Dimers: A Model for Surfactant Systems

Surfactants have been shown to exhibit a wide variety of phase behavior, both in bulk solution and at interfaces. For example, in bulk solution, surfactants have been shown to form a rich variety of microstructures, including micelles, wormlike micelles, lamellae, and cubic phases[1]. These microstructures can be used in many applications. Micelles have been used to solubilize a wide variety of organic components in aqueous solutions and supercritical fluids, media in which they otherwise would not dissolve[2]. They also have been used as nano-scale reaction vessels[3]. Micelles can be used for polymerization; the resulting chains have an exceptionally low polydispersity[4]. All of these microstructures can be used as templates to build nanomaterials. For example, cubic surfactant phases have been used to build novel porous polymer structures for use as ultrafiltration membranes[5]. In addition to the spontaneous formation of bulk structures, surfactants have been shown to exhibit a wide variety of surface phase behavior. By using experimental techniques such as fluorescence microscopy and Brewster angle microscopy, these surface phases can be probed. Many different phase transitions have been observed. In an effort to classify this rich and complex surface phase behavior, an analogy between surfactant phases and those of liquid crystals has been established[6]. It has been shown that there are no less than four order parameters required to describe the resulting surface phases. Surfactants have many uses in industrial processes; one example is the stabilization of foams and emulsions. Surfactants also have been used as the basis of soft lithographic methods in nanofabrication, a process that may have a huge impact in the microelectronics industry[7]. With such a diverse range of applications and phase transitions, it is of paramount importance to be able to accurately model and predict the behavior of surfactants both at interfaces and in solution.

Many experimental studies of surfactant systems rely on adsorption models that are based on the behavior of monomers, such as the Langmuir isotherm. A more realistic model would divide a surfactant into two distinct regions consisting of a hydrophilic head group and a hydrophobic tail group. While there are surfactants that defy this classification, such as the boloform and gemeni surfactants, the tail group is often is a single hydrocarbon chain. To facilitate the development of more realistic and accurate models for surfactants, we have undertaken a project to understand the behavior of dimers. This is the first step in understanding both surfactant behavior as well as the behavior of block copolymers.
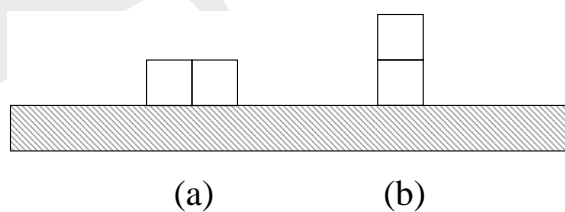

Figure 1: Dimers in the (a) parallel configuration, and (b) perpendicular configuration. The results of this study show that dimers in the parallel configuration are preferentially adsorbed over perpendicular dimers, even at very high dimer concentrations.

We are using lattice density functional theory (DFT) to model the behavior of symmetric and asymmetric dimers, both in bulk solution and at an interface. Nearest neighbor interactions are specified, and configurations that result in overlap of two dimers have been excluded, in some cases out to the first three nearest neighbors. For symmetric dimers at a surface, it is found

Professor Marc Donohue
Department of Chemical Engineering
Johns Hopkins University

that the preferred conformation upon adsorption is parallel to the surface, with the long side oriented toward the wall (see Figure 1). For the interactions that have been studied so far, there is no case in which the perpendicular orientation is favored, which has the short side oriented toward a wall and extends out into solution. A (bulk) phase transition was identified, although the microstructure of the solution after this transition has not yet been determined. These results extend to amphiphilic (asymmetric) dimers at a surface also, although a phase transition was not identified in this system.

The case of asymmetric dimers in the bulk are also being modelled; phase transitions have been identified in this system which lead to both micelles and lamellar phases. These phases have been identified by Monte Carlo simulation; the predicted lamellar phase is shown in Figure 2. Current work on this project involves a reformulation of the DFT equations to allow their solution beyond the two-phase region. It is hoped that the improved theory will help us identify new phase transitions in the system. This knowledge of phase boundaries will then guide Monte Carlo studies aimed toward visualizing the new phases formed. We hope that the improved knowledge of the phase behavior can then be extended to experimental systems to aid in the design and interpretation of experiments and the formulation of new surfactants capable of exhibiting novel behaviors and structures.
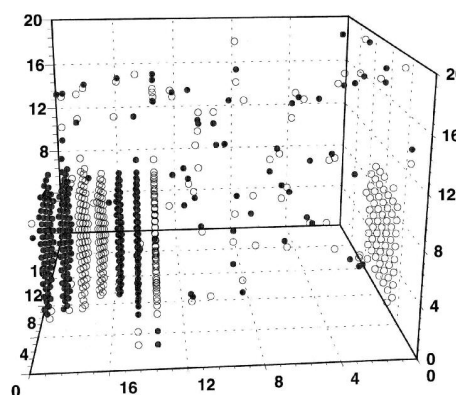

Figure 2: Lamellar phase predicted by Monte Carlo simulation for asymmetric dimers.

[1] Langevin, D. *Studies Surf. Sci. Catal.* **1998**, 117, 129.

[2] McClain, J. B.; Betts, D. E.; Canelas D. A.; Samulski, E. T.; DeSimone, J. M.; Londono, J. D.; Cochran, H. D.; Wignall, G. D.; Chillura-Martino, D.; Triolo, R. *Science* **1996**, 274, 2049.

[3] Anderson, K.; Kizling, J.; Holmberg, K.; Bystroom, S. *Colloids Surf. A* **1998**, 144, 259.

[4] Lusvardi, K. M.; Schubert, K.-V.; Kaler, E. W. *Ber. Bunsenges. Phys. Chem.* **1996**, 100, 373.

[5] Li, T. D.; Gan, L. M.; Chew, C. H.; Teo, W. K.; Gan, L. H. *Langmuir* **1996**, 12, 5863.

[6] Bibo, A. M.; Knobler, C. M.; Peterson, I. R. *J. Phys. Chem.* **1991**, 95, 5591.

[7] Zhao, X.-M.; Xia, Y.; Whitesides, G. M. *J. Mater. Chem.* **1997**, 7, 1069.

Professor Marc Donohue
Department of Chemical Engineering
Johns Hopkins University