

Dynamics of Surfactant Adsorption from Solution Considering Aggregation within the Adsorption Layer

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The theory of diffusion-controlled adsorption kinetics is developed for adsorption layers of surfactant molecules able to form two-dimensional aggregates. It is shown that the formation of such aggregates within the adsorption layer results in a deceleration of the surface tension decrease and in a reduction of the dynamic surface pressure when the system is far from the equilibrium state. If no aggregation of adsorbed molecules is considered, then any decrease in adsorption rate is ascribed usually to the existence of an adsorption barrier. However, assuming this two-dimensional aggregation, the diffusion model provides a much better description of phenomena that actually take place. A good correspondence is found between the experimental dynamic surface tensions and theoretically calculated dependencies for the solutions of 1-decanol for a mean aggregation number of 2.5 within the monolayer. The same aggregation number was estimated for decanol equilibrium monolayers.

Introduction

The well-known integro-differential equation derived by Ward and Tordai¹ is the most general relationship between the dynamic adsorption $\Gamma(t)$ and the subsurface concentration $c(0,t)$ for fresh nondeformed surfaces:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}[c_0\sqrt{t} - \int_0^{\sqrt{t}} c(0,t-\lambda) d\sqrt{\lambda}] \quad (1)$$

where D is the diffusion coefficient, c_0 is the bulk concentration, t is a time, λ is a dummy integration variable. Equation 1 is valid for kinetic-controlled, pure diffusion-controlled, and mixed adsorption mechanisms. In the latter case the adsorption isotherm is an additional relation between the adsorption and the subsurface concentration. Therefore, even for a diffusion-controlled adsorption mechanism eq 1 predicts different Γ dependencies on t for different types of isotherms. For example, the Frumkin adsorption isotherm with the corresponding equation of state predicts a slower initial rate of surface tension decrease than the Langmuir isotherm does.^{2,3} At the same time, the isotherm considering interfacial reorientation,⁴ which assumes two modifications of adsorbed surfactant molecule with corresponding partial molar surface areas, leads to a more rapid surface tension decrease within the entire time range, as compared to the Langmuir isotherm.⁵ Experimental evidence of this rapid surface tension decrease was presented in refs 5–7. Attempts to explain a slower surface tension decrease, a case that is often experimentally observed, were also reported in literature. For example, in refs 2 and 3 the adsorption isotherm was modified to provide such an explanation, while in refs 8 and 9 this was achieved assuming a special structure of the

surface layer and a nonequilibrium surface layer, respectively. Note that the adsorption barrier concept^{10–17} is generally accepted in this case. The adsorption barrier model may, of course, be employed to explain any deviations from the diffusion-controlled adsorption kinetics (for a Langmuir isotherm); however, the reasons for a slower surface tension decrease often remain obscure.

Van den Tempel proposed processes within the adsorption layer to be considered instead of hypothetical adsorption barriers.^{18–20} We believe that such models which account for actual physical processes within adsorption layers, such as reorientation of molecules, their dimerization, and formation of clusters, although explanations for all known cases of anomalous adsorption kinetics do not exist yet, have to be preferred over any formal model. Reliable experimental evidence for a slower surface tension decrease caused by aggregation within the adsorption layer does not allow the conclusion that this is an exclusive mechanism. For example, the dynamic surface tension for aqueous solutions of the slightly soluble *N*-dodecyl- γ -hydroxybutyric acidamide (DHBA) exhibits a sharp decrease of the slope when the surface pressure attains a critical value which corresponds to the beginning of 2D aggregation of DHBA molecules within the adsorption layer.²¹ Theoretical calculations based on an approximate diffusion model that assumes the formation of large two-dimensional aggregates (with aggregation number exceeding 1000 as supported by Brewster angle microscopy) show good agreement with the experiments. Studies reported in refs 2 and 3 also provide a satisfactory description for the deviation of the adsorption kinetics of 1-decanol from the Langmuir-type behavior by assuming a 2D aggregation within the surface layer. However, in these studies the adsorption isotherm proposed in ref 22 was used. Adsorption and surface tension isotherms for decanol were described in refs 2 and 3 by the Langmuir and von Szyszkowski equations, respectively. Two different adsorption equilibrium constants were employed, one for the states

