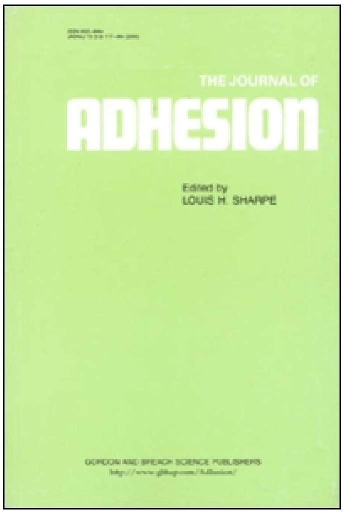

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INFLUENCE OF MOLECULAR PROCESSES AT LIQUID INTERFACES ON DYNAMIC SURFACE TENSIONS AND WETTING KINETICS

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INFLUENCE OF MOLECULAR PROCESSES AT LIQUID INTERFACES ON DYNAMIC SURFACE TENSIONS AND WETTING KINETICS

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The application of theories on the wetting kinetics of surfactant solutions requires accurate knowledge of the adsorption kinetics of the surfactant molecules at the involved interfaces. Studies on dynamic surface tensions give access to a quantitative understanding of the mechanisms governing this part of the complex wetting process. It is shown that besides the surface activity and the bulk concentration of a surfactant, the adsorption mechanism and the peculiarities of the interfacial dynamics play a significant role at the liquid–air interface. Due to interfacial processes, such as change in orientation or aggregation of molecules in the surface layer, differences in the adsorption time of more than one order of magnitude are observed.

Keywords: Surfactant adsorption; Molecular processes at interfaces; Diffusion-controlled adsorption; Dynamic surface tension; Wetting kinetics

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INTRODUCTION

It is commonly known that good wettability of a solid surface by a liquid is necessary for good adhesion. In many applications, the major problem is to increase the rate and uniformity of wetting. One possibility is the addition of surfactant to the liquid. However, surfactants employed to enhance spreading complicate the wetting process through time-dependent diffusion and adsorption at the involved interfaces. Despite the enormous technical importance of spreading of aqueous surfactant solutions on solid surfaces, spreading mechanisms are poorly understood [1–4]. Therefore, the dynamic spreading behavior cannot be easily predicted [5, 6].

For the processes of wetting and spreading occurring under nonequilibrium conditions, as far as these processes obey the Young equation, surface and interfacial tension dynamics are among the most important controlling parameters [7–9].

The solid–liquid interfacial tension, γ_{SL}, is not directly accessible by experiments, as is the case for γ_{LV}. Instead, the Young equation, $\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \cos\theta \cdot \gamma_{\mathrm{LV}}$, is often used for solving the inverse problem, *i.e.*, to determine the difference $(\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})$, which is referred to as *wetting tension* or *adhesion tension*, by means of the experimental values of contact angle, θ, and the surface liquid tension, γ_{LV}. Under dynamic conditions (Figure 1), the wetting tension is generally a function of time due to time-dependent adsorption of surfactant molecules at both the solid–liquid and the solid–vapor interfaces. For hydrophobic surfaces, the spreading dynamics can be approximated in terms of the dynamic contact angle by

$$\cos\theta(\mathrm{t}) = \frac{\gamma_{\mathrm{SV}}(\mathrm{t}) - \gamma_{\mathrm{SL}}(\mathrm{t})}{\gamma_{\mathrm{LV}}(\mathrm{t})}. \tag{1}$$

