Dynamic Surface Tension in Concentrated Solutions of C_nE_m Surfactants: A Comparison between the Theory and Experiment

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Dynamic surface tension (DST) measurements have been carried out with a series of C_nE_6-type surfactants with varying alkyl chain length (n = 10−16). Major emphasis has been placed on the DST relaxation in complex solutions containing both the micellar and monomer forms of surfactant. This paper also provides a step-by-step guidance to the theoretical interpretation of DST data for micellar solutions. Distributions of monomers and micelles in the vicinity of the gas/liquid interface, adsorption kinetics, and DST relaxation curves have been simulated in the framework of the Fainerman theory (Fainerman, V. B. *Kolloid Z.* **1981**, *43*, 94) explicitly allowing for monomer/micelle interconversation. A thorough numerical analysis has shown that although the Fainerman theory can follow the general experimental trends, it clearly lacks the flexibility needed to provide a self-consistent and quantitatively correct description of the process. Possible reasons for this disagreement are discussed.

Introduction

Surfactants in solution are known to undergo micellization as their concentration exceeds a certain critical value (cmc). Although micelles are commonly assumed not to be surface active, their presence affects the surfactant transport and, thereby, the kinetics of surfactant adsorption to the gas/liquid interface. There always exists a unique relationship between the amount of surfactant adsorbed to the gas/liquid interface and the surface tension of the solution, which permits using surface tension measurements to study the adsorption. Numerous techniques for measurement of the dynamic surface tension (DST) have been developed.[1−5]

Theoretical treatment of DST phenomena usually comes down to the diffusion-controlled adsorption model pioneered by Ward and Tordai,[6] which has been further elaborated by many others.[7,8] The model uses the so-called surface−subsurface concept,[1] assuming that the adsorbate is transported by diffusion to a thin interfacial region, called the subsurface, which gets equilibrated with the surface instantly. To describe this equilibrium, several popular adsorption isotherms, including those by Henry, Langmuir, Frumkin, and Freundlich, have been used,[9] although only the first of them permits an analytical solution. It also was realized quite a time ago that if the equilibration between the surface and subsurface is relatively slow, mixed adsorption kinetics should be observed, and a variety of models covering this specific case have been designed.[7,10−13] The mathematical formalism of the theory in its generality has been stated by Filippova.[14]

Nevertheless, it remained unclear until quite recently how the DST theory should accommodate micellization. One possible solution to the problem was proposed by Fainerman in the beginning of the 1980s,[15,16] who explicitly allowed for micellar transport and interconversation between monomers and micelles in the solution. His ideas have been further developed in a recent paper by Brinck et al.[17] who modeled the adsorption kinetics of surfactants at a solid/liquid interface. The model developed by these authors allows treatment of polydisperse multicomponent systems. Its adaptation to the adsorption at gas/liquid interfaces would be rather straightforward.

The present study is intended to analyze the adequacy of the Fainerman theory, demonstrating its advantages as well as its shortcomings. It also provides a step-by-step guidance to the interpretation of DST data for concentrated surfactant solutions. The theoretical analysis is supported by a series of experiments with hexa(ethylene glycol) monoalkyl ethers C_nE_6 (n = 10, 12, 14, 16). The experiments were planned so as to allow independent evaluation of static parameters, including the parameters of the adsorption isotherm, thus minimizing the interdependence between different parameters and, therefore, allowing more precise evaluation of dynamic parameters and characteristics of micellar equilibria. Surfactants of poly(ethylene glycol) type were the subject of recent studies by Lin et al.[18] and Eastoe et al.,[19] which provide a reference point for checking the adequacy of experimental routines and consistency of results.

Experimental Section

Surfactants. Nonionic surfactants of hexa(ethylene glycol) monoalkyl ether type, $C_nE_6 = CH_3(CH_2)_{n-1}(OCH_2CH_2)_6OH$ (n =

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(2) Miller, R.; Joos, P.; Fainerman, V. B. *Adv. Colloid Interface Sci.* **1994**, *49*, 249.
(3) Chang, C.-H.; Franses, E. I. *Colloids Surf. A* **1995**, *100*, 1.
(4) Dukhin, S. S.; Kretzschmar, G.; Miller, R. *Dynamics of Adsorption at Liquid Interfaces*; Elsevier: Amsterdam, 1995.
(5) Manning-Benson, S.; Bain, C. D.; Darton, R. C.; et al. *Langmuir* **1997**, *13*, 5808.
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(8) Mysels, K. J. *J. Phys. Chem.* **1982**, *86*, 4648.
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(12) Adamczyk, Z. *J. Colloid Interface Sci.* **1987**, *120*, 477.
(13) Chang, C.-H.; Franses, E. I. *Colloids Surf. A* **1992**, *69*, 189.
(14) Filippova, N. L. *J. Colloid Interface Sci.* **1999**, *213*, 572.
(15) Fainerman, V. B. *Kolloid. Zh.* **1981**, *43*, 94.
(16) Fainerman, V. B.; Rakita, Yu. M.; Zadara, V. M. *Zh. Fiz. Khim.* **1984**, *58*, 2006.
(17) Brinck, J.; Jönsson, B.; Tiberg, F. *Langmuir* **1998**, *14*, 5863.
(18) Lin, S.-Y.; Tsay, R.-Y.; Lin, L.-W.; Chen, S.-I. *Langmuir* **1996**, *12*, 6530.
(19) Eastoe, J.; Dalton, J. S.; Rogueda, P. G. A.; et al. *J. Colloid Interface Sci.* **1997**, *188*, 423.

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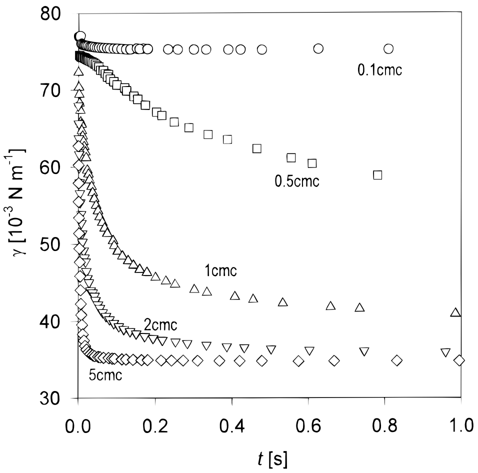

Figure 1. Dynamic surface tension curves measured at different concentrations of $C_{10}E_6$ surfactant in aqueous solutions.

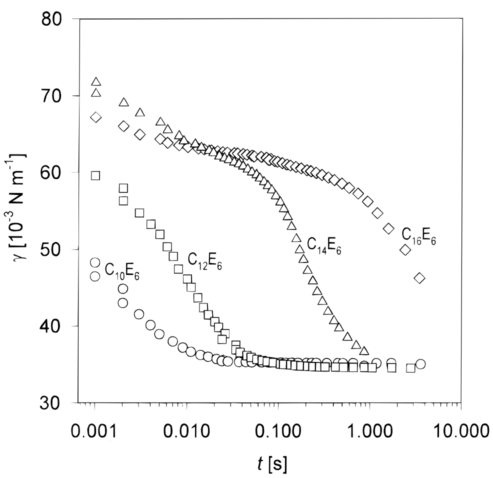

Figure 2. Dynamic surface tension curves measured for a series of C_nE_6 (n = 10, 12, 14, 16) surfactants with increasing hydrophobicity. In all cases, the concentration of surfactant was 0.01 mol dm^{-3}.

