Mechanism of Micelle Birth and Death

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In micellar surfactant solutions, changes in the total number of micelles are rare events that can occur by either of two mechanisms—by stepwise association and dissociation via insertion and expulsion of individual molecules or by fission and fusion of entire micelles. Molecular dynamics simulations are used here to estimate rates of these competing mechanisms in a simple model of block copolymer micelles in homopolymer solvent. This model exhibits a crossover with increasing degree of repulsion between solvent and micelle core components, from a regime dominated by association and dissociation to a regime dominated by fission and fusion.

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Spherical micelles are simple self-assembled structures that form in solutions of both small molecule and macromolecular surfactants [1,2]. Micelles are also the building blocks of a variety of complex phases of sphere-forming diblock copolymers [3–6]. The slowest dynamical processes in micellar systems are generally those that involve a change in the total number of micelles. Understanding of these slow processes is critical to understanding of applications that rely on adsorption of surfactant to an interface, such as wetting, emulsification, and foaming [1,2], because the rate of adsorption is closely related to the rate at which micelles can break down near an interface [7]. Analogous processes also appear to play a crucial role in phase transformations and equilibration in melts of sphere-forming block copolymers [5,6].

Experiments in which equilibrium of a micellar solution is disturbed by a small change in temperature, pressure, or concentration have demonstrated the existence of two dynamical processes with disparate timescales: a "fast" process with a typical relaxation time τ_1 of microseconds or less and a "slow" process with a much longer relaxation time τ_2 [8–14]. The fast process is one in which micelles grow or shrink slightly via insertion or expulsion of individual free molecules, without changing the number of micelles. The slow process instead involves a change in the total number of micelles [11–14].

The mechanism of the fast process is well understood, but the mechanism of the slow process has remained unclear. The slow process in an equilibrated solution could occur primarily either by association and dissociation or by fission and fusion [14]. In the association-dissociation mechanism, a new micelle can occasionally form by aggregation of dissolved free surfactant molecules, or disappear by dissociation into free molecules. In the fission-fusion mechanism, the number of micelles can instead increase by one when a micelle undergoes fission or decrease by one when two micelles undergo fusion. Several techniques can be used to measure the rate of the slow processes, but it is more difficult to devise experiments that can distinguish these two mechanisms.

The best developed theory of micelle kinetics is the stepwise-growth theory [11]. This theory assumes that both fast and slow processes arise from strictly stepwise changes in micelle size, by insertion and expulsion of individual free molecules, and that rates of fission and fusion are negligible. The resulting theory [11–20] is closely analogous to the classical Becker-Döring theory of stepwise nucleation of liquid from a vapor [21].

Theories that allow for fission and fusion processes are much less well developed. Several authors have formulated population models that allow for micelle fission and fusion as well as stepwise processes [22–26]. Such models have, however, thus far relied on estimates of the rate constants for fission and fusion that either assume that fusion is diffusion limited or that mimic the effects of a barrier to fusion via the introduction of an adjustable parameter. The predictive power of such models has thus been limited primarily by our limited understanding of the magnitude of barriers to fission and fusion.

Spontaneous creation and destruction of micelles in an equilibrated micellar solution generally occur too infrequently to be observed in straightforward molecular dynamics (MD) simulations. Simulation studies of kinetics have thus far focused instead on the comparatively rapid initial formation of micelles from a supersaturated solution [27], and on exchange of individual molecules [28]. Here, we combine MD simulation and population modeling to estimate and compare equilibrium rates of the competing association-dissociation and fission-fusion processes for a simple simulation model of a nonionic block copolymer surfactant and improve upon prior diffusion limited estimates. To do so, we analyze the behavior of a micelle population model using model parameters extracted from molecular simulations. Many details of the simulations and analysis presented here are discussed in two related longer papers [29,30].

Population model.—We consider a dilute micellar solution in which micelles coexist with a concentration c_1 of free surfactant molecules. Let $c_n(t)$ denote the concentration of micelles that contain n surfactants at time t. The equilibrium concentration of such micelles, denoted by c_n^*, is given by a Boltzmann distribution $c_n^* \propto \exp(-W_n/k_BT)$, where W_n is the free energy required to form a micelle of aggregation number n from a reservoir of free surfactants. The free energy W_n characteristically has a local minimum at some value n_e, which is the most probable micelle aggregation number.

