

# On the 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 association and dissociation of entire micelles or by fission and fusion of existing micelles. Molecular dynamics simulations are used here to estimate rates of these competing mechanisms in a simple model of block copolymer micelles. 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.

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 often 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 time scales: a “fast” process with a typical relaxation time  $\tau_1$  of microseconds or less and a “slow” process with a much longer relaxation time  $\tau_2$ . [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 [11–19] is closely analogous to the classical Becker-Döring theory of stepwise nucleation of liquid from a vapor.[20]

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 step-wise processes [21–23]. The usefulness of such models has thus far been limited, however, by the absence of quantitative estimates of rate constants for 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 [24], and on exchange of individual molecules [25]. Here, we combine MD simulation and population modelling to estimate and compare equilibrium rates of the competing association/dissociation and fission/fusion processes for a simple simulation model of a non-ionic block copolymer surfactant. To do so, we analyze the behavior of a micelle population model using model parameters that we extract from molecular simulations.

*Population Model:* We consider a dilute micellar solution in which micelles coexist with a concentration  $c_f$  of free surfactant molecules. Let  $P_{eq}(M)$  denote the equilibrium probability that a randomly chosen micelle in such a solution contains  $M$  molecules. This is given by a Boltzmann distribution  $P_{eq}(M) \propto \exp[-\Phi(M)/k_B T]$ , where  $\Phi(M)$  is the free energy required to form a micelle of size  $M$  from a reservoir of free surfactants. The free energy  $\Phi(M)$  characteristically has a local minimum at some value  $M_{eq}$ , which is the most probable micelle size.

The principle of detailed balance requires that rates of stepwise association and stepwise dissociation must be equal in equilibrium, as must rates of fission and fusion.[26] We take advantage of this by considering a model that allows for only one of each pair of opposing processes. We consider a model for a micelle that allows

for stepwise changes in  $M$  that can lead to dissociation, and that allows for fission, but that does not explicitly allow for creation of a new micelle by association or for fusion of a pair of micelles. This model is used to estimate the average time  $\tau_d$  for dissociation and the time  $\tau_f$  for fission of an existing micelle.

Let  $P(M, t)$  denote the probability that a micelle selected from an equilibrium distribution  $P_{eq}(M)$  at time  $t = 0$  contains  $M$  molecules at time  $t$ , and has undergone neither fission nor dissociation since time 0. Molecules are randomly expelled from such a micelle at a rate  $k^-(M)$ , and are randomly inserted at rate  $k^+(M)c_f$  that is proportional to  $c_f$ . Detailed balance requires that

$$P_{eq}(M)k^+(M)c_f = P_{eq}(M+1)k^-(M+1) \quad . \quad (1)$$

Let  $J(M)$  denote the net probability flux

$$J(M) = P(M)k^+(M)c_f - P(M+1)k^-(M+1) \quad (2)$$

from size  $M$  to  $M+1$  via stepwise processes. In a model that allows for both stepwise processes and fission,

$$\frac{\partial P(M, t)}{\partial t} = J(M-1, t) - J(M, t) - \frac{P(M, t)}{\tau_{fis}(M)} \quad , \quad (3)$$

where  $1/\tau_{fis}(M)$  is the rate of spontaneous fission for a micelle of size  $M$ . To allow for dissociation, we impose an absorbing boundary condition  $P(M_d, t) = 0$  at some very small value  $M = M_d$ , thus assuming that micelles of size  $M \leq M_d$  are doomed to dissociation. In the continuum limit, in which  $|\Phi(M+1) - \Phi(M)| \ll k_B T$ , Eq. (3) reduces to a Fokker-Planck equation [27]

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial M} \left[ k^- \left( \frac{\partial P}{\partial M} + P \frac{\partial(\Phi/k_B T)}{\partial M} \right) \right] - \frac{1}{\tau_{fis}} P \quad . \quad (4)$$

The independent input parameters required by this model are the free energy  $\Phi(M)$ , the expulsion rate  $k^-(M)$  and the fission rate  $\tau_{fis}(M)$ , all of which are functions of  $M$ .

