Adsorption Kinetics in Micellar Solutions of Nonionic Surfactants

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Standard models of the adsorption kinetics of surfactants at the air-water surface assume that micelles break down into monomers in the bulk solution and that only monomers adsorb. We show here that micelles of the nonionic surfactant $C_{14}E_8$ adsorb to the surface of a liquid jet at a diffusion-controlled rate. Micellar adsorption can be switched off by incorporation of a small amount of ionic surfactant into the micelle and switched on again by addition of salt. More sophisticated models of adsorption processes in micellar solutions are required that permit a kinetic flux of micelles to the air-water interface.

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The kinetics of adsorption of surfactants at the air-water interface has been the subject of extensive theoretical and experimental study for more than half a century [1,2]. More sophisticated models allow for the fact that many surfactants form small aggregates in solution, known as micelles, above a well-defined concentration [the critical micelle concentration (CMC)]. All models assume that the rate constant for adsorption of micelles is zero: a no-flux boundary condition is imposed on the mass transport equations for the micelles [3–8]. Micelles can still influence the adsorption kinetics, but they must first break down in solution to release monomers which then adsorb to the surface. This physical picture is summarized in Fig. 1.

While the no-flux boundary condition is justifiable for ionic surfactants in the absence of added electrolyte (see below), it is less obvious why micelles of uncharged surfactants should not adsorb directly to a fresh water surface. In this Letter, we show that micelles of the nonionic surfactant octaethyleneglycol tetradecylether ($C_{14}E_8$) adsorb at the air-water interface at a diffusion-controlled rate. Furthermore, we show that this direct adsorption route can be "switched off" by doping a small amount (mole fraction, $\chi < 0.1$) of a cationic surfactant into the micelle, and switched back on again by addition of a low concentration of electrolyte. We argue that this behavior is inconsistent with an adsorption mechanism that proceeds only via a flux of monomers to the surface.

Our experiments were carried out on a gravity-driven water jet [9,10] containing $C_{14}E_8$ at a bulk concentration of 1 mM (Fig. 2). The mean velocity of the jet, $\bar{u}_0 = 0.87\ \mathrm{m\,s^{-1}}$, corresponds to a Reynolds number of 1440.

Near the nozzle the surface expansion rates are very high (of the order of 10^2–$10^3\ \mathrm{s^{-1}}$) and the surface concentration of surfactant is close to zero. As the distance from the nozzle increases, the surfactant diffuses to the nascent water surface and adsorbs. We used ellipsometry to measure the coefficient of ellipticity, $\bar{\rho}$, of the free surface as a function of the axial distance, z, down the jet (see Fig. 3, solid circles). We have shown previously that for a related nonionic surfactant (C_8E_4OMe) $\bar{\rho}$ scales linearly with the surface excess, Γ, of adsorbed surfactant [11]. It is reasonable to assume a linear relationship between $\bar{\rho}$ and Γ for $C_{14}E_8$ also (right-hand axis in Fig. 3). The maximum surface coverage reached in these experiments is <40% of a saturated monolayer ($\Gamma_{\mathrm{sat}} = 3.2 \times 10^{-6}\ \mathrm{mol\,m^{-2}}$ [12]), so the interface is always far from equilibrium.

In the absence of surface tension gradients, the surface velocity, $u_s(z)$, of a free jet in boundary-layer flow takes the form $u_s(z) = az^{1/3}$, where z is the axial displacement in meters and the constant $a = 3.7\ \mathrm{m^{2/3}\,s^{-1}}$ for the conditions in Fig. 3 [10]. For pure water, the surface velocity (measured by laser Doppler velocimetry) agrees accurately with this prediction [9]. Marangoni effects vary $u_s(z)$ by less than 20% [13]. Neglecting jet contraction, the mean surface age, $\bar{t}(z)$, is given by $\bar{t}(z) = z/u_s(z) = a^{-1}z^{2/3}$ [14]. For $z = 1$–50 mm, $\bar{t}(z)$ is in the range of 2–40 ms.