We consider a general dynamical model that allows for both stepwise insertion and expulsion and fission and fusion. Fusion of clusters of aggregation number n and n' to form a cluster of size $n+n'$ is assumed to occur at a rate $r^+_{n,n'} = k^+_{n,n'}c_n c_{n'}$ per unit volume. Fission of an aggregate of size $n+n'$ into daughters of size n and n' occurs at a rate $r^-_{n,n'} = k^-_{n,n'}c_{n+n'}$. Stepwise insertion and expulsion of individual molecules is treated as a special case in which n or n' is equal to 1. The time dependence of $c_n(t)$ is controlled by a master equation,

$$\frac{dc_n}{dt} = \sum_{n'=1}^{n/2} J_{n-n',n'} - \sum_{n'=1}^{\infty} \nu_{n,n'} J_{n,n'}, \tag{1}$$

where $J_{n,n'} = r^+_{n,n'} - r^-_{n,n'}$. Here, $\nu_{n,n'} = 1 + \delta_{n,n'}$ is a coefficient giving the number of clusters of a size n consumed by fusion of clusters of size n and n'. Detailed balance requires that $J_{n,n'} = 0$ for all n and n', implying that $k^+_{n,n'}c^*_n c^*_{n'} = k^-_{n,n'}c^*_{n+n'}$. The independent input parameters required by this model are thus the equilibrium concentrations or cluster free energies W_n for all n, and the rate constants $k^+_{n,n'}$ or $k^-_{n,n'}$, which are related by detailed balance. The simpler stepwise model only requires values for the insertion rate constant $k^+_{n,1}$ or the expulsion constant $k^-_{n,1}$.

Simulation model.—We have analyzed a simple simulation model of nonionic diblock copolymer surfactants in a polymer solvent [31–34]. Each copolymer is a chain of 32 beads, with 4 B beads and 28 A beads. Each "solvent" molecule is a homopolymer of 32 A beads. Pairs of i and j beads separated by a distance r less than a cutoff σ interact via a pair potential $U_{\text{pair}}(r) = \frac{1}{2}\epsilon_{ij}(1 - r/\sigma)^2$, with $\epsilon_{AA} = \epsilon_{BB} = 25k_BT$ and $\epsilon_{AB} \geq \epsilon_{AA}$. Bonded beads also interact via a potential $U_{\text{bond}} = \kappa r^2/2$, with $\kappa = 3.048k_BT/\sigma^2$. Simulations were performed at constant temperature $k_BT = 1$ and pressure $P = 20.249k_BT/\sigma^3$, giving an average bead concentration $c \simeq 3\sigma^{-3}$ [32,33]. Simulations were performed at several values of a parameter $\alpha \equiv (\epsilon_{AB} - \epsilon_{AA})/k_BT$ that controls the driving force for micellization. Well-defined micelles form only for $\alpha > 8$. Extensive simulations were performed at $\alpha = 10$, 12, 14, and 16. Different types of simulation were performed to estimate different parameters.

Equilibrium properties.—Thermal equilibrium properties were obtained from hybrid Monte Carlo (MC) simulations that were performed in a semigrand ensemble in which the number of copolymer molecules fluctuates but the total number of copolymer and solvent chains remains constant [35]. These simulations use a MC move that can convert molecules of one type into the other by toggling the bead type of the 4 beads that form the minority block of a copolymer molecule. This allows very efficient sampling when both species are polymers of the same length, which is why we chose to study such a system. These simulations also used a hybrid MC-MD move in which short MD simulations are used as proposed MC moves [36]. We suppress the creation of states with more than one micelle in the simulation by rejecting all MC moves that produce such states [29].

The acceptance criteria for MC moves is designed to sample the Boltzmann distribution for a system with a modified potential energy $U' = U - V(N)$, in which U is the physical potential energy and $V(N)$ is an umbrella potential that depends only on the total number of copolymers in the simulation cell, which we denote by N. The potential $V(N)$ is chosen adaptively to obtain a nearly flat probability distribution $P_{\text{sim}}(N)$ for N. The Gibbs free energy $G(N)$ for the system is then given by $G(N) = -k_BT \ln P_{\text{sim}}(N) + V(N)$. Results of these biased simulations are then used to reconstruct properties that would be obtained in a semigrand canonical ensemble describing a system that can exchange molecules with a reservoir of a specified exchange chemical potential $\Delta\mu$, which is the difference between the copolymer and hompolymer chemical potential.