*Simulation Model:* Values of all parameters in Eq. (3) have been estimated for a simple simulation model of nonionic AB diblock polymer surfactants in a polymeric solvent. 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  $\sigma$  interact via a pair potential  $U_{\text{pair}}(r) = \epsilon_{ij}[1 - (r/\sigma)^2]$ , with  $\epsilon_{AA} = \epsilon_{BB} = 25k_B T$  and  $\epsilon_{AB} \geq \epsilon_{AA}$ . Bonded beads also interact via a potential  $U_{\text{bond}} = \kappa r^2/2$  with  $\kappa = 3.048k_B T/\sigma^2$ . Simulations were performed at constant temperature  $k_B T = 1$  and pressure  $P = 20.249k_B T/\sigma^3$  [28], giving an average bead concentration  $c \simeq 3\sigma^{-3}$ .

Simulations were performed at several values of a parameter  $\alpha \equiv (\epsilon_{AB} - \epsilon_{AA})/k_B T$  that controls the driving force for micellization. Well-defined micelles form only for  $\alpha \geq 10$ . 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) / molecular dynamics (MD) simulations that were performed in a semi-grand ensemble in which the number of copolymer molecules fluctuates but the total number of copolymer and solvent chains remains constant. [29] These simulations use a MC move that can convert molecules of one type into the other by the toggling the bead type of the 4 beads that form the B block of a copolymer. 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.[30] Let  $\tilde{M}$  denote the total number of copolymer molecules in a simulation unit cell. The acceptance criteria for MC moves are designed to sample the Boltzmann distribution for a system with a modified potential energy  $U' = U - V(\tilde{M})$ , in which  $U$  is the physical potential energy and  $V(\tilde{M})$  is a umbrella potential that depends only on  $\tilde{M}$ . The potential  $V(\tilde{M})$  is chosen adaptively to obtain a nearly flat probability distribution  $P(\tilde{M})$  for  $\tilde{M}$ . The Gibbs free energy  $G(\tilde{M})$  for the system is then given by  $G(\tilde{M}) = -k_B T \ln[P(\tilde{M})] + V(\tilde{M})$ .

The semigrand canonical equilibrium probability  $P_{eq}(\tilde{M}, \Delta\mu)$  for a hypothetical subsystem in which composition can fluctuate via exchange with a reservoir with a fixed exchange chemical potential  $\Delta\mu$  is given by  $P_{eq}(\tilde{M}, \Delta\mu) \propto \exp[-\Phi(\tilde{M}, \Delta\mu)/k_B T]$ , where

$$\Phi(\tilde{M}, \Delta\mu) = G(\tilde{M}) - \tilde{M}\Delta\mu \quad , \quad (5)$$

and where  $\Delta\mu$  is the difference between copolymer and homopolymer chemical potentials.

We define the critical micelle concentration  $c_c$  to be the average free molecule concentration  $c_f$  in a state in which the number of free molecules is equal to the number in micelles, or in which the total concentration  $c$  is twice  $c_f$ . Let  $\Delta\mu_c$  denote the value of  $\Delta\mu$  in this state. The mole fraction of free copolymers in this state, denoted by  $\phi_c$ , decreases exponentially with  $\alpha$ , and is found to be  $\phi_c = 0.0154, 0.0052, 0.0017, 0.00075$  for  $\alpha = 10, 12, 14, 16$ , respectively.

