Communication

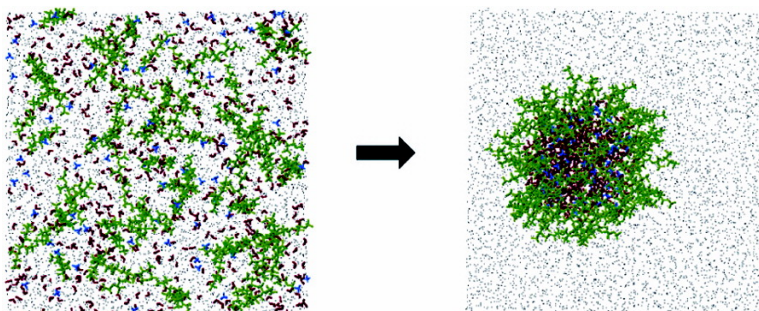# Molecular Dynamics Simulation of a Reverse Micelle Self Assembly in Supercritical CO

Lanyuan Lu, and Max L. Berkowitz

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Molecular Dynamics Simulation of a Reverse Micelle Self Assembly in Supercritical CO_2

Lanyuan Lu and Max L. Berkowitz*

*Department of Chemistry, University of North Carolina at Chapel Hill, CB 3290,
Chapel Hill, North Carolina 27599*

Received March 8, 2004; E-mail: maxb@unc.edu

Supercritical carbon dioxide ($scCO_2$) represents a nontoxic, nonflammable, easily recyclable and environmentally friendly solvent that hopefully can replace the environmentally harmful traditional solvents in the polymer industry. This is why a large amount of experimental work[1] has been done to find surfactants with an appropriate aggregation behavior and good solubility in $scCO_2$. Can computer simulations help in the search for proper surfactants? To study self-assembled aggregates such as micelles or reverse micelles (RMs) in molecular detail, computer simulations are usually performed on pre-assembled micelles. This may produce results that depend on the initial conditions. Here we report on simulations where we observed successful self-assembly of RMs in a three-component system containing $scCO_2$, water, and fluorinated surfactant starting from random configurations. Such self-assembly allows for the future computational study of structural and thermodynamic properties of microemulsions in water/CO_2 (w/c) systems that will be less dependent on the initial conditions.

To understand in detail the influence of surfactants on the properties of w/c interfaces, computer simulations were recently employed. Thus, Rocha et al. studied the PFPE surfactant-modified planar w/c interface,[2] and Stone et al.[3] investigated the molecular differences between hydrocarbon and fluorocarbon surfactants at the planar CO_2/water interface. In the study of Stone et al., the surfactants were the recently synthesized fluorinated di-chain surfactant DiF8 and its hydrogenated analogue DiH8. Senapati et al. performed molecular dynamics simulations of the RM containing DiF8 in w/c mixtures.[4] In another simulation of a RM in w/c system Senapati and Berkowitz[5] also investigated the difference between the fluorinated and hydrogenated surfactant. This time the surfactants in the system were PFPE and its hydrogenated analogue PE. In the simulations of Senapati et al.[4,5] the micelles were not self-assembled but, for the purpose of saving computational time, were initially preassembled. Although micelles were in a nonequilibrium state at the beginning of the simulations, they changed their conformations during the molecular dynamics run and presumably reached their equilibrium state. Experimental information about micellar sizes is needed to prepare the initial micelle. If this information is unavailable, one cannot pre-assemble the micelle, and therefore a self-assembly has to be performed on the computer.

In general, the self-assembly of a micelle should be preferred in computational studies, since less dependence on the initial conditions (and number of particles) is expected to appear in the simulation. Computer simulation of self-assembly is a challenge for computational studies.[6] With the increasing power of modern computers, it is now possible to study various self-assembly processes in atomic detail using MD simulations. In recent years, Marrink and co-workers[7] observed the spontaneous aggregation of direct micelles, bilayers, and vesicles. In these simulations the typical time scale of self-assembly was $\sim$10–100 ns or even longer. The self-assembly of a RM in a three-component system containing water/surfactant/oil (or $scCO_2$) has never been simulated satisfactorily, although has been attempted.[8]

In our molecular dynamics simulations the sCO_2/surfactant/water system was chosen to study self-aggregation behavior. We used the fluorinated polyether, $CF_3-(O-CF_2-CF(CF_3))_3-O-CF_2-COO^-NH_4^+$ (PFPE), as the surfactant, which is a commercially available surfactant found to form aqueous reverse micelles in $scCO_2$. Experiments show[9] that PFPE forms aqueous RMs in $scCO_2$ with water–surfactant mole ratios (W_o) up to 30. We also performed simulations with the hydrogenated analogue of the PFPE surfactant. In the simulations, the force field for the anionic surfactants and water were the same as those used by Senapati and Berkowitz.[5] Also, the temperature (298 K) and the pressure (20 MPa) in the ensemble (NPT) we used here were the same as in the above-mentioned work of Senapati and Berkowitz.[5] For reasons of computational economy, a single-point model was used for the CO_2 molecules.[10] We demonstrated previously[4] that this model gives a good description of the $scCO_2$ equation of state. Each simulation lasted for more than 50 ns to ensure thermodynamic equilibrium.

