Molecular Modeling of Microstructure and Solubilization of Single and Multiple Micelles by a Novel FFT Solution Density Functional Theory

Shun Xi [C, S] and Walter Chapman
Department of Chemical Engineering, Rice Unviersity, Houston, TX, U.S.A.
shun.xi@rice.edu

Classical density functional theory (DFT) has been successful in modeling thermodynamic properties of inhomogeneous fluids. Various DFT theories have been developed to approximate the Helmholtz free energy functional. Interfacial statistical associating fluid theory (iSAFT) is one of the most successful molecular DFTs. It is a perturbation theory that allows us to model inhomogeneous systems such as self-assembly or confined fluids of simple alkanes, colloids, associating fluids, and heteronuclear polymers. This work focuses on applying iSAFT theory to block copolymer micelles. Block copolymer micelles have been of interest to both academia and industry over decades for their extensive applications in enhanced oil recovery, cosmetic products, and drug delivery. A few chemical potential models have been developed to predict sizes, aggregation number, solubilization ability, critical micelle concentration (CMC), etc. Most of the theories are phenomenological equation of state types of theories and thus cannot fully capture the physics at the molecular level. iSAFT in this work is demonstrated to predict different influences of the hydrophobic tail and hydrophilic head of block copolymer surfactants on the size and CMCs of a single micelle. iSAFT predicted that radii and CMCs of single micelles are strongly dependent on the length of the hydrophobic tail. The radii of triblock surfactant micelles are smaller than diblock copolymer surfactants. These results agree with the experimental finding of Pluronic micelles. We also studied the distribution of solute, solvent, and surfactants within micelles using iSAFT. We are able to show the enhanced solubility of hydrocarbons in water with surfactants. A novel Fast Fourier Transform(FFT) solution method was recently developed by our group to solve iSAFT. This new method can encompass associating contributions, chain contributions, and complex geometry effects. This work also includes some of the latest results with the new method such as modeling of hydrophobic effects, and systems having multiple micelles.