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below a certain critical decanol bulk concentration, which corresponds to the onset of aggregation within surface layer, and another one above this concentration. Another more rigorous thermodynamic theory for the adsorption at solution/fluid interfaces was proposed in ref 23, where the aggregation of adsorbed molecules was taken into account. A multicomponent adsorption layer was assumed comprised of monomers and aggregates that are in equilibrium. It was shown that the experimental decanol adsorption isotherm of refs 2 and 3 agrees perfectly with the new equations assuming a mean surface aggregation number of 2.5.

The purpose of the present study is to develop a theoretical model for the diffusion-controlled adsorption kinetics based on simultaneous solution of eq 1 and the isotherm equations presented in ref 20 accounting for a possible 2D aggregation in the adsorption layer and to compare the theoretical predictions with experimental data.

Theory

For monodisperse aggregates formed within the adsorption layer, the theory developed in ref 23 yields the equation of state

$$\Pi = -\frac{RT}{\omega_{\Sigma}} \ln[1 - \omega_{\Sigma} \Gamma_{\Sigma}] \quad (2)$$

and the adsorption isotherm

$$bc(0,t) = \frac{\Gamma_1 \omega_{\Sigma}}{[1 - \omega_{\Sigma} \Gamma_{\Sigma}]^{\omega_1/\omega_{\Sigma}}} \quad (3)$$

where Π is the surface pressure (the difference between surface tension of the solvent and that of the solution), R is the gas constant, T is the temperature, Γ_1 and Γ_n stand for the values of adsorption of monomers and aggregates, respectively, n is the aggregation number, b is the adsorption equilibrium constant, ω_1 is the partial molar area for monomers, and ω_{Σ} is the mean partial molar area of monomers and aggregates. Note that if the formation of aggregates takes place within the surface layer, then the adsorption in eq 1,

$$\Gamma = \Gamma_1 + n\Gamma_n \quad (4)$$

is the total adsorption of monomers and aggregates recalculated in terms of monomers, because only monomers exist within the solution bulk and diffuse toward the surface. At the same time, the adsorption that enters eqs 2 and 3,

$$\Gamma_{\Sigma} = \Gamma_1 + \Gamma_n \quad (5)$$

is the total adsorption of monomers and aggregates assumed to be the kinetic entities. The theory presented in ref 23 leads to approximate expressions for the adsorption of aggregates and the mean partial molar surface area of a kinetic entity, respectively,

$$\Gamma_n = \Gamma_1 \left(\frac{\Gamma_1}{\Gamma_c} \right)^{n-1} \quad (6)$$

$$\omega_{\Sigma} = \omega_1 \frac{1 + n(\Gamma_1/\Gamma_c)^{n-1}}{1 + (\Gamma_1/\Gamma_c)^{n-1}} \quad (7)$$

where Γ_c is the critical adsorption of aggregation. It follows from eq 6 that the lower the value of Γ_c , the lower the portion of monomers within the surface layer. Calculations summarized

in ref 23 show that for $\Gamma_c \leq 10^{-9}$ mol/m² the adsorption layer is almost entirely comprised of aggregates, while for $\Gamma_c \geq 10^{-4}$ mol/m² the portion of aggregates in the surface layer is negligibly small. (The value itself has no physical meaning; however it was chosen so large to ensure absence of any aggregates.) Therefore, if $\Gamma_c \ll \Gamma_1$, then $\Gamma_n \gg \Gamma_1$, and from eqs 4 and 5 one obtains the important relations $\Gamma_{\Sigma} = \Gamma_n$ and $\Gamma = n\Gamma_n = n\Gamma_{\Sigma}$. These relations are valid provided complete aggregation of all adsorbed molecules takes place. In this special case, within the short time range and for low adsorption layer coverage, one can derive an approximate solution to eqs 1 and 2, retaining the first term in eq 1 and the leading term of the expansion of the logarithm in eq 2,

$$\Pi = \frac{2c_0 RT}{n} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (8)$$