Fig. 1 shows the calculated free energy  $\Phi$  at  $\Delta\mu = \Delta\mu_c$  as a function of the average number of molecules in a micelle, which we denote by  $M$ . The average micelle aggregation number  $\bar{M}$  has been calculated for each value of  $\tilde{M}$  by subtracting the average number of free molecules from  $\tilde{M}$ , as discussed in detail in supplemental material (SM).[31] The most probable aggregation number  $M_{eq}$  is the value at which  $\Phi(M)$  is minimum, for which we obtain  $M_{eq} \simeq 49, 66, 84$ , and  $105$  for  $\alpha = 10, 12, 14$ , and  $16$ . The local maximum in  $\Phi(M)$ , at a value of  $M$  denoted by  $M^*$ , is the transition state for stepwise dissociation

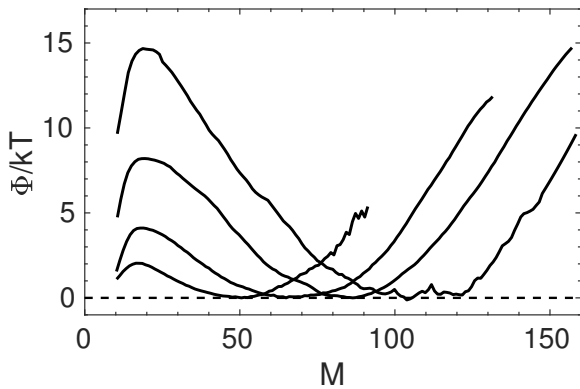


FIG. 1. Micelle free energy  $\Phi$  plotted vs. average micelle aggregation number  $M$  at  $\Delta\mu = \Delta\mu_c$ . Results are shown for  $\alpha = 10, 12, 14$ , and  $16$ , from lowest to highest free energy barrier. Results are shown shifted so that  $\Phi(M) = 0$  at the micellar minimum,  $M = M_{eq}$ , and cutoff at a minimum value  $M_d = 10$ .

or association. The barrier to dissociation, denoted by  $\Delta\Phi_d = \Phi(M^*) - \Phi(M_{eq})$ , increases from 2-15  $k_B T$  over this range of  $\alpha$  values.

*Molecular Insertion and Expulsion Rates:* The rate constants  $k^+(M)$  and  $k^-(M)$  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 simply measuring the rates at which copolymers enter and leave the micelle. Details are discussed in SM. [31]

*Estimating Fission Rates:* Preliminary MD simulations of pre-assembled micelles of varying size showed that micelles with sizes somewhat larger than  $M_{eq}$  spontaneously fission frequently enough to be observed in long MD simulations, with an intrinsic lifetime  $\tau_{fis}(M)$  that decreases rapidly with increasing  $M$ . The observation that  $\tau_{fis}(M)$  decreases rapidly with  $M$  suggests a picture of fission as a two step process involving a random fluctuation of  $M$  to a value greater than  $M_{eq}$  via stepwise insertion, followed by fission of the enlarged micelle. This picture suggested that the study of fission in enlarged micelles might allow us to estimate the overall rate.

To estimate  $\tau_{fis}(M)$ , MD simulations of individual pre-assembled micelles were performed for each value of  $\alpha = 10 - 16$  at several values of  $M$ . For each choice of values for  $\alpha$  and  $M$ , independent MD simulations were performed for many similar systems, each containing one micelle. All fission events were identified, and the resulting set of values for the lifetimes of similar micelles was used to estimate an average fission lifetime  $\tau_{fis}$ . [31]

Fig. 2 shows the resulting estimates of  $\ln \tau_{fis}(M, \alpha)$  vs.  $M$  for  $\alpha = 10, 12, 14$ , and  $16$ . The value of  $M$  in this plot is the average number of copolymers in the micelle just prior to fission. For each value of  $\alpha$ ,  $\ln \tau_{fis}$  is found to depend nearly linearly on  $M$ , with similar slopes for