10, 12, 14, and 16), purity >99%, were purchased from Nikko Chemicals (Tokyo, Japan) and used without further purification. The surfactant solutions were prepared by using double-distilled deionized water (Milli-Q system, Millipore) as solvent. Freshly prepared solutions were used for each surface tension measurement.

Surface Tension Measurements. The dynamic surface tensions (Figures 1 and 2) were measured by using a MPT2 maximum bubble pressure tensiometer (Lauda), which allows measurements to be conducted with a time-resolution from 1 ms to several seconds. A detailed description of the instrument and measurement procedure can be found elsewhere.[20] Equilibrium surface tensions (Figure 3) were measured with a Sigma 70 tensiometer (KSV) equipped with a du Nouy ring. Addition of surfactant was controlled by a Methron Dosimat microtitration device. Zuidema−Waters's correlation method[21] was used to compensate the ring weight. All measurements were carried out at 20.0 ± 0.1 °C.

Overview of the Fainerman Theory

According to Gibbs law, adsorption of surfactant to the gas/liquid interface leads to a reduction in the surface tension of the solution. However, Gibbs law applies to equilibrium systems. When a fresh interface is created, surfactant starts to migrate to the interface, and until all concentration gradients disappear, the system does not qualify as an equilibrium system from a thermodynamic viewpoint. The concomitant surface tension relaxation process in general involves several different mechanisms:

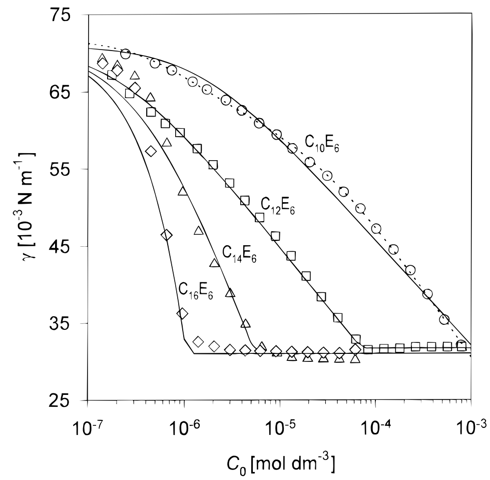

Figure 3. Static (quasi-static) surface tension of C_nE_6 (n = 10, 12, 14, 16) surfactant solutions as a function of concentration. The experimental data (discrete points) are approximated by the Langmuir−Szyszkowski equation using the following parameters: ($C_{10}E_6$, cmc = 9 × 10^{-4} mol dm^{-3}) K_L = 7 × 10^5 dm^3 mol^{-1}, Γ_m = 2.4 × 10^{-6} mol m^{-2}; ($C_{12}E_6$, cmc = 8 × 10^{-5} mol dm^{-3}) K_L = 5 × 10^6 dm^3 mol^{-1}, Γ_m = 2.7 × 10^{-6} mol m^{-2}; ($C_{14}E_6$, cmc = 6 × 10^{-6} mol dm^{-3}) K_L = 3 × 10^6 dm^3 mol^{-1}, Γ_m = 6 × 10^{-6} mol m^{-2}; ($C_{16}E_6$, cmc = 1 × 10^{-6} mol dm^{-3}) K_L = 8 × 10^4 dm^3 mol^{-1}, Γ_m = 2 × 10^{-4} mol m^{-2}. The dotted line shows the improvement achieved when using the generalized Frumkin isotherm instead of the Langmuir isotherm in the case of $C_{10}E_6$ adsorption (K_F = 1.4 × 10^6 dm^3 mol^{-1}, Γ_m = 2.9 × 10^{-6} mol m^{-2}; p = 3.7; q = 1.7).

(i) Solvent Relaxation. This is a sufficiently fast relaxation process involving rearrangement and reorientation of solvent molecules near a freshly created interface. It would occur even in the absence of surfactant and is only little affected by surfactant in diluted solutions. [Sometimes it is erroneously asserted that a fresh surface has the surface tension of solvent (cf. Chang et al., ref 3).]

(ii) Diffusional Transport, Reorientation, and Adsorption of Surfactant Molecules. This process, sometimes followed by reorganization in the adsorbed layer, is commonly agreed to dominate the surface tension dynamics in surfactant solutions. It occurs at any concentration of surfactant, tapering off as the adsorption approaches its equilibrium value.

(iii) Diffusional Transport and Desorption of Micelles. This process can only occur at concentrations of surfactant above the cmc, when a part of surfactant exists in the aggregated form.

(iv) Decay and/or Conversion of Micelles. Since there exists an exchange between the monomer and micellar form of surfactant, diffusional flows of monomers and micelles are interrelated. Low molecular aggregates, such as hemimicelles, may be able to "patch" the surface directly.

To extend the area of applicability of the Gibbs law to such systems, the concept of local equilibrium between the surface and subsurface was introduced. Instead of referring to the bulk concentration of adsorbate, one now refers to its concentration in the subsurface. The transport of surfactant between the bulk solution and the subsurface

(20) Miller, R.; Fainerman, V. B.; Schano, K.-H.; et al. *Tenside Surf. Det.* **1997**, *35*, 357.
(21) Zuidema, H. H.; Waters, G. *Ind. Eng. Chem.* **1941**, *13*, 312.

is described by the diffusion equations[15,16]

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} + Q(x,t)$$

$$\frac{\partial c_N}{\partial t} = D_N \frac{\partial^2 c_N}{\partial x^2} - Q(x,t) \qquad (1)$$

where c_1 is the concentration of monomers, c_N is the concentration of micelles, and D_1 and D_N are the corresponding diffusion coefficients. The source function, $Q(x,t)$, accounts for generation of monomers in the first equation and for decay of micelles in the second equation. According to Fainerman et al.,[16] the latter is given by

$$Q(x,t) = k[\mathrm{cmc} - c_1(x,t)][1 - \xi \exp(-t/\tau)][\eta + c_N(x,t)/\mathrm{cmc}] \quad (2)$$

where cmc states for the critical micellization concentration, k is the frequency factor, τ is the activation time of micelle decay, and ξ and η are some parameters. It should be noted that the latter parameter, η, must be taken equal to zero. Otherwise, the decay of micelles in a region not containing micelles will violate the conservation of mass. It is kept here only for compliance with the original Fainerman definition.

The above empirical equation is found to describe experimental micelle decay kinetics reasonably well. It can be deduced by reasoning as follows: First, the micelle decay rate should be proportional to the difference between the local concentration and the equilibrium concentration of monomers, which contributes the first term in the above product. Rillearts and Joos restricted themselves to using only this term in the source function.[22] Second, as in accord with the theory of nucleation, the aggregation rate is proportional to the degree of oversaturation. In equilibrium, the aggregation (micelle formation) and disaggregation (micelle decay) rates are equal. This explains the last term. Finally, if micelle decay is an activated process, some induction period proportional to the activation time has to exist. This is reflected in the middle term.