In contrast to the known relation valid for nonaggregating molecules,²⁴ the denominator of eq 8 is proportional to the aggregation number n . This means that if the formation of aggregates within the monolayer takes place, then the rate of surface tension decrease becomes lower, and the value of dynamic surface pressure becomes inversely proportional to the aggregation number.

For arbitrary times, monolayer coverage and critical adsorption Γ_c , the set of eqs 1–7 has to be solved numerically. This model assumes that the aggregation process itself does not require additional time; that is, there is always equilibrium between monomers and aggregates in the adsorption layer. Introducing dimensionless variables (cf. ref 25),

$$\tau = \frac{Dtc_0^2}{\Gamma_0^2}, \quad C(\tau) = c(0,t)/c_0, \quad \bar{\Gamma}(\tau) = \Gamma(t)/\Gamma_0 \quad (9)$$

where $\Gamma_0 = \lim_{t \rightarrow \infty} \Gamma(t)$ is the equilibrium adsorption value, one reduces eq 1 to the form

$$\bar{\Gamma}(\tau) = \frac{2}{\sqrt{\pi}} \left[\sqrt{\tau} - \int_0^{\sqrt{\tau}} C(\tau - \tau') d(\sqrt{\tau'}) \right] \quad (10)$$

To solve this equation numerically, first-order finite difference schemes can be applied as described in detail in the Appendix of ref 5. This requires a procedure to calculate C for given $\bar{\Gamma}$ at any Γ_c , ω_1 , and n . To construct this procedure, one transforms eqs 2–7 into the dimensionless variables $\bar{\Gamma}$,

$$\bar{\Gamma}_{\Sigma} = \Gamma_{\Sigma}/\Gamma_0, \quad \bar{\Gamma}_1 = \Gamma_1/\Gamma_0, \quad \bar{\Gamma}_n = \Gamma_n/\Gamma_0, \quad \bar{\Gamma}_c = \Gamma_c/\Gamma_0 \quad (11)$$

$$B = bc_0, \quad w_1 = \omega_1 \Gamma_0, \quad w_{\Sigma} = \omega_{\Sigma} \Gamma_0 \quad (12)$$

and introduces an auxiliary variable

$$\kappa = \Gamma_1/\Gamma_c = \bar{\Gamma}_1/\bar{\Gamma}_c \quad (13)$$

It can then be easily shown that the dependence of C on $\bar{\Gamma}$ is given by the expression

$$C = \frac{1}{B} \frac{\Gamma_c \omega_1 \kappa \Omega(\kappa)}{[1 - \Gamma_c \omega_1 \kappa (1 + \kappa^{n-1}) \Omega(\kappa)]^{1/\Omega(\kappa)}} \quad (14)$$

where for each given set of Γ_c , ω_1 , and n , the product $\Gamma_c \omega_1$ is constant, and $\kappa = \kappa(\bar{\Gamma})$ is the only solution of the equation

$$\bar{\Gamma} - \bar{\Gamma}_c \kappa (1 + n\kappa^{n-1}) = 0 \quad (15)$$

Here the function $\Omega(\kappa)$ was introduced for convenience.

$$\Omega(\kappa) = \frac{1 + n\kappa^{n-1}}{1 + \kappa^{n-1}} \quad (16)$$

Dimensionless adsorption values introduced by eqs 11 can be expressed via system parameters and κ .