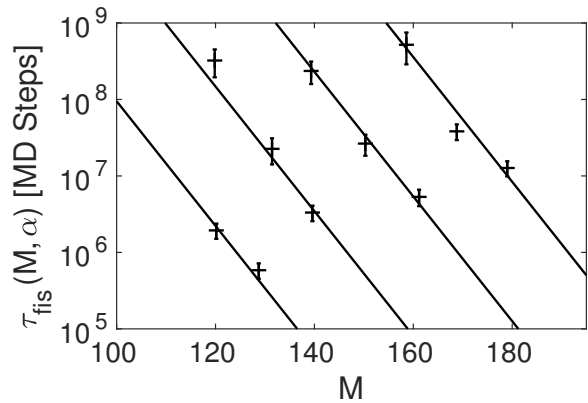


FIG. 2. Semi-log plot of the intrinsic fission time lifetime  $\tau_{fis}$  as a function of micelle aggregation number  $M$ , for values of  $\alpha = 10, 12, 14$ , and  $16$  (left to right). Error bars show root-mean-squared statistical errors. Solid lines are predictions of the global fit to Eq. (6), plotted at these four values of  $\alpha$ .

different values of  $\alpha$ . The dependence of  $\ln \tau_{fis}$  upon both  $M$  and  $\alpha$  is found to be well described over this range as a linear function of both  $M$  and  $\alpha$ , of the form

$$\ln \tau_{fis}(M, \alpha) = A + B\alpha + CM \quad (6)$$

with  $A = 16.1538$ ,  $B = 2.0984$  and  $C = -0.1877$ .

*Analysis of Slow Processes:* To analyze population dynamics, estimates of  $\Phi(M)$ ,  $k_-(M)$ , and  $\tau_{fis}(M)$  that were obtained from the simulations described above were used as inputs to Eq. (3). For this purpose, Eq. (6) was used to approximate  $\tau_{fis}(M)$ . The analysis for each value of  $\alpha$  was carried out at  $\Delta\mu = \Delta\mu_c$ .

Let  $P(t) = \sum_M P(M, t)$  denote the total probability that a micelle that is selected at random from  $P_{eq}(M)$  time 0 survives to time  $t$  without undergoing either dissociation or fission. The function  $P(t)$  decreases with time  $t$  as a result of both fission and dissociation, and decays as  $P(t) \propto e^{-t/\tau}$  at long times, where  $1/\tau$  is an overall decay rate. Separate values for the rate  $1/\tau_f$  of fission and the corresponding rate  $1/\tau_d$  of dissociation were obtained by analyzing the long-time decay of  $P(t)$  in variants of the model in which we either artificially suppress fission to measure  $\tau_d$  or artificially suppress dissociation to measure  $\tau_f$ . To measure  $\tau_f$ , dissociation is suppressed by replacing the absorbing boundary condition at the lower boundary  $M = M_d$  by a reflecting boundary condition. All simulations use a lower cutoff  $M_d = 10$ .

Fig. 3 shows the resulting predictions for the lifetime  $\tau_d$  for stepwise dissociation (solid diamonds) and the lifetime  $\tau_f$  for fission (solid circles) at  $\alpha = 10, 12, 14$  and  $16$ . The predicted dissociation lifetime  $\tau_d$  increases much more rapidly with increasing  $\alpha$  than  $\tau_f$ . As a result, we predict that association / dissociation occur much more frequently than fission or fusion for low values of  $\alpha$ ,  $\alpha < 14$ , but that fission and fusion dominate at the highest value,  $\alpha = 16$ .

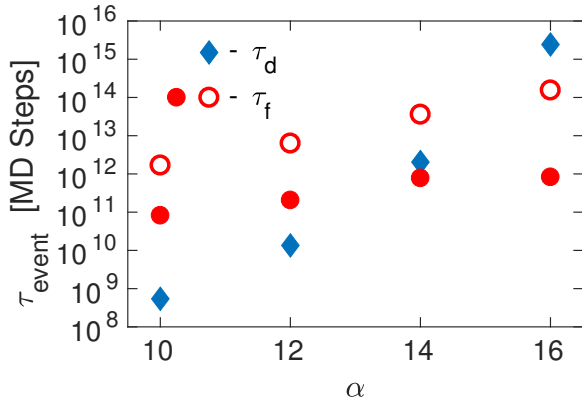


FIG. 3. Predicted values of the dissociation lifetime  $\tau_d$  (blue diamonds) and fission lifetime  $\tau_f$  (red circles) plotted vs.  $\alpha = (\alpha_{AB} - \alpha_{AA})/k_B T$ , for  $\alpha = 10, 12, 14$ , and  $16$ . Solid circles are estimates of  $\tau_f$  computed using Eq. 6 for all values of  $M$ , while open circles are an upper bound obtained by only accounting for fission events that occur in the range  $\tau_{fis}(M)$  for which the intrinsic lifetime was directly measured.