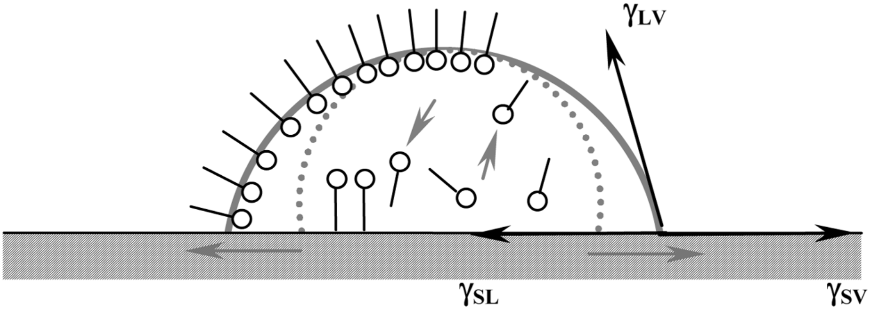

FIGURE 1 Schematic representation of a water drop containing surfactant molecules that spreads over a hydrophobic surface.

If we assume that the solid–vapor interfacial tension is a constant, then it can be calculated from the experimentally determined contact angles of water using Neumann's equation of state [10]. In this case the dynamic solid–liquid interfacial tension, $\gamma_{SL}(t)$, can be determined from Equation (1) knowing the dynamic contact angle and dynamic surface tension of the surfactant solution. On the other hand, the models proposed by Starov *et al.* [11] assume that surfactant molecules move to the liquid–gas interface and to the three-phase contact line, adsorb, and decrease the interfacial tension, γ_{SV}. The exact mechanism of the surfactant transfer is not yet clear; however, experimental data on wetting kinetics show that the adsorption at the solid–gas interface can be described by first-order kinetics [11]. In this process the rate constant of surfactant transfer depends on the coverage of the water–gas surface. As adsorption kinetics of surfactant molecules at liquid–vapor and solid–liquid interfaces mainly affect both the dynamic contact angle and dynamic surface tension, the knowledge of molecular processes at interfaces is of crucial importance for understanding of spreading mechanisms.

The purpose of this article is to demonstrate that the dynamic interfacial tension of the liquid–gas interface, and the adsorption kinetics of surfactant molecules at this interface, depend strongly on molecular processes, such as aggregation or change of orientation of adsorbed molecules. Therefore, under the same conditions, *i.e.*, at the same surfactant concentration and diffusion coefficient, different rates of surface tension can result in different rates of wetting of the solid surface.

THEORY

The equation proposed by Ward and Tordai [12] represents a relationship between the dynamic adsorption, $\Gamma(t)$, and the subsurface concentration, $c(0,\ t)$. For freshly formed and nondeformed surfaces, the equation can be written in the form

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \int_0^{\sqrt{t}} c(0, t-t')\,d\left(\sqrt{t'}\right)\right], \tag{2}$$

where t is the time, t' is a dummy integration variable, D is the surfactant diffusion coefficient in the solution bulk, and c_0 is the bulk concentration of the surfactant.

To solve Equation (2) we need, in addition to initial and boundary conditions, a supplementary equation associating adsorption with subsurface concentration [13, 14]. If the process of adsorption is a quasi-equilibrium one, the adsorption isotherm is used, while for a nonequilibrium process a kinetic equation will have to be used. In what follows we shall consider quasi-equilibrium adsorbed layers.

Depending on the exact mechanism of the process of adsorption, the following models of adsorption are distinguished: ideal (Langmuir) model, nonideal (Frumkin) model, aggregation model (surfactant molecules are able to form small aggregates or to condense in the surface layer), and reorientation model (surfactant molecules in the surface layer change their orientation as adsorption progresses) [15, 16]. All of these models have specific adsorption isotherms (unique to the respective model) and equations of the surface layer state expressing the dependence of surface tension on adsorption, which are given below.

Frumkin's Model

The adsorption isotherm and the equations of surface layer state have the form

$$\mathrm{bc}(0,\mathrm{t}) = \frac{\Gamma\omega}{1-\Gamma\omega}\exp(-2\mathrm{a}\Gamma\omega), \tag{3}$$

$$\Pi = -\frac{\mathrm{RT}}{\omega}\left[\ln(1-\Gamma\omega) + \mathrm{a}(\Gamma\omega)^2\right], \tag{4}$$

where Π is the surface pressure, R is the gas law constant, T is the temperature, b is the adsorption constant, a is the intermolecular interaction parameter, and ω is the molecular area of adsorbed molecules. For the sake of simplicity in Equations (3) and (4), the simplified notation $\Gamma(\mathrm{t}) = \Gamma$ is used. These equations transform into the Szyszkowski-Langmuir model for $\mathrm{a} = 0$.