Some caution note regarding the form of the last term should be stated. In the above formulation, it is assumed that micelles manage to “feel” the creation of the interface instantly at any point of the solution, so that their decay in the superficial region and in the bulk of the solution starts at the same time. Although this does not conflict with the mathematical theory of diffusion, where any perturbation of the concentration profile instantly propagates throughout the system, common logic suggests that the decay in deeper regions should start later: micelles would not likely notice that anything has changed if the monomer concentration fell down by, say, 10^{-100} percent or so. An appropriate formulation reflecting this circumstance is

$$1 - \xi \exp\left[-\frac{t}{\tau}\left(1 - \frac{c_1(x,t)}{\mathrm{cmc}}\right)\right] \qquad (3)$$

For $x \gg (D_1 t)^{1/2}$, $c_1(x,t) \simeq \mathrm{cmc}$; i.e., the local environment is essentially the same as it was at equilibrium, and for the time being, micelles occupying this region remain unaware that a new interface has been created. The effect on the surface tension dynamics, resulting from replacement of the activation term in eq 2 by the more elaborate expression (3), is significant only at short time, as shown by direct numerical simulations in Figure 4.

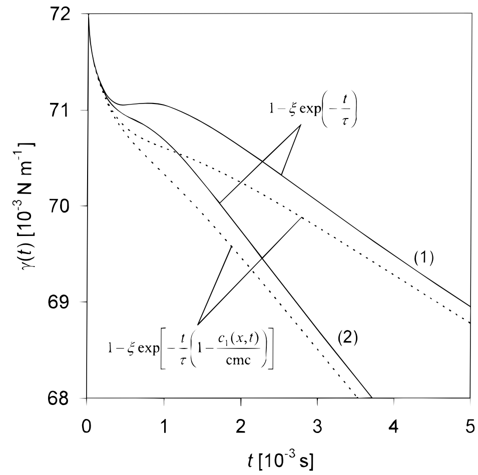

Figure 4. Effect of the form of the activation factor in the source function $Q(x,t)$ on the short-time surface tension dynamics. The following simulation parameters have been used: $\mathrm{cmc} = 9 \times 10^{-4}$ mol dm^{-3}; $C_0 = 2$ cmc; $K_L = 7 \times 10^5$ dm^3 mol^{-1}, $\Gamma_m = 2.4 \times 10^{-6}$ mol m^{-2}; $\tau = 0.01$ s; $k = 10^5$ s^{-1}; $\xi = 1$; $\eta = 0$; $D_1 = 5 \times 10^{-10}$ m^2 s^{-1}, $D_N = 5 \times 10^{-11}$ m^2 s^{-1} (1), and $D_N = 1 \times 10^{-10}$ m^2 s^{-1} (2).

The mathematical formulation of the problem becomes complete on adding the initial conditions

$$c_1(x,0) = \mathrm{cmc}; \qquad c_N(x,0) = C_0 - \mathrm{cmc} \qquad (4)$$

where C_0 is the total concentration of surfactant (assumed to be greater than cmc) and the boundary conditions

$$D_1 \frac{\partial c_1}{\partial x}\Big|_{x=0} = \frac{\mathrm{d}\Gamma}{\mathrm{d}t}; \qquad D_N \frac{\partial c_N}{\partial x}\Big|_{x=0} = 0; \qquad c_1(\infty,t) = \mathrm{cmc};$$
$$c_N(\infty,t) = C_0 - \mathrm{cmc} \quad (5)$$

The boundary conditions reflect the fact that only monomers are capable of adsorbing to the gas/liquid interface. The solution phase is assumed to be semi-infinite. Integration by time produces a familiar mass conservation relation,

$$\Gamma(t) = \int_0^t \mathrm{d}t \left[D_1 \frac{\partial c_1}{\partial x}\Big|_{x=0} + D_N \frac{\partial c_N}{\partial x}\Big|_{x=0}\right] = \int \mathrm{d}t \int \mathrm{d}x \left[\frac{\partial}{\partial x}\left(D_1 \frac{\partial c_1}{\partial x} + D_N \frac{\partial c_N}{\partial x}\right)\right]$$
$$= \int \mathrm{d}x \int \mathrm{d}t \left(\frac{\partial c_1}{\partial t} + \frac{\partial c_N}{\partial t}\right) = \int_0^\infty \{C_0 - c_1(x,t) - c_N(x,t)\}\, \mathrm{d}x \quad (6)$$

It should be noted that in Fainerman’s definition of the source function only the decay of micelles is allowed for, while the formation is not. Consequently, only equilibrium initial conditions (4) are acceptable. The following symmetrized definition is free of this limitation,

$$Q(x,t) = k_1(t)[\mathrm{cmc} - c_1(x,t)]c_N(x,t) - k_2(t)[(C_0 - \mathrm{cmc}) - c_N(x,t)]c_1(x,t)$$
$$= [\mathrm{cmc} - c_1(x,t)][k_1(t)c_N(x,t) + k_2(t)c_1(x,t)] \qquad (7)$$

Here, the activation factors have been incorporated into the corresponding frequency factors, k_1 and k_2, making the latter time-dependent.

(22) Rillaerts, E.; Joos, P. *J. Phys. Chem.* **1982**, *86*, 3471.

For the forthcoming numerical solution, it is convenient to represent the boundary condition for $c_1(x,t)$ in the form

$$c_1(0,t) = c_s(t) \qquad (8)$$

where c_s is the monomer concentration in the vicinity of the gas/liquid interface. Since the adsorption is only controlled by diffusion, the equilibrium between the neighboring interfacial region, called the subsurface, and the interface itself, termed in this context the surface, is established instantly (i.e., much faster than the mass transport can caus any noticeable changes in the concentration profile). Hence, the magnitude of adsorption, Γ, must be a unique function of the concentration of monomers at the subsurface,

$$\Gamma(t) = F\cdot c_s(t) \qquad (9)$$

A common type of the adsorption isotherm is[21,22]

$$\theta = \left[1 + \frac{A}{c_s}\exp\left(\psi - \frac{E + \omega\theta}{RT}\right)\right]^{-1} \qquad (10)$$

where $\theta = \Gamma/\Gamma_m$, Γ_m being the monolayer capacity. Here, E is the adsorption energy, ω is the energy of lateral interactions, and A is a parameter. For $\psi = 0$, the Langmuir, Frumkin, and Fowler–Guggenheim isotherms are obtained, whereas taking $\psi = \theta/(1 - \theta)$ one gets the Hill–de Boer isotherm. (The Frumkin isotherm known in electrochemistry has the same functional form as the Fowler–Guggenheim isotherm known in gas adsorption. The Fowler–Guggenheim isotherm reduces to the Langmuir isotherm if lateral interactions are neglected.) As $c_s \to 0$, all the three isotherm reduce to the Henry law, $\Gamma = K_H c_s$, where $K_H = (\Gamma_m/A)\exp(E/RT)$ is the Henry constant. The above isotherms are nearly the only isotherms that have a solid statistical-mechanical substantiation and comprehensible equations of state. Nonetheless, some semiempirical relations, like the generalized Frumkin isotherm, are often found to be in better agreement with experimental data.[18] What is important to note here is that c_s can always be found by inverting the functional (9),

$$c_s(t) = F^{-1}\cdot\Gamma(t) \qquad (11)$$

provided that the magnitude of adsorption is known and a decision has been made which isotherm to use. Then, taking into account the mass conservation relation (6), one can write,

$$c_1(0,t) \equiv c_s(t) = F^{-1}\cdot\left\{\int_0^{\infty}[C_0 - c_1(x,t) - c_N(x,t)]\,\mathrm{d}x\right\} \qquad (12)$$

On putting eqs 1, 2, 4, 5, and 12 together, a closed system of equations having a unique solution is obtained.

