

Kinetic exchange of copolymer surfactants in micelles.

Fabián A. García Daza, Josep Bonet Avalos, and Allan D. Mackie

Universitat Rovira i Virgili, Spain.

The exchange of surfactants in micelles with the bulk involves several processes which are difficult to characterize experimentally [1-4]. Microscopic simulations have the potential to reveal some of the key aspects that take place when a surfactant spontaneously exits a micelle. We present a study based on a dynamic version of a single-chain mean field theory [5] using a coarse-grained model for poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer systems [6]. The kinetics described in our simulations involves three different regimes which span over a large range of time [7]. After a fast initial rearrangement of the labeled chains, the system undergoes a logarithmic relaxation [8], which has been experimentally observed [1-2]. Contrary to what has been stated in previous analyses, this regime is caused by the intrinsic physical behaviour of the system, and not only due to the polydispersity of the samples. Finally, the terminal regime is characterized by an exponential decay. The exit rates predicted by our simulations are in good agreement with the ones experimentally reported. In addition, we find a subtle variation of the radius of gyration of the hydrophobic block while exiting the micelle, which challenges the vision of either a complete collapse or a full stretching commonly accepted in current theoretical and experimental literature [9].

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