Two-State Reorientation Model

In the event of two possible states of a surfactant molecule in the surface layer (**1** and **2**) differing by the molecular area (where it is assumed that $\omega_1 > \omega_2$), the equations of the adsorption isotherm for both states read

$$\mathrm{bc}(0,\mathrm{t})\beta = \frac{\Gamma_1\omega}{(1-\Gamma\omega)^{\omega_1/\omega}}, \tag{5}$$

$$\mathrm{bc}(0,\mathrm{t}) = \frac{\Gamma_2\omega}{(1-\Gamma\omega)^{\omega_2/\omega}}, \tag{6}$$

where

$$\beta = \left(\frac{\omega_1}{\omega_2}\right)^{\alpha} \exp\left(\frac{\omega_1 - \omega_2}{\omega}\right), \tag{7}$$

with Γ and ω defined by

$$\Gamma = \Gamma_1 + \Gamma_2, \quad \omega\Gamma = \omega_1\Gamma_1 + \omega_2\Gamma_2. \tag{8}$$

Equations (5) and (6) give the distribution function of equilibrium adsorption in the states **1** and **2**:

$$\frac{\Gamma_1}{\Gamma_2} = \beta \exp\left[-\frac{\Pi(\omega_1 - \omega_2)}{\mathrm{RT}}\right]. \tag{9}$$

The equation of state in the reorientation model reads

$$\Pi = -\frac{\mathrm{RT}}{\omega}\left[\ln(1 - \Gamma\omega) - \mathrm{a}(\Gamma\omega)^2\right]. \tag{10}$$

Aggregation Model

The main model parameters are the aggregation number, n, and the critical value of adsorption, Γ_c. The adsorption isotherm of monomers is defined by the equation

$$\mathrm{bc}(0, \mathrm{t}) = \frac{\Gamma_1\omega}{(1 - \Gamma\omega)^{\omega_1/\omega}}, \tag{11}$$

with Γ, Γ_1, and ω being interrelated by

$$\Gamma = \Gamma_1 + \Gamma_n = \Gamma_1 + \Gamma_1 \cdot (\Gamma_1/\Gamma_c)^{n-1}, \tag{12}$$

$$\omega = \omega_1 \frac{1 + n(\Gamma_1/\Gamma_c)^{n-1}}{1 + (\Gamma_1/\Gamma_c)^{n-1}}. \tag{13}$$

The equation of state in the aggregation model has the form

$$\Pi = -\frac{\mathrm{RT}}{\omega}\ln(1 - \Gamma\omega). \tag{14}$$

The physical peculiarities of the given models are discussed in more detail elsewhere [16], and we analyse their impact on the adsorption dynamics here to show the importance of the chosen thermodynamic quantities on the adsorption dynamics.

MATERIALS AND METHODS

For studies of the dynamic surface tensions of surfactant solutions, two methods were used, a maximum bubble pressure tensiometer BPA-1P and a bubble profile analysis tensiometer PAT1, both from SINTERFACE Technologies, Berlin, Germany. Detailed descriptions of these methods are given in Fainerman and Miller [17] and Loglio *et al.* [18], respectively. The surfactants Triton® X-100 and $C_{12}EO_6$ (hexaethyleneglycol monododecylether) used in the present studies were purchased from SigmaAldrich (Munich, Germany). The solutions were prepared with Milli-Q water.