We define the critical micelle concentration c_c to be the average free molecule concentration c_1 in a state in which the average number of free molecules is equal to the number of molecules in micelles, or in which the total concentration c is twice c_1. Let $\Delta\mu_c$ denote the value of $\Delta\mu$ in this state. The mole fraction of free copolymers in this state, denoted by ϕ_c, decreases exponentially with α, and is found to be $\phi_c = 0.0163$, 0.0054, 0.0017, 0.00072 for $\alpha = 10$, 12, 14, 16, respectively.

Values of the cluster formation free energy W_n have been extracted from measurements of the frequency of appearance of cluster of each size in a semigrand canonical ensemble [29]. The most probable aggregation number n_e is the value at which W_n is at a local minimum, for which we obtain $n_e \simeq 55$, 70, 83, and 97 for $\alpha = 10$, 12, 14, and 16. Figure 1 shows the calculated values of free energy W_n as a function of n at $\Delta\mu = \Delta\mu_c$. The local maximum in W_n, at a value of n denoted by n_t, is the transition state for stepwise dissociation or association. The barrier to dissociation,

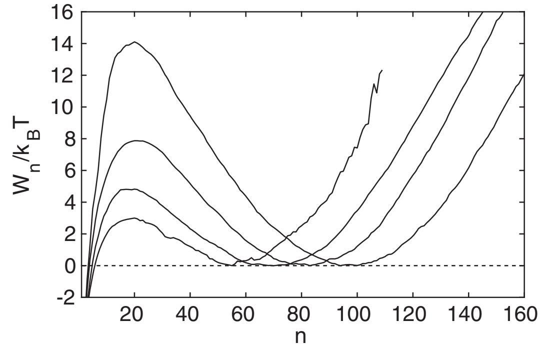

FIG. 1. Micelle free energy W plotted versus micelle aggregation number n at $\Delta\mu = \Delta\mu_c$. Results are shown for $\alpha = 10$, 12, 14, and 16, from lowest to highest free energy barrier. Results are shifted so that $W_n = 0$ at the micellar minimum, $n = n_e$.

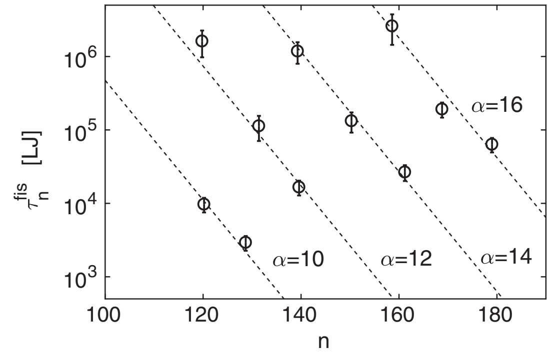

FIG. 2. Semilog plot of the intrinsic fission lifetime τ_n^{fis} in units of Lennard-Jones time as a function of micelle aggregation number n, for values of $\alpha = 10$, 12, 14, and 16 (left to right). Error bars show root-mean-squared statistical errors. Solid lines are predictions of the global fit to Eq. (2), plotted at these four values of α.

denoted by $\Delta W_d = W_{n_t} - W_{n_e}$, increases from 3 to $14 k_B T$ over this range of α values.

Molecular insertion and expulsion rates.—The rate constants $k_{n,1}^{+}$ and $k_{n,1}^{-}$ for copolymer insertion and expulsion were measured for micelles of varying size in MD simulations of systems that contain a single micelle in coexistence with a few free copolymer molecules, by directly measuring the rates at which copolymers enter and leave the micelle [30].

Equilibrium dissociation lifetime.—Given estimates of W_n and the insertion rate constant $k_{n,1}^{+}$, it is straightforward to compute the average time required for an existing micelle to undergo dissociation via purely stepwise processes. We call this time the equilibrium dissociation lifetime, denoted by τ_d. Values of τ_d have been computed for each value of α at $\Delta\mu = \Delta\mu_c$ by a method closely analogous to that used to compute nucleation rates in the Becker-Döring theory of stepwise vapor phase nucleation [30].

