Research Report

Modeling the Micellization Behavior of Surfactants Having Increased Chemical Complexity, Including Fluorosurfactants and Fluorocarbon-Based/Hydrocarbon-Based Surfactant Mixtures

Personnel: J. Iyer and D. Blankschtein
Sponsorship: Industrial Funds

Fluorocarbon-based surfactants are utilized in a wide variety of practical applications, including: (i) reducing surface tension in many products, such as adhesives, waxes, polishes, and paints, (ii) providing better control over the emulsion polymerization of fluoropolymers, (iii) serving as artificial oxygen carriers, and (iv) solubilizing membrane proteins. The efficacy and superior performance of fluorocarbon-based surfactants in these types of applications and in comparison to other types of common surfactants, such as those based on hydrocarbons, is due to the unique properties of the fluorine atoms. However, in spite of the advantages resulting from the use of fluorosurfactants, there has recently been growing concern about their incorporation into commercial products due to their potential toxicity. This has prompted major fluorocarbon manufacturers and industrial consumers to search for benign alternatives, which ideally would behave in solution similarly to the surfactants being replaced.

In most applications involving surfactant solutions, both the surface and bulk properties of the solution are affected by the surfactant micellization behavior, characterized by a critical micelle concentration (CMC), above which surfactants aggregate into micelles, and by the shape, size, and composition (in mixed surfactant systems) distributions of these micelles, which can vary with surfactant concentration, surfactant composition, and other solution conditions. Accordingly, developing a theoretical framework to predict micellization behavior based on the chemical structures of the constituent surfactants and the solution conditions would greatly assist the formulator searching for alternatives to fluorosurfactants, by reducing the need for costly trial-and-error experimentation.

As part of this project, we are studying the micellization behavior of both traditional fluorocarbon-based surfactants (in order to understand their fundamental properties) and some of their potential substitutes. Such substitutes include: partially-fluorinated surfactants with methylene, ether, ester, and possibly other groups in the surfactant tail, surfactants with one head and two tails – both partially-fluorinated tails or one hydrocarbon-based and one fluorocarbon-based tail, and mixtures of fluorinated surfactants with hydrocarbon-based surfactants. The advantage of inserting methylene groups in the fluorocarbon backbone is that it may make the carbon backbone more susceptible to degradation, since hydrogen atoms do not shield the carbon backbone as effectively as the fluorine atoms. Adding ester and ether linkages in the carbon backbone also makes the chain more susceptible to degradation. The presence of these linkages with oxygen in the surfactant tail can aid in the breakdown of the long partially-fluorinated surfactant tail into smaller, less toxic fluorocarbon segments. Mixing fluorocarbon-based surfactants with hydrocarbon-based surfactants may lead to a reduction in the amount of fluorocarbon-based surfactant required to attain properties similar to those attained by fluorocarbon-based surfactants alone, and is, therefore, preferable from an environmental standpoint.