RESULTS AND DISCUSSION

The theoretical models discussed above predict quite different courses of the time dependence of adsorption, *i.e.,* of the measurable dynamic surface tension. This is shown in Figure 2 as dynamic surface pressure for the three mentioned models. The data were calculated by using the program package developed by Aksenenko [19]. Equal values of equilibrium surface pressure (30 mN/m), bulk concentration of surfactants

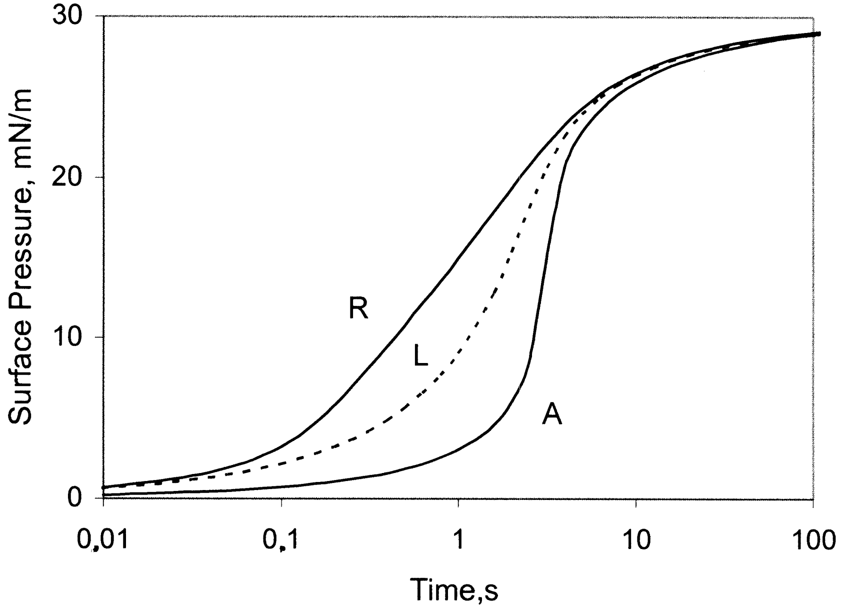

FIGURE 2 Dynamic surface pressure, Π, calculated for model solutions using the aggregation model (A), reorientation model (R), and Langmuir model (L).

($c_0 = 0.1$ mmol/l), molecular surface area, ω ($2.5 \cdot 10^5$ m^2/mol), and diffusion coefficient ($D = 5 \cdot 10^{-10}$ m^2/s) were assumed for all models. For the aggregation model an aggregation number of $n = 3$ (with $\Gamma_c \ll 1/\omega_1$), typical for surfactants with linear chains and small hydrophilic groups was used, while the reorientation model made use of the relations $\omega_1/\omega_2 = 4$ and $\alpha = 1$, typical for oxyethylated surfactants [16]. It is evident that reorientation (the ability of the surfactant molecule to occupy a maximum area at small surface coverage) contributes to a drastic acceleration of surface pressure change, whereas aggregation (*i.e.*, a strong interaction between adsorbed surfactant molecules and, hence, reducing the number of kinetically free units in the surface layer) slows the growth rate of Π drastically down. For small surface pressures as discussed here (less than 10 mN/m), the time necessary to achieve the specified surface pressure differs by more than an order of magnitude. In contrast, the adsorption values calculated for the three models practically do not differ in the same range of surface pressures (Figure 3).

