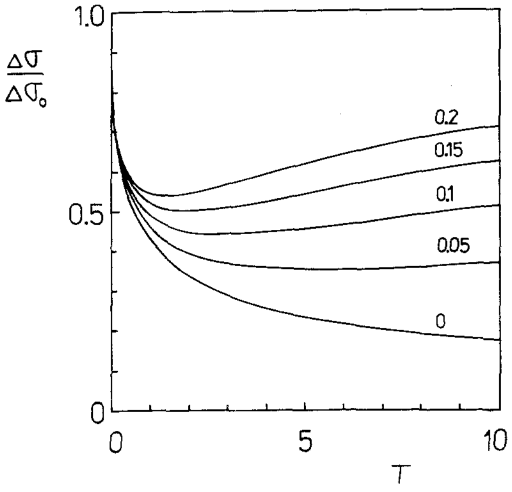

Fig. 2. Dynamic surface tension as a function of time calculated by Eq. (2.18) at different expansion rates a (for details see Appendix A)

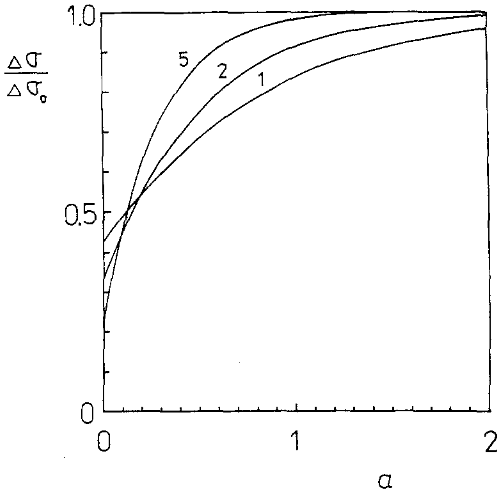

Fig. 3. Dynamic surface tension as a function of the expansion rate a calculated by Eq. (2.18) at different times T

At the beginning of relaxation (end of perturbation) the surface tension equals its initial value $\sigma(0)$, i.e., $\Delta\sigma/\Delta\sigma_0 = 1$. The first term on the right-hand side of Eq. (2.18) accounts for the relaxation of the surface tension due to diffusion of surfactant, while the second term accounts for the effect of expansion of the bubble surface. Both terms are affected by the convection and expansion through the parameter a. The first term always decreases with time, which leads to a decrease of the surface tension. At small times, $T \leq 1$ ($t \leq \tau_D$), this term predominates because the diffusion of surfactant molecules prevails over the expansion of the bubble surface. As a result, the number of adsorbed surfactant molecules is larger than the number of surface sites created by the expansion of the monolayer. At that, the smaller the rate of expansion the more effective the diffusion of surfactant (Fig. 2). At $T \geq 1$ ($t \geq \tau_D$) the second term starts to dominate and the surface tension increases. Since the bubble expansion prevails over the surfactant diffusion, the local disturbance in the monolayer cannot be compensated by adsorption of surfactant molecules. Similar behavior of the interfacial tension was observed experimentally with an oil drop expanding at constant rate in surfactant solution [28].

To compare the model with the experiment, as a first step we fitted the MBP-data assuming $a = 0$ because the rate of expansion $\dot{\alpha}$ was not known in our experiment [1]. Since the initial value of the surface tension, $\sigma(0)$, was also not known, it was better to transform the data for the surface tension $\sigma(t)$ in data for the subsurface concentration $\Phi(t)$. According to ref. [9], $\Phi(t)$ is assumed equal to the surfactant concentration $\bar{c}$ of a solution of equilibrium surface tension σ equal to the dynamic surface tension $\sigma(t)$ at the same moment t. The experimental values of $\Phi(t)$ thus obtained are plotted in Fig. 4 where different figures correspond to solutions with different surfactant concentration $\bar{c}$.