In a 1 mM solution of $C_{14}E_8$, 99% of the surfactant is present in the form of micelles. The established models of adsorption kinetics from micellar solutions assume that micelles have to break down to monomers in the subsurface region before adsorption can occur [3,6,7]. A widely supported mechanism for micelle formation and breakdown in dilute solutions was elucidated by Aniansson and Wall [15,16] and is characterized by two relaxation times. The fast relaxation time, τ_1, corresponds to exchange of a surfactant monomer between a micelle and

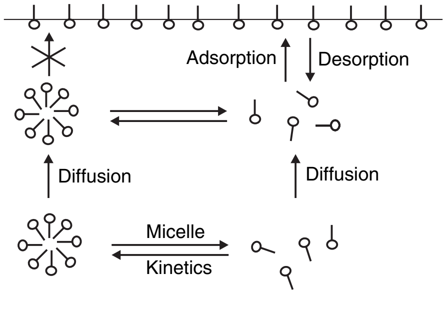

FIG. 1. Standard model for adsorption process in micellar solutions (after [2]). The crossed arrow indicates that the direct adsorption of micelles is forbidden in the standard model.

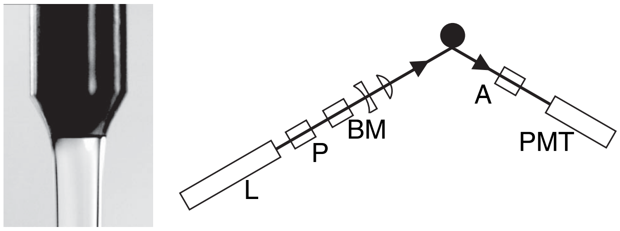

FIG. 2. (left) Photograph of the liquid jet. (right) Schematic of the phase-modulation ellipsometer in the plane perpendicular to the jet axis. L: laser, P: polarizer, BM: birefringence modulator, A: analyzer, PMT: photomultiplier tube. Details can be found in Ref. [9]. Nozzle radius, $R_0 = 0.8$ mm, $T = 293$ K. The spatial resolution of the ellipsometer is 0.1 mm.

the solution and occurs at a rate close to the diffusion-controlled limit [17]. The slow relaxation time, τ_2, corresponds to the total disintegration of the micelle.

For $C_{14}E_8$, the diffusion-controlled value of $\tau_1 = (4\pi a D c_{\mathrm{cmc}})^{-1} \sim 10^{-5}$ s (where $a \sim 3$ nm is the radius of the micelle, $D \sim 4 \times 10^{-10}$ m^2 s^{-1} is the monomer diffusion coefficient and $c_{\mathrm{cmc}} = 10$ μM is the free monomer concentration) [18]. On the time scale of our experiments, exchange of monomers between micelles and solution is therefore fast. There is a limit, however, to how many monomers a micelle can lose by the "fast" process. For spherical micelles, the typical standard deviation, s, of the micellar distribution is $\sqrt{\bar{N}}$, where $\bar{N}$ is the mean aggregation number [19]. (For the homologous surfactant C_8E_8, studied by ultrasound by Zana and coworkers, $\bar{N} = 72$ and $s = 9$ [17].) For $C_{14}E_8$, $\bar{N} \cong 120$ [20], giving a half-width of about 10% of $\bar{N}$. Once the aggregation number drops more than 10% below $\bar{N}$, the free energy of the micelle rises rapidly and the rate constant for loss of monomers drops sharply. Thus micelles of $C_{14}E_8$ can only shed about 10% of their monomers by the fast process.

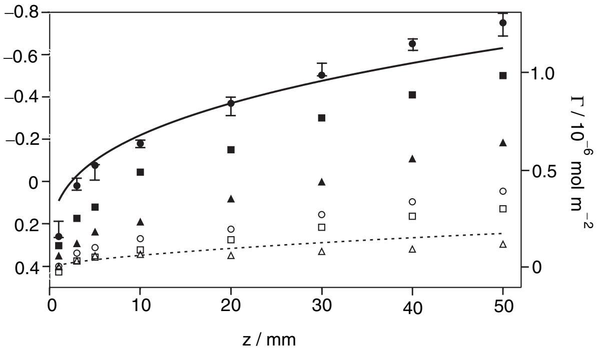

FIG. 3. Coefficient of ellipticity $\bar{\rho}$ and surface excess Γ as a function of axial distance down the jet, z. (solid line) Diffusion-controlled limit for 1 mM $C_{14}E_8$; (●) 1 mM $C_{14}E_8$; (dashed line) 0.1 mM $C_{12}E_8$; (■) 1 mM $C_{14}E_8$ + 1/40 mM C_{16}TAB; (▲) 1 mM $C_{14}E_8$ + 1/30 mM C_{16}TAB; (○)1 mM $C_{14}E_8$ + 1/20 mM C_{16}TAB; (□)1 mM $C_{14}E_8$ + 1/10 mM C_{16}TAB; (△) 1/10 mM C_{16}TAB. Random errors lie within the symbols. Reproducibility is indicated by the error bars on the 1 mM $C_{14}E_8$ data, which show the range of values obtained in three experiments over a six-month period.