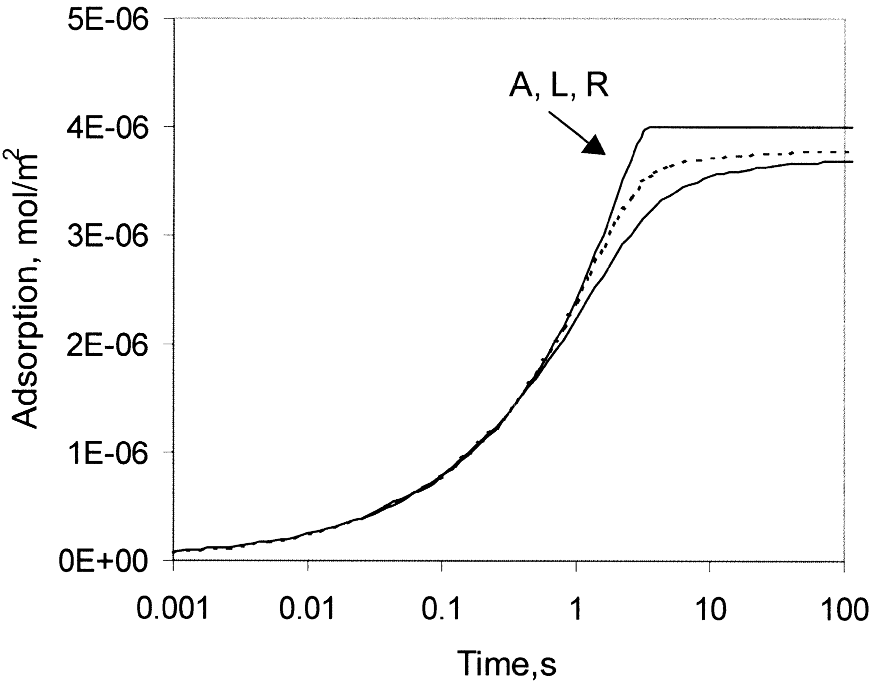

FIGURE 3 Adsorption, Γ, as function of time, t, calculated for model solutions using the aggregation model (A), reorientation model (R), and Langmuir model (L).

Hence, in order to decrease the surface tension rapidly and simultaneously accelerate the wetting process, it is not enough to have a high rate of adsorption at the solution–air interface. Adsorption activity of surfactant molecules and their ability to change orientation or to form aggregates in the surface layer exerts essential influence on the dynamic surface tension and, thus, on the wetting kinetics. These theoretical conclusions are supported by experimental results.

In Figure 4 measured dynamic surface tensions are shown of Triton X-100 solutions at 0.005 mmol/l and 0.01 mmol/l and 22°C. The theoretical calculations were performed for the Langmuir and reorientation models using model parameters obtained from the surface tension isotherm of Triton X-100 [16]. The molecular surface area in both adsorption states agrees well with the geometry of the molecule. The parameters used are: for the Langmuir model $\omega = 4 \cdot 10^5\,\mathrm{m^2/mol}$; for the reorientation model $\omega_1 = 1.2 \cdot 10^6\,\mathrm{m^2/mol}$, $\omega_2 = 4 \cdot 10^5\,\mathrm{m^2/mol}$, and $\alpha = 0.5$. For either model, a diffusion coefficient of $D = 3 \cdot 10^{-10}\,\mathrm{m^2/s}$