Intrinsic fission lifetimes.—Preliminary MD simulations of preassembled micelles of varying size showed that micelles with sizes somewhat larger than n_e spontaneously fission frequently enough to be observed in long MD simulations, with an average lifetime that decreases rapidly with increasing n. The fact that the fission lifetime decreases rapidly with increasing n suggests a picture of fission as a two-step process in which fission typically occurs via a rare fluctuation of n to a value greater than n_e via stepwise insertion, followed by fission of the enlarged, less stable micelle. This picture suggested that a study of fission in enlarged micelles, with $n > n_e$, might allow us to estimate the overall rate.

To quantify fission rates, MD simulations of individual preassembled micelles were performed for each value of $\alpha = 10$–16 with several values of n. For each choice of values for α and N, independent MD simulations were performed for many equivalent systems, each containing one micelle. The times at which all fission events occurred were recorded, and the resulting set of times was used to estimate an intrinsic fission lifetime for a micelle of known size n, which we denote by τ_n^{fis} [30].

Figure 2 shows the resulting estimates of $\ln \tau_n^{\mathrm{fis}}$ versus n for $\alpha = 10$, 12, 14, and 16. The value of n in this plot is the average number of copolymers in the micelle just prior to fission. For each value of α, $\ln \tau_n^{\mathrm{fis}}$ is found to depend nearly linearly on n, with similar slopes for different values of α. The dependence of $\ln \tau_n^{\mathrm{fis}}$ upon both n and α is found to be well described over this range as a linear function of both n and α, of the form

$$\ln \tau_n^{\mathrm{fis}}(\alpha) = A + B\alpha + Cn, \tag{2}$$

with $A = 10.855$, $B = 2.0984$, and $C = -0.1877$.

Equilibrium fission lifetime.—Given estimates of W_n and τ_n^{fis} as functions of n, we can compute the time it would take a randomly chosen micelle to undergo fission, in the absence of stepwise dissociation. We call this the equilibrium fission lifetime, denoted by τ_f. The corresponding rate $1/\tau_f$ is given by

$$\frac{1}{\tau_f} = \sum_n P_n \frac{1}{\tau_n^{\mathrm{fis}}}, \tag{3}$$

where $P_n \propto e^{-W_n/k_B T}$ is the probability that a randomly chosen micelle has size n. We have computed τ_f at $\Delta\mu = \Delta\mu_c$ at each value of α using MC results for P_n and using Eq. (2) to approximate the dependence of τ_n^{fis} on n.

In Ref. [30], for comparison, we also analyze a simplified theory that is based on the assumption that fusion is diffusion limited. Because predicted fusion and fission rates are related by detailed balance, this assumption can be used to compute corresponding predictions for τ_n^{fis}. Within the range of values of n in which we were able to measure τ_n^{fis}, measured values for τ_n^{fis} exceed those predicted by this

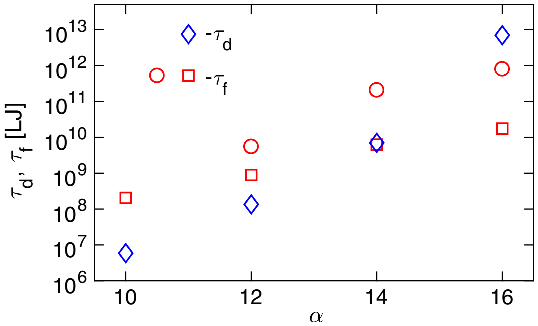

FIG. 3. Predicted values of the dissociation lifetime τ_d (blue diamonds) and fission lifetime τ_f plotted versus $\alpha = (\alpha_{AB} - \alpha_{AA})/k_BT$, for $\alpha = 10$, 12, 14, and 16. Squares are estimates of τ_f computed using Eq. (2) for all values of n, while circles are an upper bound obtained by only accounting for fission events that occur in the range $\tau_n^{\rm fis}$ for which the intrinsic lifetime was directly measured.

model by factors of 10^3 or greater, confirming the existence of a substantial barrier to fusion.