$$\bar{\Gamma}_1 = \Gamma_c \omega_1 \kappa / w_1, \quad \bar{\Gamma}_\Sigma = \bar{\Gamma}_1 (1 + \kappa^{n-1}), \quad \bar{\Gamma}_n = \Gamma_1 \kappa^{n-1} \quad (17)$$

and the pressure dependence on $\bar{\Gamma}$ can be calculated via the relation

$$\Pi = -RT\Gamma_0 \frac{1}{w_\Sigma} \ln(1 - \bar{\Gamma}_\Sigma w_\Sigma) \quad (18)$$

$w_\Sigma = w_1 \Omega(\kappa) = \omega_1 \Gamma_0 \Omega(\kappa)$, and the dependence of $\bar{\Gamma}_\Sigma$ on κ is given by eqs 17.

It is thus seen that to calculate the value of C for any $\bar{\Gamma}$ and all related quantities from the solution $\kappa = \kappa(\bar{\Gamma})$ of eq 15, one needs to determine the equilibrium value Γ_0 , which defines the value of $\bar{\Gamma}_c = \Gamma_c / \Gamma_0$, and the value of B . To do this, equilibrium conditions have to be used, $\lim_{\tau \rightarrow \infty} C(\tau) = 1$, $\lim_{\tau \rightarrow \infty} \bar{\Gamma}(\tau) = 1$. Introducing the equilibrium value κ_0 defined as the root of the equation that follows from eq 18 at $\tau \rightarrow \infty$,

$$\frac{\Pi_0 \omega_1}{RT} + \frac{1 + \kappa_0^{n-1}}{1 + n\kappa_0^{n-1}} \ln[1 - \Gamma_c \omega_1 \kappa_0 (1 + n\kappa_0^{n-1})] = 0 \quad (19)$$

one can see that this root for any set of model parameters n , ω_1 , Γ_c depends on the equilibrium surface pressure Π_0 only. This root determines the equilibrium adsorption Γ_0 via the relation

$$\Gamma_0 = \Gamma_c \kappa_0 (1 + n\kappa_0^{n-1}) \quad (20)$$

which follows from eq 15 at $\tau \rightarrow \infty$. All other equilibrium values can then be calculated from eqs 17 with $\kappa = \kappa_0$, while the value of B can be determined from the relation

$$B = \frac{\Gamma_c \omega_1 \kappa_0 \Omega_0}{[1 - \Gamma_c \omega_1 \kappa_0 (1 + n\kappa_0^{n-1}) \Omega_0]^{1/\Omega_0}} \quad (21)$$

which follows from eq 14. Here $\Omega_0 = \Omega(\kappa_0)$ is calculated from eq 16.

To summarize, the procedure used to obtain the numerical solution of the problem was as follows. First, for any given set of parameters n , ω_1 , Γ_c and equilibrium surface pressure Π_0 , the root κ_0 of eq 19 was calculated, which determines Γ_0 via relation 20, the other equilibrium adsorption values via eqs 17, and the value of B from eq 21. Then the numerical procedure described in ref 5 was applied which calculates the value of C for any $\bar{\Gamma}$ at each successive step of the procedure from the solution $\kappa = \kappa(\bar{\Gamma})$ eq 15 introduced into eq 14.

Results and Discussion

Figure 1 illustrates the dependence of dynamic surface pressure for a surfactant solution of $c_0 = 0.05 \text{ mol/m}^3$ and $D = 6 \times 10^{-10} \text{ m}^2/\text{s}$ assuming a dimerization within the surface layer. The calculations were performed for various values of the critical adsorption of aggregation Γ_c . In all cases the equilibrium surface pressure Π_0 was set to 25 mN/m . It is seen from the curves that for $\Gamma_c \geq 10^{-4} \text{ mol/m}^2$ the dynamic surface pressure is equal to that calculated from the Langmuir isotherm. With