The estimate of  $\tau_f$  shown by solid circles in Fig. 3 was obtained by using Eq. (6) for  $\tau_{fis}(M)$  to extrapolate our results to values of  $M$  somewhat below the range over which we actually measured  $\tau_{fis}(M)$ . To check whether our main conclusion is sensitive to this extrapolation, we have also considered a variant of the model in which fission is artificially suppressed for all  $M$  for which Eq. (6) yields  $\tau_{fis}(M)$  greater than a cutoff of  $10^9$  MD steps, which is near the upper limit of values that we measured. This more conservative analysis yield an upper bound for  $\tau_f$ . The resulting bounds on  $\tau_f$  (open circles) are 1-2 orders of magnitude greater than those obtained by extrapolating, but still yield  $\tau_f \ll \tau_d$  at  $\alpha = 16$ . The conclusion that fission and fusion dominate at  $\alpha \geq 16$  thus appears to be robust.

Our analysis thus predicts a crossover with increasing  $\alpha$  (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  $\alpha$  in which fission and fusion dominate. This crossover occurs because  $\tau_d$  increases much more rapidly than  $\tau_f$  with increasing  $\alpha$ . Note that  $\tau_d$  increases by six orders of magnitude over the range shown in Fig. 3, while  $\tau_f$  increases by only about one order of magnitude. The theory of step-wise dissociation [15–17] predicts a dissociation rate  $\tau_d^{-1} \sim k_-(M^*) \exp(-\Delta\Phi_d/k_B T)$  in which  $\Delta\Phi_d$  is the barrier to dissociation, corresponding to the difference between minimum and maximum values of  $\Phi(M)$  in Fig. 1. The value of the elementary rate  $k_-(M^*) \simeq k_+(M^*)c_f$  in a system with  $c_f = c_c$  varies with  $\alpha$  nearly proportionately to  $c_c$ , which decreases by a factor of 50 over this range. The more important factor in the increase in  $\tau_d$  is the increase in the Arrhenius factor  $\exp(-\Delta\Phi_d/k_B T)$ , which decreases by a factor of more than  $10^4$  as a result

of the increase in the barrier  $\Delta\Phi_d$  visible in Fig. 1. The magnitude of the increase in  $\Delta\Phi_d$  is not particularly surprising in light of prior analysis. [15, 16] What is more surprising, in our view, is how little the estimate of  $\tau_f$  changes with  $\alpha$ .

Since the seminal work of Aniansson and Wall [11], most detailed theoretical analyses of micelle kinetics have assumed the validity of the step-wise growth mechanism for the slow process [11–13, 15–19, 32] and dismissed the relevance 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 step-wise association and dissociation to a strongly-immiscible regime in which fission and fusion dominate. Most block copolymer systems presumably lie in the strongly-immiscible regime. This conclusion is consistent with the conclusions of several authors who have argued on experimental grounds for the relevance of fission and fusion in solutions of relatively insoluble nonionic surfactants [14, 17, 22, 33, 34] and of ionic surfactants at high salt concentrations [14, 35, 36], on the basis of analysis of the concentration dependence [14, 33, 35] or the absolute magnitude [17, 22, 34] of the measured slow relaxation time  $\tau_2$ . Our results are not consistent with the theoretical predictions of Halperin and Alexander [32], who considered kinetics of strongly immiscible block copolymers micelles and argued for the irrelevance of fission and fusion 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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