558a Complementary Use of Simulations and Molecular-Thermodynamic Theory to Model Micellization and Micellar Solubilization

Brian C. Stephenson, Kenneth J. Beers, and Daniel Blankschtein

Micellar solubilization is relevant to many industrial, pharmaceutical, and biological processes and applications. Because it is such a broadly applicable phenomenon, gaining a fundamental understanding of the factors that drive surfactant and solubilizate self-assembly is of great practical relevance. Frequently, a highly specific set of surfactant/solubilizate solution characteristics is required for a given application. These characteristics typically include: the critical micelle concentration (CMC), the extent of solubilization, and the shape and size of the surfactant/solubilizate micellar aggregates.

Theoretical work relying on a thermodynamic model of self-assembly (referred to as the molecular-thermodynamic approach) permits prediction of solution properties for relatively simple surfactants and solubilizates where it is possible to identify a priori what equilibrium position each component will adopt in a self-assembled micellar aggregate. Unfortunately, for many surfactants possessing more complex chemical structures, it is not clear a priori how the system components will assemble and locate themselves within micellar aggregates.

An alternative to molecular-thermodynamic modeling is to use computer simulation methods to study the self-assembly of surfactants and solubilizates in solution. However, an atomistic-level description of micelle formation is computationally challenging because of the size and density of the micellar aggregates.

We have recently implemented a combined computer simulation/molecular thermodynamic approach to model micellization and micellar solubilization. This approach permits modeling of more complex surfactant/solubilizate systems using less computational time than has been possible to date. In this approach, molecular dynamics simulations are used to simulate a surfactant or solubilizate at an oil/water interface (modeling the micellar core/water interface) to determine the local environment of each portion of the molecule. After identifying the hydrated and the unhydrated atoms, molecular-thermodynamic modeling is performed to predict: (i) the free-energy change associated with forming a micellar aggregate, (ii) the critical micelle concentration (CMC), and (iii) the optimal shape and size of the micellar aggregate.

Our results indicate that a combined computer simulation/molecular thermodynamic modeling approach can be used to extend the applicability of molecular-thermodynamic theory to significantly more complex surfactants and solubilizates than has been possible to date.