While τ_1 is fast on the experimental time scale, τ_2 is very slow. For the homologous surfactant $C_{12}E_8$, a value of $\tau_2 = 4$ s has been reported [21]. Increasing the length of the alkyl chain will increase τ_2 further: disintegration of micelles in bulk solution will therefore not occur to any significant extent in our liquid jet.

Figure 3 shows the coefficient of ellipticity and the derived value of the surface excess as a function of z for a 1 mM solution of $C_{14}E_8$. The solid line shows the theoretical prediction of the surface excess based on a boundary-layer treatment of the hydrodynamics of the jet [10] and the assumption of diffusion-controlled adsorption of surfactant micelles [Eq. (1)]:

$$\Gamma = 0.244\left(\frac{D_{\mathrm{mic}}}{\bar{u}_0}\right)\left(\frac{2R_0\bar{u}_0\rho}{\mu}\right)^{2/3}\left(\frac{\mu}{D_{\mathrm{mic}}\rho}\right)^{1/2} c_b \left(\frac{1}{R_0}\right)^{1/3} z^{1/3}, \tag{1}$$

where μ is viscosity, ρ is density, c_b is bulk concentration, and the micellar self-diffusion coefficient $D_{\mathrm{mic}} = 0.6 \times 10^{-10}$ m^2 s^{-1} [20]. The agreement of the experimental results with the diffusion-controlled prediction is remarkably good.

For $C_{14}E_8$ at its CMC of 10 μM, is $\bar{\rho}$ indistinguishable from that of pure water, as would be expected from Eq. (1). To estimate the possible effect of the fast relaxation process on the adsorption rate, we show data in Fig. 3 for the homologous surfactant $C_{12}E_8$ at its CMC of 0.1 mM. The value of 0.1 mM provides a reasonable estimate of the number of monomers that could be released in a 1 mM micellar solution of $C_{14}E_8$ by the τ_1 process (the maximum free monomer concentration at any point is limited by the CMC to 10 μM). The results for $C_{12}E_8$ suggest that the fast process could account for around 10% of the adsorption observed with $C_{14}E_8$. Given that neither the fast nor the slow relaxation processes can explain the experimental data, we deduce that micelles of $C_{14}E_8$ adsorb to the air-water interface without first breaking down into monomers.

Since this conclusion runs contrary to conventional models for surfactant adsorption kinetics, it is essential to test the hypothesis further. We therefore designed an experiment with opposing outcomes depending on whether monomers or micelles adsorb to the surface of the liquid jet. To validate (or disprove) our hypothesis, we doped the nonionic surfactant with a small amount (mole fraction $\chi \leq 0.1$) of a cationic surfactant, hexadecyltrimethylammonium bromide (C_{16}TAB). In the presence of C_{16}TAB, the nonionic micelles acquire a charge. Migration fields then increase the "mutual" diffusion coefficient, D_m, of the micelles. D_m is given by $D_m = (1 + q)/(1/D_{\mathrm{mic}} + q/D_{\mathrm{Br}^-})$, where q is the magnitude of the charge (in electrons) on the micelle and D_{Br^-} is the self-diffusion coefficient of the counterion, Br^- [22]. D_{Br^-} is 35 times larger than D_{mic} [23], so for small q, the rate of diffusion of the micelles increases linearly with q. This equation has been validated by Tominaga for mixtures of $\mathrm{C}_{12}\mathrm{E}_8$ with long-chain ionic surfactants for $\chi < 0.1$ [24].

If the micelles decompose to monomers which then adsorb to the surface, doping the micelles with $\mathrm{C}_{16}\mathrm{TAB}$ should increase the adsorption rate by increasing the mass transport of the micelles towards the surface of the jet [the surface excess scales as ${D_m}^{1/2}$, Eq. (1)]. Conversely, if the micelles adsorb without first breaking down into monomers, then there will be an electrostatic barrier to adsorption and the adsorption rate will decrease with increasing charge q on the micelle.