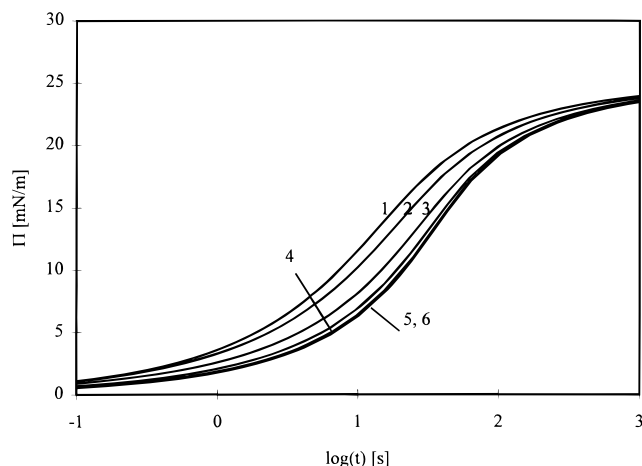


Figure 1. Dynamic surface pressure of an adsorption layer with dimerization: curve 1, Langmuir isotherm; aggregation isotherm for $\Gamma_c \geq 10^{-4} \text{ mol/m}^2$ with $\Gamma_c = 10^{-5} \text{ mol/m}^2$ (curve 2), $\Gamma_c = 10^{-6} \text{ mol/m}^2$ (curve 3), $\Gamma_c = 10^{-7} \text{ mol/m}^2$ (curve 4), $\Gamma_c = 10^{-8} \text{ mol/m}^2$ (curve 5), $\Gamma_c \leq 10^{-9} \text{ mol/m}^2$ (curve 6).

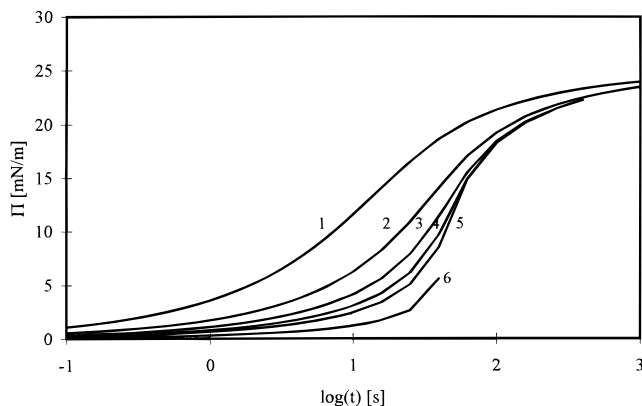


Figure 2. Dynamic surface pressure of adsorption monolayer for the case of n -mers formation ($\Gamma_c \leq 10^{-9} \text{ mol/m}^2$). Curve 1, Langmuir isotherm; curve 2, $n = 2$; curve 3, $n = 3$; curve 4, $n = 4$; curve 5, $n = 5$; curve 6, $n = 10$;

decreasing Γ_c , the values of Π for a given surface lifetime also decrease, but for $\Gamma_c \leq 10^{-9} \text{ mol/m}^2$ the values of Π become independent of Γ_c . Therefore the threshold value of Γ_c under dynamic conditions coincides with that characteristic for equilibrium conditions,²³ which can be ascribed to the fact that in both these cases the dependence of the adsorption layer composition on Γ_c is similar. For $\Pi < 3 \text{ mN/m}$ the surface tensions for the upper curve in Figure 1 are 2 times higher than those for the lower one, which agrees with the approximate expression of eq 8.

Figure 2 illustrates the effect of the aggregation number on the dynamic surface pressure of a surfactant solution. The values of c_0 , D , and Π_0 were the same as before. For all cases the value Γ_c was taken as 10^{-13} mol/m^2 ; that is, the monolayer consisted of aggregates only. One can see that an increasing aggregation number leads to a sharp deceleration of the surface tension decrease for low and intermediate surface lifetimes. However, when the system approaches the equilibrium state, then the effect of aggregation within the adsorption layer becomes negligibly small, and all dynamic curves approach the one calculated from the Langmuir isotherm. The approximate eq 8 agrees well with the results of the rigorous calculations for $t < 1 \text{ s}$.