Finally, the link to the surface tension is established by the Gibbs equation,

$$\gamma(t) = \gamma_0 - RT\int_{c=0}^{c=c_s(t)}\Gamma\,\mathrm{d}\ln c \qquad (13)$$

How to Explain the Initial Delay in the Surface Tension Dynamics

Thus far, it has been assumed that the equilibrium between the surface and subsurface is established instantly, which means—in accordance with eq 11—that the adsorption, $\Gamma(t)$, at time t is fully correlated with the concentration, $c_s(t)$, determined at the same time. This assumption, however, is no longer valid if there exists an activation barrier of adsorption, in which case a certain finite time is required for the adsorption equilibrium to get settled. As a result, the typical DST curve will have an induction region, followed by a fast fall region.[26]

If the activation time of adsorption is small compared to the time needed for any noticeable changes in $c_s(t)$ to occur, the following relaxation kinetics can be assumed,

$$\Gamma(t'|t) = \Gamma(\infty|t)\chi(t' - t) \qquad t \le t' < \infty \qquad (14)$$

where $\Gamma(\infty|t)$ is the adsorption value at time t if adsorption equilibrium is achieved instantly, i.e., $\Gamma(\infty|t) = F\cdot c_s(t)$, and χ is the relaxation function such that $\chi(0) = 0$ and $\chi(\infty) = 1$. A typical relaxation function describing the dynamics of processes of the kind “amount transferred is proportional to the amount present” is

$$\chi(t) = 1 - \exp(-\beta t) \qquad (15)$$

where β is the relaxation rate constant.

It should be kept in mind that the aforesaid formulation is based on the assumption of quasi-stationarity of c_s,

$$\left|\frac{1}{c_s}\frac{\mathrm{d}c_s}{\mathrm{d}t}\right| \ll \left|\frac{1}{\chi}\frac{\mathrm{d}\chi}{\mathrm{d}t}\right| \qquad (16)$$

If this is not the case, the more general equation should be used,

$$\Gamma(t) = \int_0^t \frac{\mathrm{d}\chi}{\mathrm{d}t}(t')F\cdot c_s(t - t')\,\mathrm{d}t' \qquad (17)$$

Asymptotically, as $t \to 0$, $\Gamma(t)$ goes as

$$\Gamma(t) \cong F\cdot c_1(x,0)\chi'(0)t \qquad t \to 0 \qquad (18)$$

Consequently, using the Langmuir–Szyszkowski equation, one gets

$$\gamma(t) - \gamma_0 = \Gamma_m RT\ln\left(1 - \frac{\Gamma(t)}{\Gamma_m}\right) \cong -RT\chi'(0)F\cdot c_1(x,0)t \qquad (19)$$

whereas for purely diffusion-controlled kinetics one would get

$$\gamma(t) - \gamma_0 \cong -2RT\left(\frac{D_1}{\pi}\right)^{1/2} c_1(x,0)t^{1/2} \qquad (20)$$

In the former case, the derivative $\mathrm{d}\gamma/\mathrm{d}t|_{t\to 0}$ is finite, while in the latter, $\mathrm{d}\gamma/\mathrm{d}t|_{t\to 0} \sim t^{-1/2} \to \infty$. This proves that, in the short-time limit, the activated adsorption results in slower surface tension dynamics, which looks like a “delay” when

(23) Jagiello, J.; Schwarz, J. A. *J. Colloid Interface Sci.* **1991**, *146*, 415.

(24) Jagiello, J.; Schwarz, J. A. *J. Colloid Interface Sci.* **1992**, *154*, 225.

(25) Fainerman, V. B.; Zholob, S. A.; Miller, R. *Langmuir* **1997**, *13*, 283.

(26) Hua, X. Y.; Rosen, M. J. *J. Colloid Interface Sci.* **1988**, *124*, 652.

plotted in γ vs $t^{1/2}$ coordinates. (Some authors call eq 19 the Frumkin equation (see, e.g., Chang, et al., ref 3), reserving the term "Szyszkowski equation" for a modified form of the same equation (eq 33), others call it the Langmuir–Szyszkowski equation, highlighting its relationship with the Langmuir isotherm (see, e.g., Fainerman et al., ref 25). We would prefer keeping association of the term "Frumkin equation" with the Frumkin isotherm.[16,27])

Activation Control Limit

If the relaxation function, $\chi(t)$, changes very slowly, one has

$$\Gamma(t) = \int_0^t \chi'(t') F\cdot c_s(t - t')\, dt' \cong \chi'(t)\langle F\cdot c_s\rangle \quad (21)$$

and the resultant is governed by $\chi(t)$. The existence of an activation-controlled step in the surface tension relaxation for nonionic surfactants of C_nE_m type has been reported by Eastoe et al.[19,28] However, their evidence, based on the temperature-dependence of DST relaxation kinetics, is somewhat inconclusive since both the diffusion coefficient and the adsorption rate constant depend on the temperature.

Diffusion Control Limit

The mass conservation condition must be satisfied independent of whether the adsorption process exhibits an initial delay,

$$\int_0^t F\cdot c_1(0,t - t')\chi'(t')\, dt' = \int_0^\infty [C_0 - c_1(x,t) - c_N(x,t)]\, dx \quad (22)$$

If the adsorption equilibrium the surface and subsurface is established instantly, one has

$$\int_0^t F\cdot c_1(0,t - t')\chi'(t')\, dt' \cong F\cdot c_1(0,t) \quad (23)$$

and then, eq 23 becomes identical to eq 12. This situation was analyzed by Ward and Tordai[6] for the Henry isotherm,

$$K_H c_1(0,t) = \int_0^\infty [C_0 - c_1(x,t) - c_N(x,t)]\, dx \quad (24)$$

On neglecting interconversation between monomers and micelles and substituting the classical solution of eq 1 corresponding to the boundary conditions (4) and (5),

$$c_1(x,t) = c_1(x,0)\, \mathrm{erf}\left(\frac{x}{2(D_1 t)^{1/2}}\right) + \frac{1}{2\pi^{1/2}}\int_0^t \frac{x}{[D_1(t - t')^3]^{1/2}} \exp\left(-\frac{x^2}{4D_1(t - t')}\right) c(0,t')\, dt' \quad (25)$$

into the mass balance eq 24, a simple integral equation defining $c_1(0,t)$ is arrived at,

$$K_H c_1(0,t) = \left(\frac{D_1}{\pi}\right)^{1/2}\left(2c_1(x,0)t^{1/2} - \int_0^t \frac{c_1(0,t')\, dt'}{(t - t')^{1/2}}\right) \quad (26)$$

which is easily solved by Laplace's transform, yielding

(27) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley: New York, 1990.

