577a Molecular Modeling of Transport across Surfactant-Covered Interfaces of Microemulsions

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Microemulsions are dispersions of oil in water or water in oil that are thermodynamically stable due to the significant lowering of the interfacial tension by adsorption of surfactants on the surface. They have received considerable attention due to numerous applications in a wide variety of areas such as separations, reactions, drug delivery, and detoxification. In all these applications, the process of mass transfer across the surfactant-covered interface plays a key role and the densely packed surfactant monolayer on the surface of the drops offers a significant resistance to the mass transfer.

We present results of molecular modeling of solute transport across an interface of hexadecane-in-water microemulsions covered by Brij surfactants. In order to assess the effects of the interfacial curvature on the solute transport, the investigations are performed for microemulsion droplets of various radii as well as a flat oil-water-surfactant interface. The studies are performed using a coarse-grained molecular dynamics (CGMD) model, which represents groups of several atoms as united atoms (beads). This allows one to significantly speed up the calculations while retaining the key system dynamics. The intermolecular interactions in these simulations are modeled by the Lennard-Jones potential. The simulations are performed in an NPT ensemble in a cubic 10x10x10 nm^3 box.

The simulations begin with a random distribution of the surfactant, oil and water molecules, and this distribution evolves into self-assembled structures. Depending on the surfactant concentrations, these simulations yield spherical microemulsion droplets of various radii, a flat oil-water-surfactant interface, as well as other microstructures consistent with an experimental phase diagram. The validity of the model is further confirmed by comparing the computed surface tension and surface coverage with the experimental values.

In order to obtain the transport rates for the solute, which is modeled as a spherical coarse-grained bead, we obtain an effective stochastic Langevin equation for the solute diffusion across the interface. The components of this equation (the mean potential force and the magnitude of the random force) are obtained using a novel kinetic method based on a statistical analysis of a series of short-scale molecular dynamics simulations with judiciously chosen initial conditions. The obtained Langevin equation is solved to obtain the solute transport rates. These rates are compared with available experimental data. In order to gain detailed understanding of the mechanism of the solute transport, we further analyze an internal microstructure of the surfactant monolayer and correlations between dynamics of the solute and dynamics of the surfactants.