1 mM $\mathrm{C}_{14}\mathrm{E}_8$ was mixed with $\mathrm{C}_{16}\mathrm{TAB}$ at concentrations of 1/40 mM, 1/30 mM, 1/20 mM, and 1/10 mM. A recent study [25] found an interaction parameter, $\beta \approx -3$, for mixed micelles of $\mathrm{C}_{12}\mathrm{E}_8$ with the cationic surfactant $\mathrm{C}_{14}\mathrm{TAB}$. In our experiment, the chain length of each surfactant is two carbons longer, so a similar value of β is expected. With $\beta = -3$, 95% of the added $\mathrm{C}_{16}\mathrm{TAB}$ should partition into the micelles. Tominaga has shown that for $\chi < 0.1$, ionic surfactants in predominantly nonionic micelles are almost fully dissociated [22]. Thus for total concentrations of $\mathrm{C}_{16}\mathrm{TAB}$ of 1/40, 1/30, 1/20, and 1/10 mM, the average charge q on the micelles is 3, 4, 6, and 11 electrons, respectively.

Figure 3 plots the coefficient of ellipticity $\bar{\rho}$ against z for the four mixed surfactant solutions. The contribution of an adsorbed $\mathrm{C}_{16}\mathrm{TAB}$ molecule to $\bar{\rho}$ is similar to, but slightly smaller than, that of a $\mathrm{C}_{14}\mathrm{E}_8$ molecule [26]. The extent of adsorption of nonionic surfactant decreased smoothly as the concentration of $\mathrm{C}_{16}\mathrm{TAB}$, and hence the micellar charge q, increased. For $\chi = 0.1$, the adsorbed amount was reduced by ~80%. These results support the direct micellar adsorption mechanism.

To rationalize semiquantitatively the observed behavior, we consider a simple mean-field model in which all the micelles have the same charge q and the adsorbed surface layer has the same composition as the micelles. Under the conditions of the experiment, the surface potential ψ_0 is determined by the concentration of the bromide counterions and the surface charge density σ due to adsorbed hexadecyltrimethylammonium ($\mathrm{C}_{16}\mathrm{TA}^+$) ions. The Grahame equation relates these quantities [27]:

$$\sigma^2 = 2\varepsilon\varepsilon_0 k_B T(e^{e\psi_0/k_B T} - 1)[\mathrm{Br}^-]_\lambda, \tag{2}$$

where ε is the relative permittivity of water and $[\mathrm{Br}^-]_\lambda$ is the concentration of bromide ions at the edge of the electrical double layer. For simplicity, we take $[\mathrm{Br}^-]_\lambda$ to be equal to the bulk concentration, $[\mathrm{Br}^-]_0$. In practice, due to the presence of a diffusion layer, $[\mathrm{Br}^-]_\lambda < [\mathrm{Br}^-]_0$; neglecting this difference underestimates the surface potential (for a given surface charge) and hence provides an upper limit on the adsorption rate. Assuming that the only barrier to adsorption is electrostatic, we can estimate the maximum rate constant k for adsorption of micelles of charge q from the Eyring equation [28],

$$k = (k_B T/h)e^{-\Delta G^\dagger/k_B T}, \tag{3}$$

where the activation free energy for adsorption, $\Delta G^\dagger = qe\psi_0$. To observe adsorption of micelles on the time scale of the liquid jet, we require that $k \geq \bar{t}^{-1} \sim 10^2\ \mathrm{s}^{-1}$. From Eqs. (2) and (3), we can then estimate the surface charge density required to prevent adsorption of micelles. Converting these values into surface excess of $\mathrm{C}_{16}\mathrm{TAB}$, we obtain values of $\Gamma = 2 \times 10^{-7}$, 7×10^{-8}, 3×10^{-8}, and $2 \times 10^{-8}\ \mathrm{mol\,m}^{-2}$ for $\mathrm{C}_{16}\mathrm{TAB}$ concentrations of 1/40, 1/30, 1/20, and 1/10 mM respectively. This calculation suggests that the 1/40 mM $\mathrm{C}_{16}\mathrm{TAB}$ would have a minimal effect on the adsorption of the mixed micelles, because even at saturation coverage the surface charge due to adsorbed $\mathrm{C}_{16}\mathrm{TA}^+$ ions in the mixed monolayer of $\mathrm{C}_{14}\mathrm{E}_8/\mathrm{C}_{16}\mathrm{TAB}$ would be insufficient to prevent adsorption of micelles; 1/30 mM $\mathrm{C}_{16}\mathrm{TAB}$ would have an effect near monolayer coverage; while 1/20 mM $\mathrm{C}_{16}\mathrm{TAB}$ and 1/10 mM $\mathrm{C}_{16}\mathrm{TAB}$ would provide an effective barrier to adsorption at a fraction of a monolayer coverage. Qualitatively, these predictions are in agreement with the observed trends. In reality, there is a distribution of charges on the micelles, so the differences are not as sharp as predicted, and the adsorption rates appear to be lower than the upper limits calculated (so the effects of potential barriers are manifested at lower surface charge densities). The presence of a double layer potential could also affect the monomer adsorption rate by increasing the distance from the surface at which monomers are released from micelles. Calculations of the magnitude of this effect show that this alternative mechanism cannot explain the experimental observations.