Experimental dependencies of dynamic surface tensions for 1-decanol solutions as reported in refs 2 and 3 are compared in

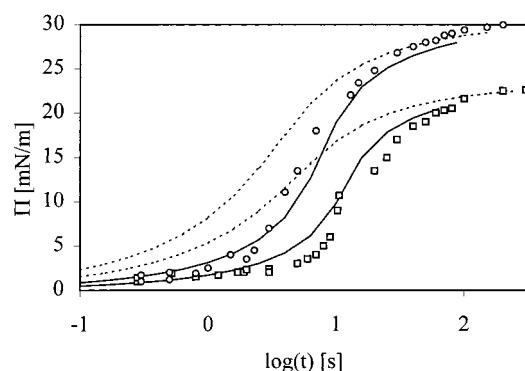


Figure 3. Dynamic surface tension for 1-decanol solutions. experimental results from refs 2 and 3 for $c_0 = 6.32 \times 10^{-5}$ mol/L (○) and $c_0 = 1.018 \times 10^{-4}$ mol/L (□); dotted curves calculated from Langmuir isotherm; solid curves correspond to the aggregation model for $n = 2.5$ and $\Gamma_c \leq 10^{-9}$ mol/m².

Figure 3 with the results calculated from the present aggregation model. Similarly to the case of equilibrium adsorption of decanol at the solution/air interface studied in ref 23, an aggregation number of 2.5 was used in the calculations of dynamic surface tension. It is seen that the model proposed in this paper provides satisfactory agreement with experimental data, while the curves calculated from the Langmuir isotherm differ significantly within the short time range. When the aggregation number n introduced into the calculations was lower than 2 or higher than 3, the agreement with experimental data became also significantly worse. We believe that these results strongly support the supposition that aggregation of decanol molecules actually takes place within the adsorption layer.

The importance of the demonstrated agreement between the results of dynamic experiments and those performed under equilibrium conditions is of special importance and can be illustrated by the following example. We have made an attempt to employ the aggregation model for the description of a nondiffusional adsorption kinetics for normal low-molecular alcohols (1-propanol to 1-heptanol) studied earlier.⁹ Note that the results presented in ref 9 agree satisfactorily with data reported elsewhere and have been interpreted earlier in the framework of an adsorption barrier model (effects related to entropy factors) or a diffusion model for a nonequilibrium surface layer (that is, assuming the existence of concentration gradients in the subsurface). It was found that small deviations from the diffusion model for a Langmuir isotherm for heptanol solutions could be completely compensated by dimerization with $\Gamma_c = 5 \times 10^{-8}$ mol/m². At the same time, for homologues possessing lower molecular mass only the cluster model was found to be appropriate (that is, complete aggregation of all molecules within the monolayer with $\Gamma_c \leq 10^{-9}$ mol/m² had to be assumed), for which the aggregation number had to be increased with decreasing molecular mass. For example, for pentanol the optimum value was $n = 4$, while for propanol $n = 30$ was found. No reasonable physical considerations can be presented to explain this dependence of n on the alkyl chain length. Moreover, the attempts to employ the aggregation model for the description of equilibrium characteristics have failed: instead of 2% difference obtained for propanol solution when a Langmuir isotherm was employed,⁴ for the aggregation model the discrepancy between theory and experiment exceeds 50%.

Therefore, in spite of a formal agreement between theoretical predictions and experimental results obtained under dynamic conditions, the entire scope of data enables us to conclude that no aggregation of low-molecular alcohols takes place within the adsorption layers, and therefore, the aggregation model cannot explain the slow adsorption in these systems.