We have recently developed a novel modeling approach that combines computer simulations with a molecular-thermodynamic theory to create a computational framework that can be used to predict the micellization behavior of complex surfactants such as those mentioned above in aqueous solution [B. Stephenson, et.al., Langmuir **22**, 1500 (2006); J. Phys. Chem. B **111**, 1029 (2007); J. Phys. Chem. B **111**, 1045 (2007); J. Phys. Chem. B **111**, 1063 (2007)]. Our short-term goals for this project include testing and extending this new modeling approach for use with fluorinated surfactants, which represent a large class of compounds that are frequently used in coating, wetting, and emulsion formulations. In addition, we are extending both our computer simulation techniques and our molecular-thermodynamic theories in anticipation of the challenges encountered when modeling: (i) surfactant molecules possessing various architectural features, including fluorinated and partially-fluorinated chains, long flexible polymeric heads, and methylene, ether, or ester groups in the surfactant tail, and (ii) the micellization behavior of surfactant mixtures, including mixtures of fluorocarbon-based surfactants with fluorocarbon-based surfactants (see Figure 1) and mixtures of fluorocarbon-based surfactants with hydrocarbon-based surfactants. Such architectural and compositional features can impact all aspects of surfactant solution modeling and pose significant theoretical challenges. For example, certain mixtures of fluorocarbon-based surfactants and hydrocarbon-based surfactants, depending on the surfactant chain lengths and solution composition, form two types of coexisting mixed micelles, one rich in fluorocarbon-based surfactants and the other rich in hydrocarbon-based surfactants. This occurs due to the antagonistic enthalpic interactions between the fluorocarbon and hydrocarbon tails. Figure 2 illustrates the type of de-mixing possible when the antagonistic enthalpic interactions are strong. Such systems cannot be accurately modeled by assuming the existence of only one type of mixed micelle, and therefore, we are extending our model to account for the population of each type of mixed micelle present in the solution to predict micellization properties of such mixtures.
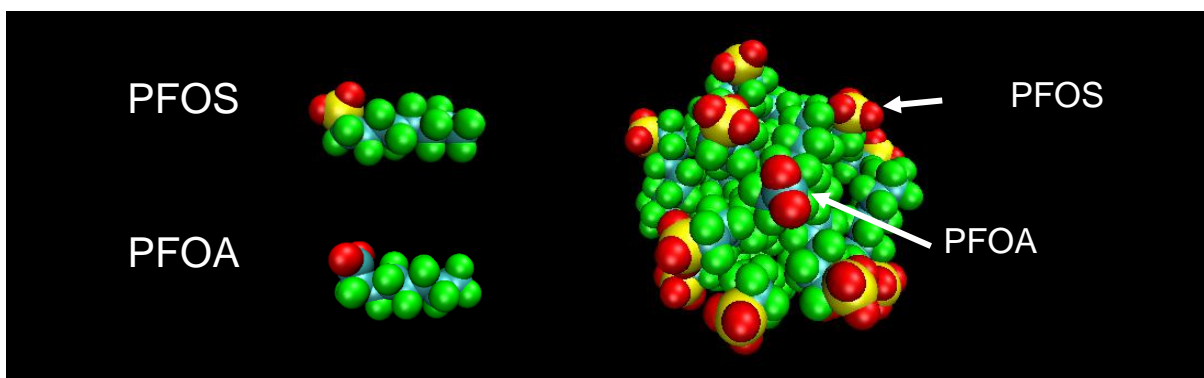
Figure 1. Snapshot of the post-equilibrium structure of the simulated surfactant monomers (Left) and mixed micelle composed of two surfactant types (Right), where PFOS is Lithium Perfluoro-octylsulfonate and PFOA is Lithium Perfluoro-octanoate. For clarity, water molecules and counterions are not shown. Color code: red – oxygen, light blue – carbon, green – fluorine, yellow – sulfur.
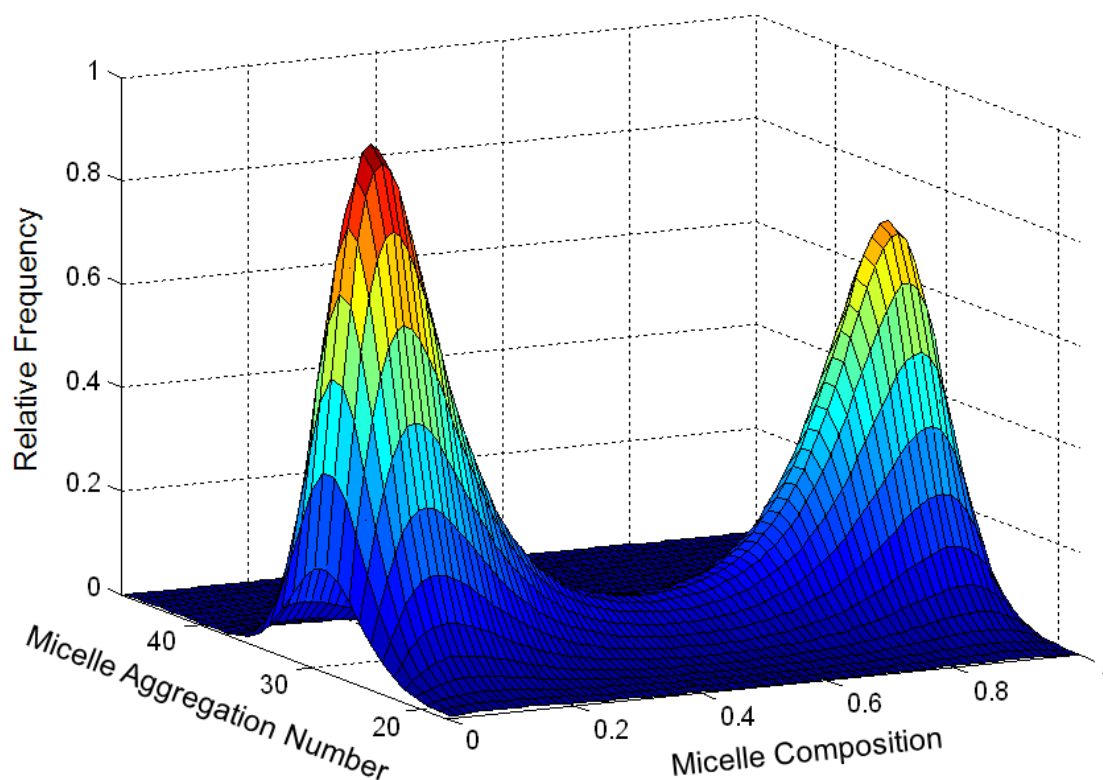
Figure 2: Sample plot of the population distribution of mixed micelles in a binary, nonionic surfactant solution above the surfactant mixture critical micelle concentration (cmc), where the two surfactant components exhibit antagonistic enthalpic interactions leading to the observed bimodality. Here, the population distribution is presented in terms of the relative frequency of occurrence of a mixed micelle of a given aggregation number and composition, normalized such that the most probable mixed micelle (located in the dark red region) has a relative frequency of 1. Note that the micelle aggregation number and micelle composition are both discrete quantities, since each mixed micelle contains only integral numbers of surfactant molecules. The surface coloring reflects the relative frequency axis values (blue – low probability of occurrence, red – high probability of occurrence).