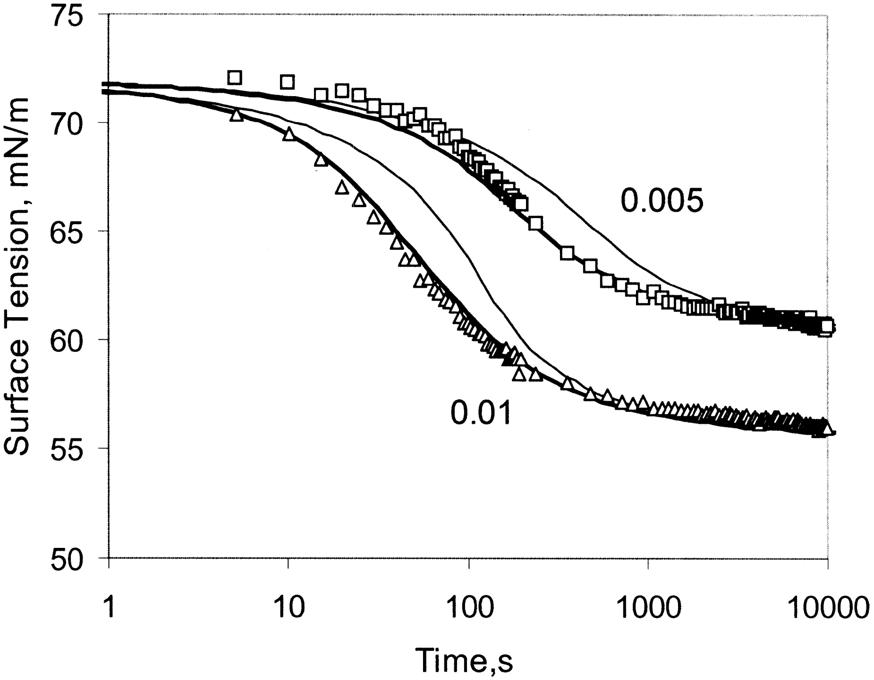

FIGURE 4 Dynamic surface tension of Triton® X-100 solutions (0.005 and 0.01 mmol/l): symbols, experimental values; thick line, calculated according to the reorientation model; thin line, calculated according to the Langmuir model.

was assumed. It is evident that calculations based on the reorientation model agree well with the experimental data, while the Langmuir model predicts a slower reduction of surface tension.

Dynamic surface tensions of 1-decanol solutions [20] are shown in Figure 5. Theoretical calculations refer to the Langmuir and aggregation models, based on the model parameters given in Fainerman *et al.* [16]. The molecular area of adsorbed 1-decanol molecules agree with results from Langmuir trough experiments and quantum-chemical calculations [21]. For the Langmuir model, $\omega = 1.7 \cdot 10^5\,\mathrm{m}^2/\mathrm{mol}$ and for the aggregation model we used $\omega_1 = 1.7 \cdot 10^5\,\mathrm{m}^2/\mathrm{mol}$ and $n = 3$. For either model, $D = 6 \cdot 10^{-10}\,\mathrm{m}^2/\mathrm{s}$ was assumed. In this example, the Langmuir model predicts faster surface tension reduction, whereas the aggregation model being in agreement with the experimental data provides a significantly slower decrease.

Finally, in Figure 6 the dynamic surface tensions of the nonionic surfactant $C_{12}EO_6$, as measured by the maximum bubble pressure tensiometer BPA1, are given. For the smallest studied $C_{12}E0_6$ concen-

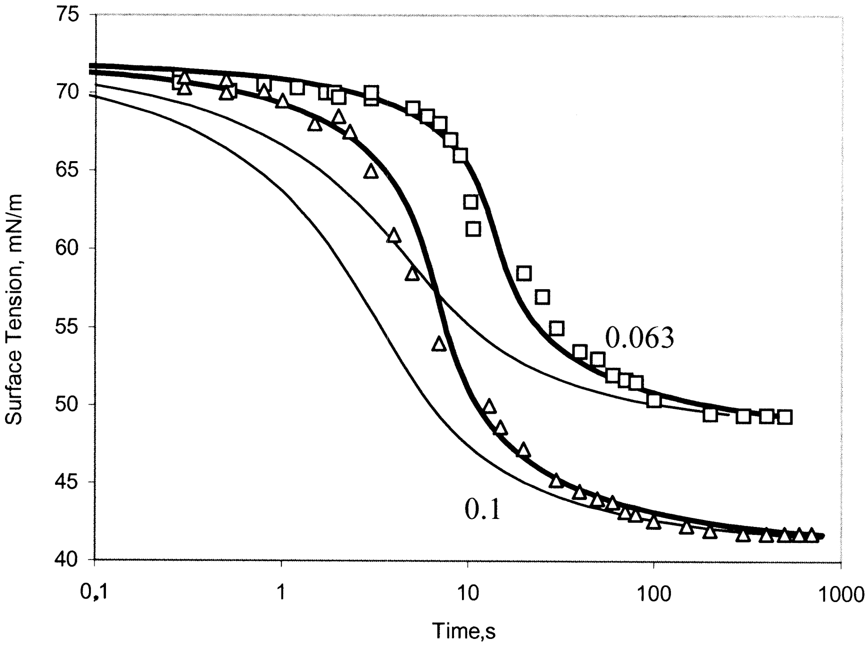

FIGURE 5 Dynamic surface tension of 1-decanol solutions (0.063 and 0.1 mmol/l): symbols, experimental values from Fainerman *et al.* [17]; thick line, calculated according to the aggregation model; thin line, calculated according to the Langmuir model.