(28) Eastoe, J.; Dalton, J. S.; Rogueda, P. G. A. *Langmuir* **1998**, *14*, 979.

$$c_1(0,t) = c_1(x,0)[1 - \exp(at)\, \mathrm{erfc}(at)^{1/2}], \quad a = D_1/K_H^2 \quad (27)$$

The short-time asymptotics,

$$\Gamma(t) \equiv K_H c_1(0,t) \cong 2c_1(x,0)(D_1 t/\pi)^{1/2}, \quad t \to 0 \quad (28)$$

have been serving for decades to describe diffusion-controlled adsorption kinetics.

As long as $t \ll \tau$, micellar decay contributes almost nothing to the replenishment of the amount of monomers. In other words, the interconversation between monomers and micelles is negligible at this early stage, and the resulting surface tension dynamics is purely diffusion-controlled as reflected in eq 28. Initially, in the bulk of the solution, the monomer and micellar forms of surfactant are homogeneously distributed and are in equilibrium with each other. Immediately after the creation of a fresh interface, monomers start to adsorb to the interface, creating a depletion zone nearby. For $t \to 0$,

$$c_1(x,0) - c_1(x,t) \cong c_1(x,0)\, \mathrm{erfc}\left(\frac{x}{2(D_1 t)^{1/2}}\right) \cong \begin{cases} 0 & \text{if } x \gg (D_1 t)^{1/2} \\ \mathrm{cmc} & \text{if } x \ll (D_1 t)^{1/2} \end{cases} \quad (29)$$

Rigorously speaking, at the beginning, micelles should migrate from the interface to the bulk—inasmuch as they are surface inactive, their adsorption has to be negative. The absolute value of the adsorption cannot be large, however, justifying the use of the boundary condition for c_N in the form (5). In some respect, this situation is similar to the redistribution of ions in an electrolyte solution near a strongly charged interface: the excess of counterions can be as large as one pleases, whereas the deficit of co-ions cannot exceed their bulk concentration.

An important point to be stressed here is that the Ward–Tordai result relies on applicability of the Henry isotherm, which means that the degree of surface coverage needs to be relatively low for the theory to be adequate. This justifies the following simplification of the Langmuir–Szyszkowski equation,

$$\gamma(t) \cong \gamma_0 - RT\Gamma(t) \quad (30)$$

Now, the dependence on Γ_m has disappeared. Notice that any changes in D_1 and K_H keeping the ratio D_1/K_H^2 constant have little effect on the DST curve.

The major drawback of eq 30 is that, when parametrized againt the experimental data measured at short times, it overestimates the magnitude of adsorption and the decrease in the surface tension at long times. This effect could be diminished to some extent by keeping the quadratic term in the logarithm expansion,

$$\gamma(t) \cong \gamma_0 - RT\Gamma(t)\left[1 - \frac{\Gamma(t)}{2\Gamma_m}\right] \quad (31)$$

However, it should be kept in mind that the Henry isotherm is nothing other than the Langmuir isotherm expansion in powers of $\Gamma(t)/\Gamma_m$ truncated on the linear term.

Evaluation of Parameters and Numerical Simulations

Parameteres of the Adsorption Isotherm. If the adsorption of surfactant is described by the Langmuir isotherm,

$$\Gamma = \frac{\Gamma_m K_L c}{1 + K_L c} \tag{32}$$

where $c = c_1(x,\infty) <$ cmc is the equilibrium concentration of surfactant, then eq 13 is transformed into the Szyszkowski equation,

$$\gamma(c) = \gamma(0) - \Gamma_m RT(1 + K_L c) \tag{33}$$

Here, K_L is the adsorption equilibrium constant and Γ_m is the monolayer capacity. The latter are determined by fitting eq 33 to the experimental surface tension data measured for several surfactant concentrations. The corresponding Henry constant is found as $K_H = \Gamma_m K_L$. The results are summarized in Figure 3. For $C_{10}E_6$ and $C_{12}E_6$ surfactants, the fitting is very good, for $C_{14}E_6$ it is getting worse, but the obtained parameters still look realistic, and finally, for $C_{16}E_6$, things obviously go awry, and the obtained parameters appear to be meaningless. Apart from conceptual limitations of the Langmuir−Szyszkowski equation, possible reasons for this is that $C_{16}E_6$ surfactant has a very low cmc value. First, practically, it is extremely difficult to quantify concentrations in the submicromolar range, where the adsorption of surfactant by glassware can substantially deplete the bulk region. Second, for ultralow surfactant concentrations, it is getting difficult to meet certain criteria of purity.[29,30] Finally, equilibration issues must be kept in mind: Since the monolayer capacity has the same order of magnitude for all surfactants, the depletion region for $C_{16}E_6$ (cmc = 1 μmol dm^{-3}) will extend about 10^3 times deeper than for $C_{10}E_6$ (cmc = 1 mmol dm^{-3}). For example, to create a surface coverage of 5 μmol m^{-2} while the bulk surfactant concentration is 1 mmol dm^{-3}, only about a 5-μm layer needs to be depleted. Given the diffusion coefficient of 5×10^{-10} m^2 s^{-1}, it takes only about 1 s for the concentration profile to develop in depth. In this case, pertinent to $C_{10}E_6$ surfactant, the typical equilibration time (10−30 min) used in static surface tension measurements is more than enough for the equilibrium to be attained. However, for $C_{16}E_6$ surfactant, the equilibration time increases by a factor of 10^6, so that seconds will turn into weeks! This proves conclusively that, in many cases, the data obtained for long-alkyl-chain surfactants by using traditional surface tension measurement techniques, which look like equilibrium ones and often claimed so in the literature, in fact refer to deeply nonequilibrium conditions. Taking into account the aforesaid complications, the experimental effort has been concentrated on studying $C_{10}E_6$ surfactant.

As pointed out by Lin et al.,[18,31] strong lateral interactions between adsorbate molecules in nonionic surfactants of the C_nE_m type may render the Langmuir isotherm inadequate, thus necessitating use of some empirical corrections allowing for nonlinear powers of Γ/Γ_m in order to best account for the surface tension relaxation profiles. The role of lateral interactions in C_nE_m surfactants also was studied by Nikas et al.,[32] who managed to derive a rather general equation of state allowing quite accurate predictions of the static surface tension in composite mixtures. However, for single-component systems, the generalized Frumkin isotherm should usually be adequate for these purposes,

$$\theta = \frac{K_F c}{K_F c + \exp(p\theta^q)} \tag{34}$$

Here K_F is another adsorption constant having the same order of magnitude as K_L, and p and q are some empirical parameters. (Note that eq 9 in ref 18 is applicable only if $|p| \ll 1$. Hence, the results reported by the authors for p in the range 5−13 appear to be completely meaningless.) As can be judged from Figure 3, for $C_{10}E_6$ surfactant, the generalized Frumkin isotherm does really provide a bit better description of the experimental γ vs c curve, whereas for $C_{12}E_6$, no improvement over the Langmuir isotherm is observed.

