Comment on "Principal Role of the Stepwise Aggregation Mechanism in Ionic Surfactant Solutions Near the Critical Micelle Concentration. Molecular Dynamics Study"

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In a recent paper,[1] Burov et al. report on the mechanisms by which micelles of ionic surfactants change size near the critical micellar concentration. From unbiased molecular dynamics simulations of model surfactants they conclude that monomer fission and fusion are the predominant mechanisms of micelle size change, for two reasons: (1) monomer fission and fusion represent 97% of all fission and fusion events and (2) solving a system of kinetic equations that neglects fission and fusion of larger fragments recovers the distribution of micelle sizes observed directly from simulation. While argument (1) unequivocally supports the main conclusion of the paper, here we will show that argument (2) is flawed and may not be used to assess the predominance of any given mechanism.

Briefly, the system of kinetic equations in question reflects the fact that the simulations were performed at constant total number of particles and were long enough to reach equilibrium. The kinetic equations thus require that both the total surfactant concentration and the concentration of micelles of any size remain constant. This system of equations contains only two types of variables: the concentration of each micellar species and the rate constants for fission and fusion of micelles of any given size. Using the rate constants for monomer fission and fusion obtained from the simulation, they solve that system of equations for the micelle size distribution (the concentration C_n of micelles with n molecules). They find that C_n obtained using this kinetic model is almost identical to that determined directly from simulation, and take this as evidence that fission and fusion of large fragments are not significant processes of micelle size change.

A thermodynamic argument shows that this conclusion may not be made. The relative concentration of different micellar species in equilibrium systems depends exclusively on their relative free energy; it does not depend on the path by which one micellar species converts into another. In other words, equilibrium systems obey detailed balance: the forward and backward reaction rates of any processes connecting any two states are identical. As an example, let us take a system that may exist in two states (A and B) connected by two processes (1 and 2) as illustrated in figure 1. Detailed balance tells us that $C_A k_{f,1} = C_B k_{b,1}$. If the two rate constants are known, clearly we can recover C_B for any given C_A. As detailed balance is always obeyed in equilibrium, $C_A k_{f,2} = C_B k_{b,2}$ is *also* true and will lead to the same C_B for the same initial C_A, even if $k_{f,1} \gg k_{f,2}$ and $k_{b,1} \gg k_{b,2}$ (if process 1 is much more frequent than 2). It
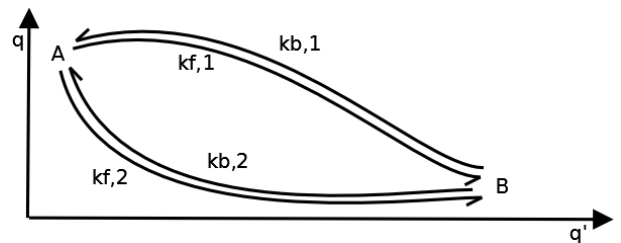

Figure 1: Diagram of a system described by two reaction coordinates q and q' with two stable states A and B connected by two distinct processes 1 and 2. $k_{f,1}$ and $k_{f,2}$ are the forward rate constants for either process; $k_{b,1}$ and $k_{b,2}$ the backward rates.

follows that the solution of a system of kinetic equations that includes only monomer fission and fusion will *always* recover the correct C_n distribution even when other processes of micelle size change are abundant, provided that the rate constants for monomer fission and fusion of micelles of any size present in the simulation are non-zero. In the thought experiment described in ref. 1 where additional transitions are switched on at some time t_{on}, the authors argue that the distribution C_n would relax to a new form at $t > t_{on}$. However, such a relaxation would

violate detailed balance and is therefore impossible in this equilibrium system.

In summary, the relative importance of different processes of micelle size change may be assessed by calculating the fraction of particular fission and fusion events (e.g. monomer addition and removal) relative to the total number of events in the system, as Burov et al. correctly did. Comparisons between C_n distributions directly obtained from simulation and as the solution of kinetic models are not appropriate to make this assessment.

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References

[1] Burov, S. V.; Vanin, A. A.; Brodskaya, E. N. *J. Phys. Chem. B* **2009**, *113, 10715.*