The solid curve in Fig. 4 represents the numerical fit of the data drawn by the equation

$$\frac{\Phi(t)}{\bar{c}} = 1 - \mathrm{E}\left(\sqrt{\frac{t}{\tau_D}}\right). \tag{3.2}$$

Equation (3.2) is a particular case of Eq. (2.20) at $\bar{c} \gg \Phi_0 \approx 0$. The diffusion time constant τ_D is given either by Eq. (1.2) or by Eq. (2.17). Both equations coincide for dilute surfactant solutions when $\mathrm{d}\bar{\Gamma}/\mathrm{d}\bar{c} = \bar{\Gamma}/\bar{c} = \delta_\mathrm{D}$. The experimental data were fitted by the method of Hooke and Jeeves [29]. The sum of squares of the differences between theoretical and experimental values of $\Phi(t)$ was minimized using one adjustable parameter, τ_D. The calculated diffusion times τ_D listed in Table 1 are in the millisecond region as are the ones reported in ref. [20]. As seen, τ_D tends to decrease with increasing the surfactant concentration because the amount of free surfactant molecules increases in the solution.

Knowing τ_D, we calculated the diffusion length δ_D. The concentration dependence of the diffusivity of SDS monomers was accounted for by the formula

$$D(\bar{c}) = 5.656 \times 10^{-6} + 2.98 \times 10^{-2}\bar{c} - 11700\bar{c}^2 ,$$

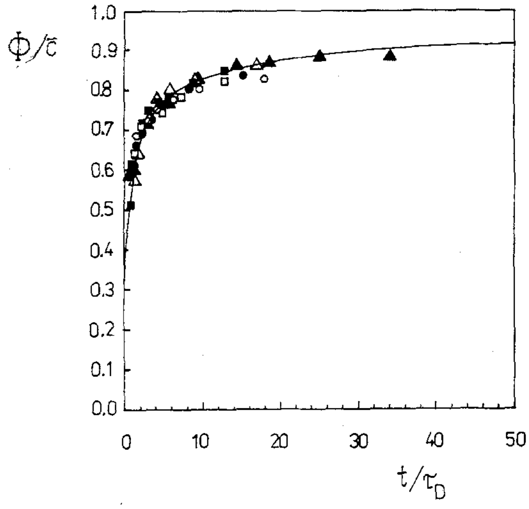

Fig. 4. The subsurface concentration of water solutions of SDS with different surfactant concentration (mol/cm^3): 2×10^{-6} (○); 3×10^{-6} (●); 4×10^{-6} (□); 6×10^{-6} (■); 7×10^{-6} (▲), data from ref. [20]; 8×10^{-6} (△). The solid line is drawn by Eq. (3.2)

which was obtained by fitting data for D published in ref. [30] ($\bar{c}$ is in mol/cm^3). Since δ_D can be identified either with the derivative $\mathrm{d}\bar{\Gamma}/\mathrm{d}\bar{c}$ or with the ratio $\bar{\Gamma}/\bar{c}$ the experimental values of δ_D are compared in Table 1 with both $\mathrm{d}\bar{\Gamma}/d\bar{c}$ and $\bar{\Gamma}/\bar{c}$. The latter were calculated from the empirical equation of Mysels [31] for $\bar{\sigma}(\bar{c})$ of SDS by the formula

$$\bar{\Gamma} = -\frac{1}{2R_\mathrm{g}T_\mathrm{a}}\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}\bar{c}} .$$

The values of δ_D computed from the MBP-data are always lower than the respective values calculated from equilibrium experimental data. This can be due to the approximations made in the theory. For example, the diffusion penetration depth is given most probably by $\delta_\mathrm{D} = \sqrt{\pi D t}$ rather than with the equilibrium values accepted in our model.

We tried also to estimate the expansion rate by fitting the data for $\Phi(t)$ using Eq. (2.18) with two adjustable parameters: $\dot{\alpha}$ and τ_D. The values of τ_D calculated in this way were only slightly different from those listed in Table 1 at $\dot{\alpha} = 0$. On the other hand, the parameter $a = \dot{\alpha}\tau_\mathrm{D}$ (dimensionless rate of expansion) was between 0 and 0.01, i.e., too small to appreciably affect the surface tension relaxation (cf. Fig. 2). Even though a seems small, the surface tension relaxes more slowly at $a \neq 0$ than at $a = 0$. Therefore, the value of the diffusion time τ_D estimated from the curve $a = 0$ will be greater than τ_D at nonzero a. This leads in turn to greater values of δ_D than the ones obtained from equilibrium data.