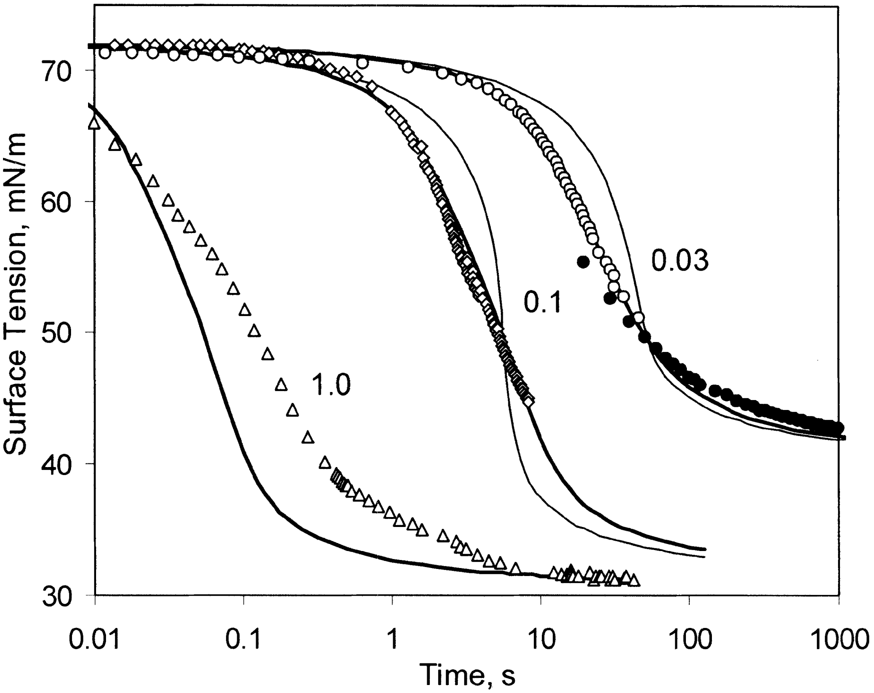

FIGURE 6 Dynamic surface tension of $C_{12}EO_6$ solutions (0.03, 0.1 and 1.0 mmol/l): open symbols, data from BPA1; closed symbols, data from PAT1; thick line, calculated according to the reorientation model; thin line, calculated according to the Langmuir model.

tration of 0.03 mmol/l, data from BPA1 were completed by data obtained from PAT1. It is evident that the data obtained by the two methods complement each other. Theoretical calculations have been performed for the Langmuir and reorientation model, while again the model parameters were taken from the monograph [16]. The molecular area, ω_2, for $C_{12}E0_6$ agrees well with results from neutron reflectivity studies [22]. For the Langmuir model we used $\omega = 3.65 \cdot 10^5\,m^2/mol$, and for the reorientation $\omega_1 = 7 \cdot 10^5\,m^2/mol$, $\omega_2 = 3 \cdot 10^5\,m^2/mol$, and $\alpha = 3$. For either model, a value of $D = 1.5 \cdot 10^{-10}\,m^2/s$ was assumed. For the two concentrations 0.03 mmol/l and 0.1 mmol/l, the reorientation model represents the experimental data very well, whereas the Langmuir model (as for Triton X-100, *cf.* Figure 4) predicts a slower reduction of the surface tension in the short time range. For the higher $C_{12}EO_6$ concentration of 1.0 mmol/l, the situation is quite different. Here also the reorientation model predicts a surface tension reduction slower than the experimental data. The reason for the disagreement is, however, not the adsorption mechanism itself. This aqueous solution is above the critical micelle concentration, which is 0.1 mmol/l for $C_{12}EO_6$ [16]). Therefore, the finite rate of the micelle dissociation process, being an additional source for monomers close to the adsorption layer, is the reason for the discrepancy between experiment and theory when micelle dissociation kinetics is not accounted for. From the experimentally obtained dynamic surface tensions of a micellar solution, the relaxation time of the micelle dissociation process, τ, can be calculated. This value can be obtained from the equation based on the ratio of the slopes at long adsorption times (close to adsorption equilibrium) of the dynamic surface tensions of the micellar solution $(d\gamma/dt^{-1})$ and the corresponding solution at c = CMC $(d\gamma/dt^{-1/2})$ [23, 24]:

