

Abstract Submitted
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Micellization kinetics of diblock copolymers in a homopolymer matrix: A self-consistent field study¹ RAGHURAM THIAGARAJAN, DAVID MORSE, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455 — Self-consistent field theory is used to calculate free energy barriers and reaction rates for the spontaneous association and dissociation of micelles formed of block copolymers in a homopolymer matrix. The barriers are prohibitively large for copolymers of typical molecular weights when the unimer (free surfactant) concentration is near the equilibrium critical micelle concentration. As a result, polymeric micelles normally cannot reach true thermodynamic equilibrium. The rates of association and dissociation are, however, sensitive to unimer concentration, making it possible to form or destroy micelles at observable rates in sufficiently highly supersaturated or subsaturated solutions, respectively, even when both reactions are suppressed near the equilibrium CMC. The barrier to disassociation is particularly sensitive to unimer concentration, and vanishes when the unimer concentration is only slightly (e.g., tens of percent) below the equilibrium CMC.

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