One important point of our treatment, as well as of the treatment of the other authors working on the same subject, is the disregard of the surface tension gradient (effect of Marangoni). Such gradient arises when the adsorption Γ varies

Table 1 Parameters of SDS solutions

$\bar{c} \times 10^6$ (mol/cm^3)	$\tau_\mathrm{D} \times 10^3$ (s)	$D \times 10^6$ (cm^2/s)	$\delta_\mathrm{D} \times 10^4$ (cm)	$(\bar{\Gamma}/\bar{c}) \times 10^4$ (cm)	$(\mathrm{d}\bar{\Gamma}/\mathrm{d}\bar{c}) \times 10^4$ (cm)
2	11.0	5.67	2.5	1.1	0.7
3	12.0	5.65	2.6	0.9	0.5
4	15.0	5.59	2.9	0.8	0.3
6	12.0	5.41	2.6	0.6	0.2
7†)	5.8	5.29	1.8	0.6	0.2
8	8.1	5.15	2.0	0.5	0.2

†) MBP-data from ref. [20].

along the bubble surface. One possibility to vary the adsorption is a nonuniform expansion of the air bubble which will result in local differences of the number of molecules per unit area. Another possibility is the removal of surfactant molecules from the subsurface layer, tangentially to the bubble surface, in the course of bubble growth. This situation resembles the one described for a fluid particle moving in surfactant solution [24]. In this case the number of adsorbed molecules on the bubble apex will decrease while the number of molecules near the bubble equator will increase. If this is so, an additional surface stress directed from the bubble equator to the bubble apex will arise. This stress can effectively alter the surface tension measured in the MBP-experiment. To account for the Marangoni effect, one should introduce two new terms in the boundary condition (2.2): one of them for the local variation of Γ and another for the surface diffusion of surfactant tending to restore the uniformity of Γ in the monolayer. However, the introduction of an additional space variable will substantially complicate the mathematical treatment. To the best of our knowledge, similar problems are solved in literature only for stationary diffusion: motion of a fluid drop [24] and thinning of a liquid film [32]. Also, the assumption (2.9) could not be applied in this case because it is valid for an uniform expansion. Finally, the procedure for experimentally calculating the dynamic surface tension from the maximum bubble pressure used in literature should also be revised since it assumes that the surface tension is uniform along the bubble surface. All these complications go beyond the scope of our paper and might be a subject of future investigation.

The theoretical approach presented in this study will be generalized in the next paper [2] for the dynamic surface tension of surfactant solutions containing micelles.

Acknowledgement

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Appendix A

The Laplace image of the subsurface concentration is

$$\frac{\hat{\xi}(0,p)}{\xi_0} = \frac{1}{p + \sqrt{p + \frac{a^2}{4} + \frac{3a}{2}}} + \frac{aE_G}{\Delta\sigma_0} \frac{1}{p\left(p + \sqrt{p + \frac{a^2}{4} + \frac{3a}{2}}\right)} . \tag{A.1}$$

By replacing the transformation parameter p with a new one, $q = p + a^2/4$, Eq. (A.1) can be written as

$$\frac{\hat{\xi}(0,p)}{\xi_0} = \frac{1}{q + \sqrt{q} + \frac{a(6-a)}{4}} + \frac{aE_G}{\Delta\sigma_0} \frac{1}{\left(q - \frac{a^2}{4}\right)\left(q + \sqrt{q} + \frac{a(6-a)}{4}\right)} . \tag{A.2}$$