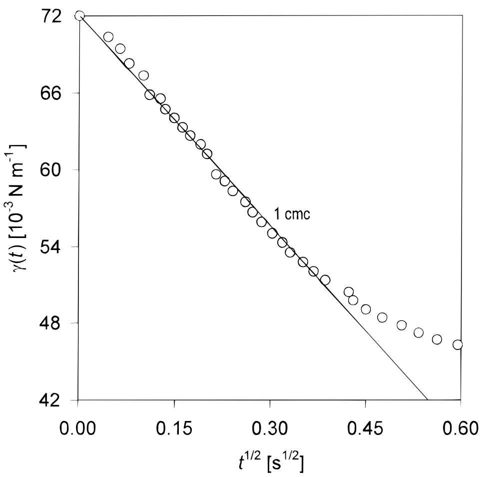

Figure 5. Evaluation of the diffusion coefficient, D_1, of monomers. The linear fit in coordinates γ vs $t^{1/2}$ according to eqs 28 and 30 produces $D_1 = 5.7 \times 10^{-9}$ m^2 s^{-1}.

Diffusion Coefficient of Monomers. The short-time experimental kinetics, γ vs t, measured in the sub-cmc concentration region, have been fitted according to the linearized eq 30. The results are represented in Figure 5. The magnitude of the diffusion coefficient found, $D_1 \sim 5 \times 10^{-10}$ m^2 s^{-1}, is typical of molecular diffusion in aqueous solutions.[18]

It is useful to estimate the minimum time required to pass by since the moment of creation of a fresh interface in order for the dynamic surface tension to qualify as the "surface tension" from a thermodynamic viewpoint. First, it should be recalled that the concept of the dynamic surface tension implies an equilibrium between the surface and subsurface. The location of the subsurface is ill-defined. One may expect that the subsurface is located on such a distance from the surface where the structure of the solution is essentially the same as in the bulk. Theoretically, this distance can be identified with the decay length of $p_{\parallel} - p_{\perp}$, where $p_{\parallel}$ and $p_{\perp}$ are the tangential and normal components of the pressure tensor. Typically, the anisotropy of p extends only over a few molecular monolayers, hence 1 nm should be a reasonable estimate. To talk about a local equilibrium, one must be sure that there exists no mass transport throughout this layer; i.e., the corresponding concentration gradient must be small. For the diffusion coefficient of 10^{-10} m^2 s^{-1}, this requires an equilibration time "much greater than" 10^{-8} s.

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Simulation of Surface Tension Dynamics. Before proceeding with the numerical solution of eqs 1−5, it is convenient to change to reduced variables, so that concentration of surfactant be expressed in units of cmc, time in units of the activation time of micelle decay, τ, and length in units of the distance traveled by the monomers over the time τ:

$$\tilde{c}_i = \frac{c_i}{\text{cmc}} \quad (i = 1, N); \quad \tilde{x} = \frac{x}{(D_1\tau)^{1/2}}; \quad \tilde{t} = \frac{t}{\tau} \qquad (35)$$

Then eqs 1−5 are transformed into

$$\frac{\partial\tilde{c}_1}{\partial\tilde{t}} = \frac{\partial^2\tilde{c}_1}{\partial\tilde{x}^2} + Q(\tilde{x},\tilde{t})$$

$$\frac{\partial\tilde{c}_N}{\partial\tilde{t}} = \frac{D_N}{D_1}\frac{\partial^2\tilde{c}_N}{\partial\tilde{x}^2} - Q(\tilde{x},\tilde{t}) \qquad (1')$$

$$Q(\tilde{x},\tilde{t}) = \tilde{k}[1 - \tilde{c}_1(\tilde{x},\tilde{t})][1 - \xi\exp(-\tilde{t})]\tilde{c}_N(\tilde{x},\tilde{t}) \qquad (2')$$

$$\tilde{c}_1(\tilde{x},0) = 1; \quad \tilde{c}_N(\tilde{x},0) = \tilde{C}_0 - 1 \qquad (4')$$

$$\frac{\partial\tilde{c}_1}{\partial\tilde{x}}\Big|_{\tilde{x}=0} = \frac{\Gamma_m}{\text{cmc}(D_1\tau)^{1/2}}\frac{\mathrm{d}\theta}{\mathrm{d}t}; \quad \frac{\partial\tilde{c}_N}{\partial\tilde{x}}\Big|_{\tilde{x}=0} = 0; \quad \tilde{c}_1(\infty,\tilde{t}) = 1;$$

$$\tilde{c}_N(\infty,\tilde{t}) = \tilde{C}_0 - 1 \qquad (5')$$

where $\tilde{k} = k\tau$.

The above equations have been solved numerically using the finite-difference method. The following information has been obtained: dynamics of the concentration profiles, $c_1(x,t)$ and $c_N(x,t)$ (Figure 6), and the source function, $Q(x,t)$ (Figure 7), the adsorption kinetics, $\Gamma(t)$ (Figure 8), and the surface tension dynamics, $\gamma(t)$ (Figures 9 and 10). Dependency of the surface tension dynamics on variations in the magnitude of different parameters, including the activation time of micelle decay, τ, frequency factor, k, diffusion coefficients, D_1 and D_N, and the concentration of surfactant, C_0, has been analyzed as well.

Discussion

Peculiarities of Mass Transport. The presence of micelles, which are a source of monomers, causes a contraction of the monomer depletion zone (see Figure 6). The contraction is stronger the larger the C_0/cmc ratio is. The source function passes through a sharp maximum located in the vicinity of the gas/liquid interface, the region suffering the strongest depletion (see Figure 7). For a fixed surfactant concentration and $D_1 > D_N$, the dynamics is found to be dominated by D_N (see Figure 9).

Adsorption Kinetics. Adsorption kinetics are very sensitive to the choice of the adsorption isotherm. If the Henry isotherm is used, the magnitude of adsorption may appear to be unrealistically high, in excess of 10 μmol m^{-2}. When no interconversation between monomers and micelles is allowed ($Q = 0$), the Langmuir isotherm leads to results similar to those obtained by using the Henry isotherm, provided that the degree of filling, θ, is less than approximately 0.9. Enabling the interconversation results in a significant change in the adsorption kinetics.

If the micelle decay needs to be activated ($\tau > 0$), a characteristic delay after the first short diffusion-controlled adsorption stage is observed. If the micelle decay can proceed without activation, no such delay occurs. In either case, the resulting kinetics are more slow because the rate of the overall process is limited by transport of micelles. The difference between the activated and non-activated decay kinetics becomes negligible after a few milliseconds. The results are summarized in Figure 8.

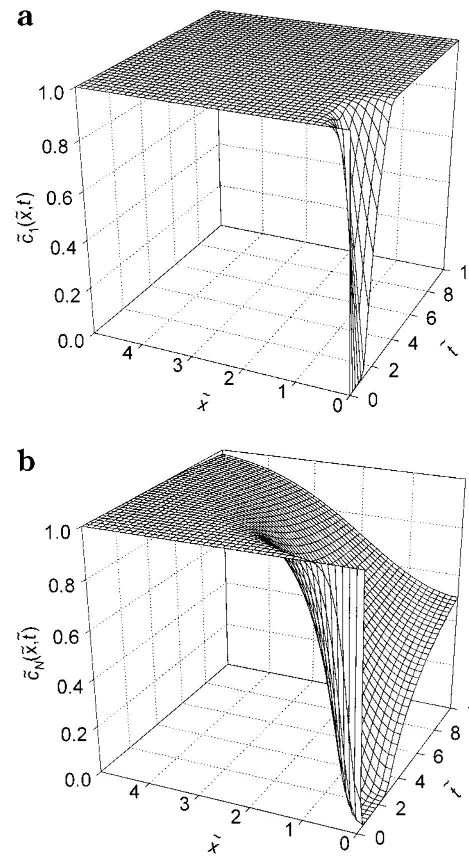

Figure 6. Dynamics of concentration profiles of monomer (a) and micellar (b) forms of surfactant calculated according to eqs 1′−5′. The simulation parameters are the same as in Figure 4 and $D_N = 1 \times 10^{-10}$ m^2 s^{-1}.