Figure 3 shows a comparison of the resulting predictions for the lifetime τ_d for stepwise dissociation (diamonds) and two different estimates of the lifetime τ_f for fission (circles and squares) at $\alpha = 10$, 12, 14, and 16 and $\Delta\mu = \Delta\mu_c$. The predicted dissociation lifetime τ_d increases much more rapidly with increasing α than τ_f. As a result, we find that association and dissociation occur much more frequently than fission and fusion for low values of α, $\alpha < 14$, but that fission and fusion dominate at the highest value, $\alpha = 16$.

The estimate of τ_f shown by squares in Fig. 3 was obtained by using Eq. (2) for $\tau_n^{\rm fis}$ to extrapolate our results to values of n somewhat below the range over which we actually measured $\tau_n^{\rm fis}$. To check whether our main conclusion is sensitive to this extrapolation, we have also considered a model in which fission is artificially suppressed outside the range of values of n in which $\tau_n^{\rm fis}$ was measured. To do this, we set $\tau_n^{\rm fis} = \infty$ for all values of n for which Eq. (2) yields $\tau_n^{\rm fis}$ greater than 5×10^6 Lennard-Jones time units, which is near the upper limit of values that we could measure. Because this model intentionally ignores the vast majority of expected fission events, most of which involve somewhat smaller micelles [29], it yields an approximate upper bound on τ_f. For $\alpha = 16$, the resulting bound on τ_f (open circles) is almost 2 orders of magnitude greater than the estimate obtained by extrapolating, but still yields $\tau_f \ll \tau_d$. The conclusion that fission and fusion dominate at $\alpha \geq 16$ thus appears to be robust.

Our analysis thus predicts a crossover with increasing α (i.e., increasing AB repulsion) from a regime in which micelle birth and death occur predominantly by stepwise association and dissociation to a regime of higher α in which fission and fusion dominate. This crossover occurs because τ_d increases much more rapidly than τ_f with increasing α. Note that τ_d increases by 6 orders of magnitude over the range shown in Fig. 3, while τ_f appears to increase by 2–4 orders of magnitude. The theory of stepwise dissociation [11,15–17] predicts a dissociation rate $\tau_d^{-1} \sim k_{n_t,1}^{-} \exp(-\Delta W_d/k_BT)$ in which ΔW_d is the barrier to dissociation, corresponding to the difference between minimum and maximum values of W_n in Fig. 1. The value of the elementary rate $k_{n_t,1}^{-} \simeq k_{n_t,1}^{+} c_1$ in a system with $c_1 = c_c$ varies with α nearly proportionately to c_c, which decreases by a factor of 20 over this range. The more important factor in the increase in τ_d is the increase in the Arrhenius factor $\exp(-\Delta W_d/k_BT)$, which decreases by a factor of nearly 10^5 as a result of the increase in the barrier ΔW_d. The magnitude of the increase in τ_d is not surprising in light of previous predictions for polymeric micelles [15,16]. What we find more surprising is how much less τ_f changes with α.

Since the seminal work of Aniansson and Wall [11], most detailed theoretical analyses of micelle kinetics have assumed the validity of the stepwise growth mechanism for the slow process [11–13,15–19,37], thus dismissing the possibility of fission and fusion. Here, we have combined several simulation and analysis techniques to construct the first quantitative comparison of rates for these competing mechanisms for a simple simulation model of block copolymer micelles. The results show the existence of a crossover with increasing degree of repulsion between unlike components (corresponding to increasing interfacial tension and decreasing solubility) from a weakly immiscible regime in which micelles are created and destroyed primarily by stepwise association and dissociation to a strongly immiscible regime in which fission and fusion dominate. Most block copolymer systems presumbably lie in the strongly immiscible regime. This conclusions is consistent with the conclusions of several authors who have argued for the relevance of fission and fusion in solutions of relatively insoluble nonionic surfactants [14,17,23,38,39] and ionic surfactants at high salt concentrations [14,40,41] on the basis of analyses of the concentration dependence [14,38,40] and absolute magnitude [17,23,39] of the slow relaxation time τ_2. Our results are not consistent with the predictions of Halperin and Alexander [37], who considered strongly immiscible block copolymers micelles and predicted that fission and fusion would be irrelevant in this limit. Further simulation and theoretical work is clearly needed to determine the generality of our conclusions and to study the mechanisms and barriers for fission and fusion. We hope that this work inspires renewed experimental and theoretical interest in this prototypical example of a slow dynamical process in soft matter.

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