$$\tau^{1/2} \cong \frac{(d\gamma/dt^{-1})_{c>cmc}}{(d\gamma/dt^{-1/2})_{cmc}}. \tag{15}$$

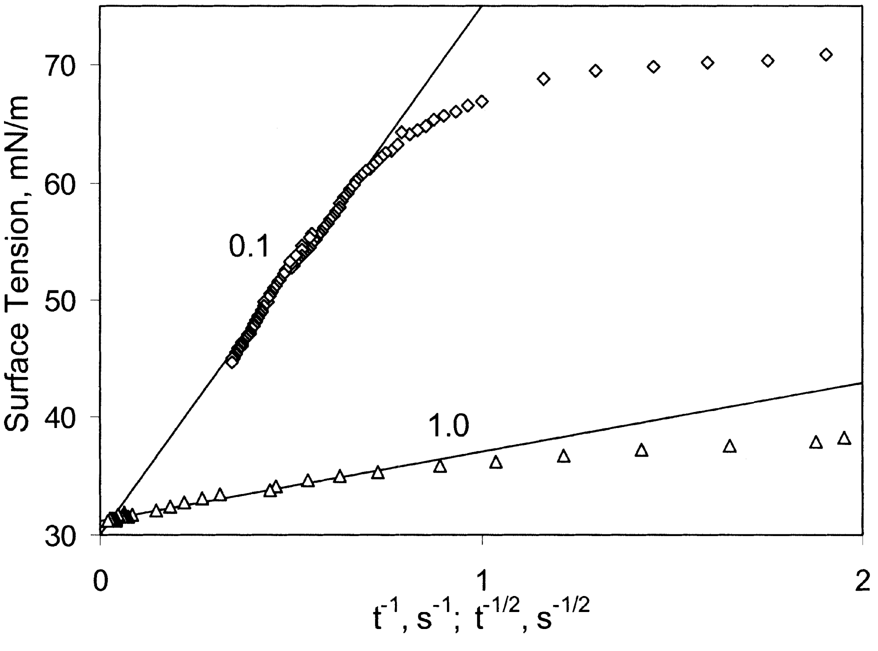

FIGURE 7 Dynamic surface tension of $C_{12}EO_6$ solutions (0.1 and 1.0 mmol/l) as function of $t^{-1/2}$ and t^{-1}, respectively; lines show the way to determine the derivatives of Equation (15).

Figure 7 shows the dependence of γ on t^{-1} and $t^{-1/2}$ for aqueous $C_{12}EO_6$ solutions at two concentrations 1.0 and 0.1 mmol/l, respectively. The micelle dissociation constant can be calculated from the derivatives (as shown in Figure 7) and amounts to $\tau = 0.02\,s$.

CONCLUSIONS

The theoretical approach of Starov *et al.* [11] and other theories on the dynamics of wetting require accurate knowledge of the dynamic surface tension of the droplet surface when the spreading behaviour on solid surfaces has to be understood. The change in dynamic surface tension with time at the liquid–air interface of a drop is not only a function of the surfactant concentration but is significantly governed by the surface activity and the interfacial properties of the adsorbed molecule. Depending on the adsorption mechanism the change in surface tension with time can differ by more than one order of magnitude for different surfactants with comparable surface activity and bulk concentration.

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