The first term on the righthand side of Eq. (A.2) can be expressed as

$$\frac{1}{q + \sqrt{q} + \frac{a(6-a)}{4}} = \frac{1}{\beta - \gamma} \times \left(\frac{1}{\beta + \sqrt{q}} - \frac{1}{\gamma + \sqrt{q}}\right),$$

where $\beta = (1 - G)/2$ and $\gamma = (1 + G)/2$, while the second term can be expanded as

$$\frac{1}{\left(q - \frac{a^2}{4}\right)\left(q + \sqrt{q} + \frac{a(6-a)}{4}\right)} = -\frac{1}{a^2} \frac{1}{\frac{a}{2} + \sqrt{q}} - \frac{1}{2a^2} \frac{1}{\frac{a}{2} - \sqrt{q}} + \frac{1 - \beta - \frac{3a}{2}}{2a^2(\beta - \gamma)} \frac{1}{\beta + \sqrt{q}} - \frac{1 - \gamma - \frac{3a}{2}}{2a^2(\beta - \gamma)} \frac{1}{\gamma + \sqrt{q}} .$$

By inverting the Laplace images, we obtain Eq. (2.18).

There are three cases of Eq. (2.18) in dependence on the parameter a:

i) $a < 3 - 2\sqrt{2} = 0.1716$ or

$a > 3 + 2\sqrt{2} = 5.8284$ $(0 < G \leq 1)$.

In this case the function $\mathrm{E}(z)$ is computed by numerical integration of (2.19c) when $z \leq \sqrt{10}$, or by the approximate formula

$$\mathrm{E}(z) \cong \frac{1}{\sqrt{\pi z}}\left[1 + \sum_{n=1}^{6}(-1)^n \frac{1.3.5\ldots(2n+1)}{(2z^2)^n}\right],$$

when $z \geq \sqrt{10}$ [17].

ii) $a = 3 - 2\sqrt{2}$ or $a = 3 + 2\sqrt{2}$ $(G = 0)$.

In this very special case, one should take the limit $G \to 0$ in Eq. (2.18) to obtain

$$\frac{\Delta\sigma(T)}{\Delta\sigma_0} = \mathrm{e}^{-\frac{a^2T}{4}}\left[\left(1 + \frac{T}{2}\right)\mathrm{E}\left(\frac{\sqrt{T}}{2}\right) - \sqrt{\frac{T}{\pi}}\right]$$
$$+ \frac{\mathrm{E}_G}{2\Delta\sigma_0}\Bigg\{1 + \frac{1}{2}\mathrm{e}^{-\frac{a^2T}{4}}\Bigg\{\mathrm{E}\left(\frac{a\sqrt{T}}{2}\right) - 3\mathrm{E}\left(\frac{\sqrt{T}}{2}\right)$$
$$- (3 - a)\Bigg[\sqrt{\frac{T}{\pi}} + \frac{T}{2}\mathrm{E}\left(\frac{\sqrt{T}}{2}\right)\Bigg]\Bigg]\Bigg\}\Bigg\}, \qquad \text{(A.4)}$$

iii) $3 - 2\sqrt{2} < a < 3 + 2\sqrt{2}$ (G-imaginary number).

In this case, we substitute $G = iG_0$ in Eq. (2.18) where i is the imaginary unit and $G_0 = \sqrt{a(6 - a) - 1}$. Using the complex variable $z = \zeta + i\omega$ with $\zeta = G_0\sqrt{T}/2$ and $\omega = \sqrt{T}/2$, one can write $\mathrm{E}(-iz) = w(z)$ and $\mathrm{E}(iz^*) = w^*(z)$ where the function

$$w(z) = \mathrm{e}^{-z^2}\operatorname{erfc}(-iz) = u + iv$$

is tabulated in ref. [33] ($z^* = \zeta - i\omega$ and $w^* = u - iv$). As shown in ref. [17] the functions u and v can be expressed as

$$u(\zeta, \omega) = \frac{2}{\sqrt{\pi}}\mathrm{e}^{\omega^2}\int_{\omega}^{\infty}\mathrm{e}^{-\tau^2}\cos[2\zeta(\tau - \omega)]\,\mathrm{d}\tau$$

$$v(\zeta, \omega) = \frac{2}{\sqrt{\pi}}\mathrm{e}^{\omega^2}\int_{\omega}^{\infty}\mathrm{e}^{-\tau^2}\sin[2\zeta(\tau - \omega)]\,\mathrm{d}\tau\,.$$

Particular cases of the last two equations are

$$u(\zeta, 0) = \mathrm{e}^{-\zeta^2} \quad \text{and} \quad v(\zeta, 0) = \frac{2}{\sqrt{\pi}}\mathrm{e}^{-\zeta^2}\int_0^{\zeta}\mathrm{e}^{\tau^2}\,\mathrm{d}\tau\,,$$

and $u(0, \omega) = \mathrm{E}(\omega)$ and $v(0, \omega) = 0$, respectively.