As a final test of our hypothesis, we observed the effect of adding a low concentration of an electrolyte (10 mM NaBr) to a solution of 1 mM $\mathrm{C}_{14}\mathrm{E}_8$ + 1/20 mM $\mathrm{C}_{16}\mathrm{TAB}$. This amount of salt would have a negligible effect on the adsorption of monomers of a nonionic surfactant. However, from Eq. (2), the effect of the salt would be to reduce the electrostatic barrier to adsorption to only a few kT, even at monolayer coverage. Figure 4 shows the ellipticity of 10 mM NaBr, 1 mM $\mathrm{C}_{14}\mathrm{E}_8$ + 10 mM NaBr, and 1 mM $\mathrm{C}_{14}\mathrm{E}_8$ + 1/20 mM $\mathrm{C}_{16}\mathrm{TAB}$ + 10 mM NaBr in the liquid jet. The presence of the NaBr creates a small negative offset in the ellipticity, the origin of which is unclear. But most importantly, there is now no difference in the adsorption rate with and without the added $\mathrm{C}_{16}\mathrm{TAB}$, in accordance with the micellar adsorption model.

The inference that the micelles adsorb to the surface as a kinetic process does not imply that adsorbed micelles exist at the air-water interface in any significant numbers at equilibrium. Once adsorbed, the local increase in surface

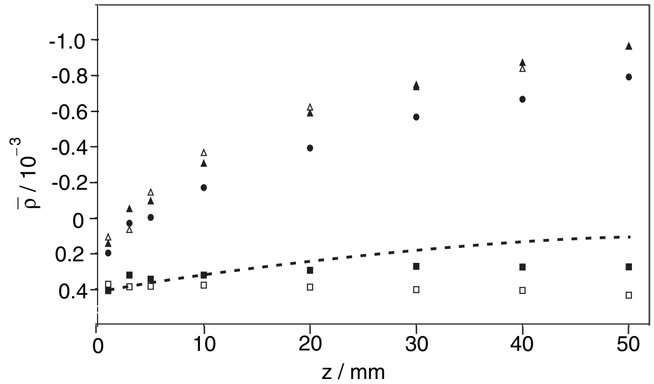

FIG. 4. Ellipticity $\bar{\rho}$ as a function of axial distance down the jet, z. (●) 1 mM $C_{14}E_8$, (▲) 1 mM $C_{14}E_8$ + 10 mM NaBr, (△) 1 mM $C_{14}E_8$ + 10 mM NaBr + 1/20 mM $C_{16}TAB$, (■) 10 mM NaBr, (dashed line) 1 mM $C_{14}E_8$ + 1/20 mM $C_{16}TAB$, (□) pure water.

coverage will lower the local surface tension and the resulting Marangoni forces will rapidly tear the aggregate apart. In one sense, the surface is acting as an efficient catalyst for micellar disintegration. (By surface, in this context, we mean the region, a few nm thick, in which the forces experienced by the molecules in the micelle are significantly different from those in micelles in the bulk solution.) The detailed mechanism by which the micelle rearranges itself as it adsorbs to the surface remains to be resolved. One would expect this process to be activated and for the activation energy to increase with increasing surface coverage, due to the steric repulsions between the polymerlike $(EO)_8$-head groups. The experiments here show that, at sparsely covered surfaces, this activation barrier is not rate-limiting on the time scale of the experiments.

In conclusion, we have provided convincing evidence that micelles of nonionic surfactants can adsorb to an air-water interface at a diffusion-controlled rate without first breaking down into monomers in the bulk solution. These results demonstrate the need for the incorporation of an additional pathway into standard models for surfactant adsorption in micellar solutions, with the relaxation of the no-flux boundary condition on the micellar distribution.

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