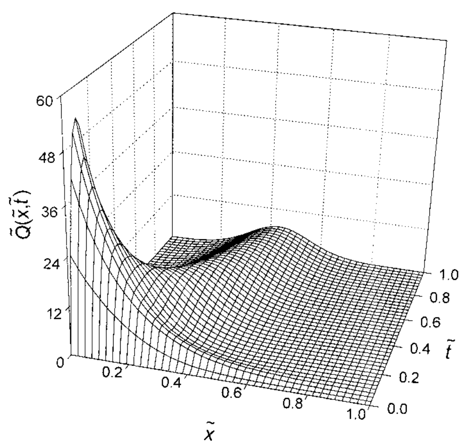

Figure 7. Source function, $Q(x,t)$, calculated according to eqs 1′−5′. The simulation parameters are the same as in Figure 4 and $D_N = 1 \times 10^{-10}$ m^2 s^{-1}.

Surface Tension Dynamics. If one expects a monotonic increase in the DST relaxation rate with increasing the surfactant concentration, the results presented in Figure 11 might appears to be a bit strange: the simulations show that immediately after passing the cmc, the DST relaxation rate suddenly falls dramatically and then starts to increase again at substantially higher surfactant concentrations. Obviously, this apparent anomaly should somehow deal with the existence of micelles. For $C_0 <$ cmc, the intensity of diffusional flow supplying the gas/liquid interface with monomers is

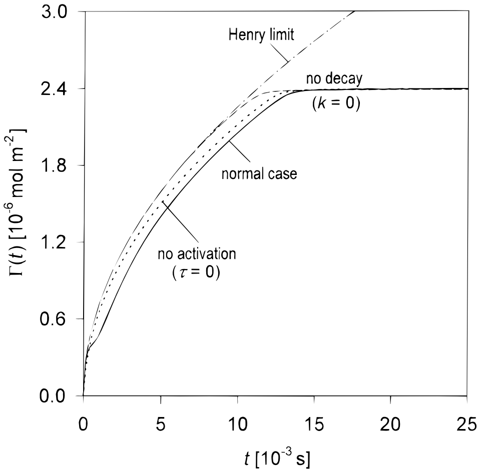

Figure 8. Comparison of adsorption kinetics. The simulation parameters are the same as in Figure 4 and $D_N = 1 \times 10^{-10}$ m^2 s^{-1}. The source function, $Q(x,t)$, is determined in accordance with eq 2.

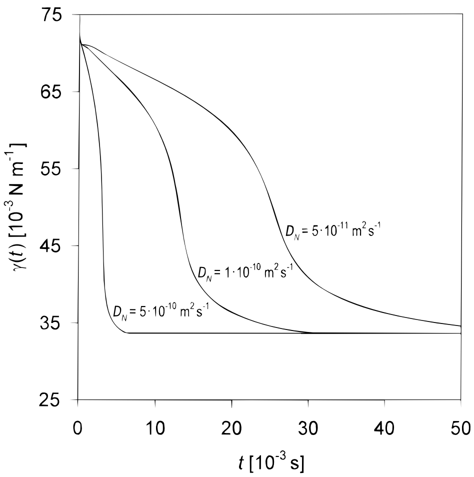

Figure 9. Dependence of the surface tension dynamics on the diffusion coefficient of micelles. Other parameters are the same as in Figure 4. On the scale shown, the results corresponding to the source function defined by eq 2 are undistinguishable from those corresponding to the source function defined in accordance with eq 3.

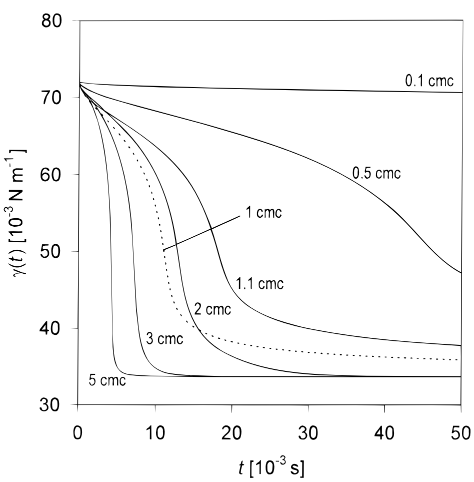

Figure 10. Dependence of surface tension dynamics on the concentration of surfactant. The simulation parameters are the same as in Figure 4 and $D_N = 1 \times 10^{-10}$ m^2 s^{-1}.

proportional to C_0. Hence, the adsorption rate, dΓ/dt, and therefore the DST relaxation rate, dγ/dt, increase steadily. Conversely, for $C_0 >$ cmc, the diffusional transport is no longer the only source supplying the monomers. Micelles are present, and their disintegration continuously replenishes the monomer supplies. As a result, the monomers to a smaller extent rely on the diffusional transport and fail to develop a sufficiently deep concentration profile. When the interfacial region gets depleted of micelles as well, new micelles need to be transported from the bulk. Their transport is slow, causing a lag in the surface tension dynamics. With further increase of the surfactant concentration, the micellar decay is finally getting so intensive that the DST relaxation rate starts to increase again. It should be recognized, however, that this depression in the DST relaxation rate predicted by the theory does not appear to have ever been observed experimentally.

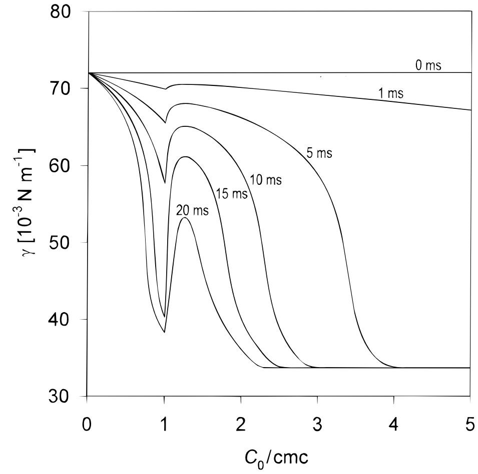

Figure 11. Constant-time contour plots showing the variation of the DST relaxation rate with increasing the concentration of surfactant. Nonactivated decay kinetics is assumed for the sake of simplicity ($\tau = 0$). Other simulation parameters are the same as in Figure 4. The derivative, dγ/dC_0, as a discontinuity point at C_0 = cmc.