Conclusions

The theory of diffusion-controlled adsorption kinetics is developed for adsorption layers of aggregating surfactant molecules. The formation of aggregates within the adsorption layer results in a deceleration of the surface tension decrease. If the aggregation in such systems is neglected, then the decrease in the adsorption rate can be ascribed to the existence of an adsorption barrier. Therefore, the extension of the theoretical model to the mechanism of aggregation within adsorption monolayer improves the descriptive ability of the diffusion-controlled adsorption kinetics theory. In addition to the agreement between experimental data and theoretical predictions under dynamic conditions, this requires agreement also under equilibrium conditions. These conditions are given for decanol solutions, for which the mean aggregation number at the solution/air interface is 2.5 for both equilibrium and dynamic experiments.

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References and Notes

- (1) Ward, A. F. H.; Tordai, L. *J. Phys. Chem.* **1946**, *14*, 543.
- (2) Ward, A. F. H.; Tordai, L. *J. Phys. Chem.* **1946**, *14*, 543.
- (3) Lin, S.-Y.; Lu, T.-L.; Hwang, W.-B. *Langmuir* **1994**, *10*, 3442.
- (4) Lin, S.-Y.; Hwang, W.-B.; Lu, T.-L. *Colloids Surf. A* **1996**, *114*, 143.
- (5) Fainerman, V. B.; Miller, R.; Wüstneck, R. *J. Phys. Chem.* **1997**, *101*, 6479.
- (6) Aksenenko, E. V.; Makievski, A. V.; Fainerman, V. B.; Miller, R. *Colloids Surf. A*, in press.
- (7) Fainerman, V. B.; Makievski, A. V.; Joos, P. *Colloids Surf. A* **1994**, *90*, 213.
- (8) Fainerman, V. B.; Miller, R.; Makievski, A. V. *Langmuir* **1995**, *11*, 3054.
- (9) Yousef, A.; McCoy, B. J. *J. Colloid Interface Sci.* **1983**, *94*, 497.
- (10) Fainerman, V. B.; Miller, R. *J. Colloid Interface Sci.* **1996**, *178*, 168.
- (11) Bley, G.; Joos, P. *J. Phys. Chem.* **1985**, *89*, 1027.
- (12) Chang, C.-H.; Franses, E. I. *Colloids Surf. A* **1995**, *100*, 1.
- (13) Li, B.; Geeraerts, G.; Joos, P. *Colloids Surf. A* **1994**, *88*, 251.
- (14) Baret, J. F. *J. Chem. Phys.* **1968**, *65*, 895.
- (15) Lindstrom, F. T.; Haque, R.; Coshov, W. R. *J. Phys. Chem.* **1970**, *65*, 495.
- (16) Fainerman, V. B. *Colloids Surf.* **1991**, *57*, 249.
- (17) Joos, P.; Serrien, G. *J. Colloid Interface Sci.* **1989**, *127*, 97.
- (18) Kimizuka, H.; Abood, L. A.; Tahara, T.; Kaibara, K. *J. Colloid Interface Sci.* **1972**, *40*, 27.
- (19) Veer, F. A.; van den Tempel, M. *J. Colloid Interface Sci.* **1973**, *42*, 418.
- (20) van den Tempel, M. *J. Non-Newtonian Fluid Mechanics* **1977**, *2*, 205.
- (21) van den Tempel, M.; Lucassen-Reynders, E. H. *Adv. Colloid Interface Sci.* **1983**, *18*, 281.
- (22) Fainerman, V. B.; Vollhardt, D.; Melzer, V. *J. Chem. Phys.* **1997**, *107*, 243.
- (23) Lin, S.-Y.; McKeigue, K.; Maldarelli, C. *Langmuir* **1991**, *7*, 1055.
- (24) Fainerman, V. B.; Miller, R. *Langmuir* **1996**, *12*, 6011.
- (25) Miller, R.; Joos, P.; Fainerman, V. B. *Adv. Colloid Interface Sci.* **1994**, *49*, 249.
- (26) Ziller, M.; Miller, R. *Colloid Polym. Sci.* **1986**, *264*, 611.