In these notations Eq. (2.18) becomes

$$\frac{\Delta\sigma(T)}{\Delta\sigma_0} = \mathrm{e}^{-\frac{a^2T}{4}}\left(u - \frac{v}{G_0}\right)$$
$$+ \frac{\mathrm{E}_G}{2\Delta\sigma_0}\Bigg\{1 + \frac{1}{2}\mathrm{e}^{-\frac{a^2T}{4}}\Bigg[\mathrm{E}\left(\frac{a\sqrt{T}}{2}\right)$$
$$- 3u - \frac{(3 - a)v}{G_0}\Bigg]\Bigg]\Bigg\}\,. \qquad \text{(A.5)}$$

Appendix B

An explicit time dependence of Γ can be obtained also if $\Phi(t)$ is a known function of time (see Eq. (1.4)). Based on the results of Section 2, we choose a model subsurface concentration in the form

$$\Phi(t) = \bar{c}\left[1 - \mathrm{E}\left(\sqrt{\frac{t}{\tau_\mathrm{D}}}\right)\right]. \qquad \text{(B.1)}$$

The constant τ_D in Eq. (B.1) will be determined thereafter. To integrate (1.4), one should calculate the integral

$$I(t) = \int_0^t \frac{\mathrm{E}\left(\sqrt{\frac{\tau}{\tau_\mathrm{D}}}\right)}{\sqrt{t - \tau}}\,\mathrm{d}\tau\,. \qquad \text{(B.2)}$$

We integrate (B.2) first by parts

$$I(t) = 2\sqrt{t} - \sqrt{\frac{\pi}{\tau_\mathrm{D}}}\,t + \frac{2J}{\tau_\mathrm{D}}\,, \qquad \text{(B.3)}$$

where

$$J(t) = \int_0^t \mathrm{E}\left(\sqrt{\frac{t - \tau}{\tau_\mathrm{D}}}\right)\sqrt{\tau}\,\mathrm{d}\tau\,.$$

By differentiating $J(t)$ with respect to time, one obtains the following differential equation

$$\frac{\mathrm{d}J}{\mathrm{d}t} - \frac{J}{\tau_\mathrm{D}} = \sqrt{t} - \sqrt{\frac{\pi}{\tau_\mathrm{D}}}\frac{t}{2}\,,$$

whose solution is

$$J(t) = \tau_{\mathrm{D}}\left\{ -\sqrt{t} + \sqrt{\frac{\pi}{\tau_{\mathrm{D}}}}\frac{t}{2} + \frac{\sqrt{\pi\tau_{\mathrm{D}}}}{2}\left[1 - \mathrm{E}\left(\sqrt{\frac{t}{\tau_{\mathrm{D}}}}\right)\right]\right\}. \qquad \text{(B.4)}$$

Combining Eqs (B.3) and (B.4), one obtains finally

$$I(t) = \sqrt{\pi\tau_{\mathrm{D}}}\left[1 - \mathrm{E}\left(\sqrt{\frac{t}{\tau_{\mathrm{D}}}}\right)\right],$$

which gives for the adsorption

$$\Gamma(t) = \bar{c}\sqrt{D\tau_{\mathrm{D}}}\left[1 - \mathrm{E}\left(\sqrt{\frac{t}{\tau_{\mathrm{D}}}}\right)\right]. \qquad \text{(B.5)}$$

In the limit $\Gamma(\infty) = \bar{\Gamma}$ it follows from (B.5) that τ_{D} is given by Eq. (1.2).

The approach demonstrated here is valid not only at small deviations from equilibrium but for any model subsurface concentration which obeys the conditions $\Phi(0) = 0$ and $\Phi(\infty) = \bar{c}$. In principal, it can be applied also to derive Eq. (2.18) by choosing $\Phi(t)$ of an appropriate form.

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