There also exist large discrepancies between the theoretical DST curves calculated according to the Fainerman model and experimental ones. Particularly confusing is the fact that eqs 27 and 30, which are based on some obviously wrong assumptions, provide a much better description of the surface tension dynamics than Fainerman's equations, which apparently are built on more realistic ideas (see Figure 12). Obviously, if a simpler model delivers a sufficiently good approximation, any more general model containing this simpler model as its subset must be able to deliver at least the same or a better quality of approximation. Hence, it would be incorrect to interpret the aforesaid as a statement that the Fainerman theory does not allow one to approximate the experimental data at all. Such approximation is possible, indeed, but in order to achieve it, one needs to accept an unrealistically high value of the monolayer capacity, Γ_m, and very low values of the adsorption equilibrium constant, K_L, and the interconversation frequency factor, k, in which case eq 1 describing the micelle and monomer transport get decoupled, and the linearized expression (30) becomes valid. Thereby, the Fainerman model is projected into the Ward–Tordai model. The problem is that, so defined, Γ_m and K_L are inconsistent with the concentration-dependence of the equilibrium surface tension measured in a separate experiment (Figure 3). Conversely, the success of the Langmuir–Szyszkowski equation in describing the equilibrium surface tension gives strong evidence that the Langmuir isotherm is an adequate choice under given conditions. Therefore, there must be something wrong in the "dynamic" part of the model. A possible reason for the

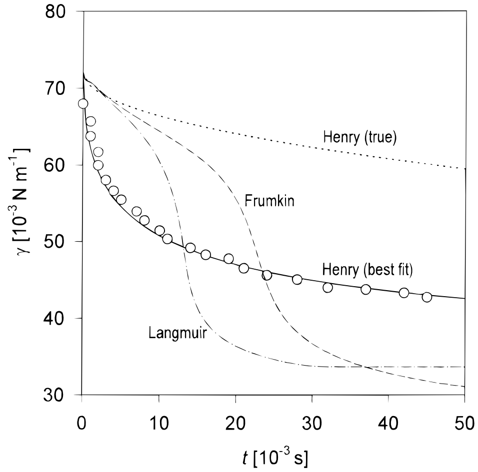

Figure 12. Quantitative comparison between the theory and experiment: (○) Experimental data obtained for 2 mM solution of $C_{10}E_6$; (—) Best-fit DST curve calculated assuming the Henry adsorption (eqs 27 and 30 with $c_1(x,0) = C_0 = 2$cmc, $K_H = 8.9 \times 10^{-6}$ m, and $D_1 = 6.0 \times 10^{-9}$ m^2 s^{-1}); (– · –) DST curve calculated by using the Langmuir adsorption isotherm (eqs 1–5, 13, and 32 with the same parameters as given in caption to Figure 4); (- - -) DST curve calculated by using the generalized Frumkin adsorption isotherm (eqs 1–5 and 34 with the same parameters as given in caption to Figure 3); and (···) DST curve calculated by using the correct asymptotic form of the Henry isotherm with $c_1(x,0) =$ cmc, $K_H = \Gamma_m K_L \sim 10^{-3}$ m, and $D_1 = 5 \times 10^{-10}$ m^2 s^{-1}.

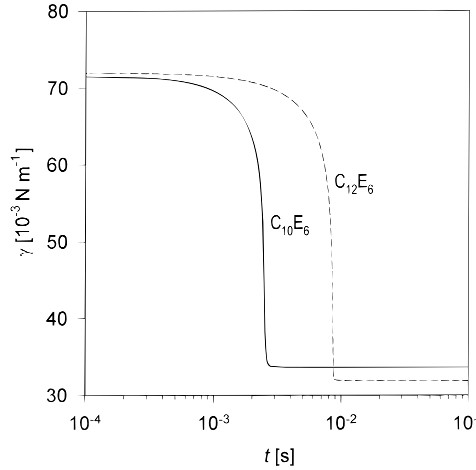

Figure 13. Simulated DST curves for 10 mM solutions of $C_{10}E_6$ and $C_{12}E_6$ surfactants. The adsorption isotherm parameters are as follows: $C_{10}E_6$ (cmc $= 9 \times 10^{-4}$ mol dm^{-3}, $K_L = 7 \times 10^5$ dm^3 mol^{-1}, $\Gamma_m = 2.4 \times 10^{-6}$ mol m^{-2}) and $C_{12}E_6$ (cmc $= 8 \times 10^{-5}$ mol dm^{-3}, $K_L = 5 \times 10^6$ dm^3 mol^{-1}, $\Gamma_m = 2.7 \times 10^{-6}$ mol m^{-2}) in accordance with Figure 3. Diffusion coefficient of micelles is 1×10^{-10} m^2 s^{-1} in either case. Other parameters are identical to those used in Figure 4.

failure is the oversimplified treatment of micellar equilibria: It is well-known that the aggregation and disintegration of surfactant are stepwise processes.[33,34] This implies that the aggregates present in the solution are essentially polydisperse in size. Consequently, a system of N coupled diffusion equations of the type

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + Q_{\langle i+1|i\rangle} - Q_{\langle i-1|i\rangle} \qquad i = 1, 2, ..., N \quad (36)$$

is needed in order to describe the mass transport in such a system. Here N is the number of different species present in the solution, $Q_{\langle i+1|i\rangle}$ describes generation of i molecular aggregates due to disintegration of $(i + 1)$ molecular aggregates, and $Q_{\langle i-1|i\rangle}$ describes dissociation of i molecular aggregates into $(i - 1)$ molecular aggregates. Such an idea has been implemented in an earlier work by Brinck et al.[17] Even if the micelles themselves are not surface active, some smaller species, such as dimers, trimers, etc., certainly are. Hence, taking into account the multispecies composition of aggregated surfactant should add flexibility to the model and swamp the unwanted minimum at $\gamma(t)$ vs C_0 plots shown in Figure 11.

Coexistence of several species capable of adsorption to the gas/liquid interface and interconversion between each other can substantially increase the mass transport of surfactant to the interface. This hypothesis is partly supported by the fact that the effective diffusion coefficient determined by fitting the experimental data shown in Figure 1 according to eqs 27 and 30 increases steadily with increasing surfactant concentration. It should be recognized that, at a quantitative level, the Fainerman model correctly accounts for this increased mass transfer (see Figure 10). Another advantage of the Fainerman model is its ability to account for, though only qualitatively again, the enlargement of the induction time observed for surfactants with lower cmc (cf. Figures 2 and 13).

Lin et al.[18,35] have observed strong dependence of the diffusion coefficient on the bulk concentration of surfactant even in the sub-cmc region. This has led them to conclude that there may exist a transition from diffusion-controlled adsorption kinetics at low concentration to mixed kinetics at higher concentration of surfactant. Mixed kinetics are recognized by a characteristic delay in the short-time limit (cf. eqs 19 and 20). In this connection, it is important to note that the results obtained in the present study show that the experimental kinetics are not slower, but faster than expected for a diffusion-controlled adsorption mechanism (see Figure 12).

Summarizing, one can see that although the Fainerman theory gives a qualitatively correct picture of DST relaxation in concentrated surfactant systems, it lacks the flexibility needed to describe the process quantitatively, at least in the case of nonionic surfactants of the poly(ethylene glycol) type. Neglect of polydispersity of micelles is one of the major drawbacks of the theory. To account for the increased mass transport to the interface at above-cmc concentrations of surfactant, one has to assume that at least some aggregated forms of surfactant are capable of adsorption to the gas/liquid interface. Even though micelles are thought not to be surface active, one cannot exclude the possibility of their conversion (unfolding) into some two-dimensional structures patching the interface directly.

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