To understand the factors that determine micelle formation, a series of simulations was performed. In two of the simulations, the simulation box contained 554 water molecules, 66 fluorinated surfactant molecules ($W_0 = 8.4$), and 6359 CO_2 molecules. These numbers of particles are exactly the same as in the simulation of Senapati and Berkowitz.[5] In the first simulation the molecules were initially distributed randomly, and in the second, the initial positions were distributed on a regular lattice. In both simulations, we observed the evolution of the system from the initial configuration to a spherically shaped RM configuration. Figure 1 displays a series of snapshots illustrating this evolution. Analysis of the average distances between molecules showed that the self-assembly process was completed after $\sim$5 ns, indicating that the process is rather fast.

From our simulation we observed that during the first stage of rearrangement ($\sim$1 ns) water molecules and surfactant molecules clustered into several small micelle-like aggregates. The fast first stage was followed by a slower process during which three or four small micelles merged into two. The final rearrangement of the last two micelles into one spherical RM was the most time-consuming process. From the plot of the number of aggregates as a function of time (not shown here) we observed that our self-assembly dynamics was similar to the dynamics observed by Marrink et al.[7a] Analysis of the RM structure (we calculated the core radius, area per headgroup, eccentricity, and the fraction of gauche angles for surfactant chains) obtained after $\sim$5 ns of self-assembly showed no difference from that of the simulation of Senapati and Berkowitz.[5] As a reminder, the latter simulation was started from a pre-assembled micelle configuration and was performed with a three-site model of CO_2.

We investigated the effect of different W_0's on the process of the micellar formation. Thus, we performed three more simulations
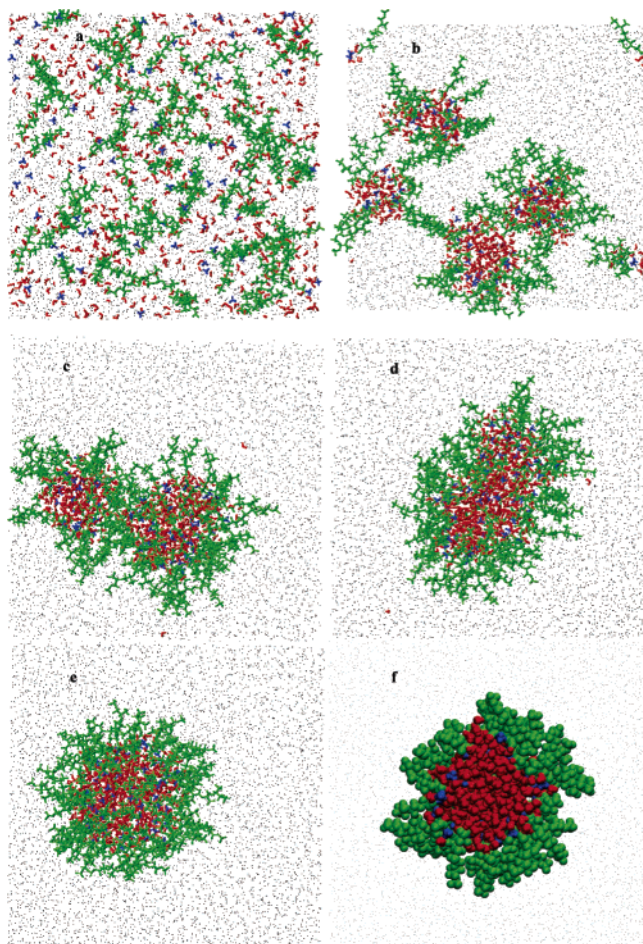
Figure 1. Snapshots of the PFPE RM self-assembly (554 water and 66 surfactant molecules). Red, blue, and green particles are water, ammonium ions, and PFPE anions, respectively. Small black dots are carbon dioxide molecules. The snapshots are taken at (a) 0 ns; (b) 1 ns; (c) 4 ns; (d) 4.4 ns; (e) 5 ns; (f) 50 ns; This snapshot in (f) is of a cut across the micelle to show water in the core and surfactants at the surface.
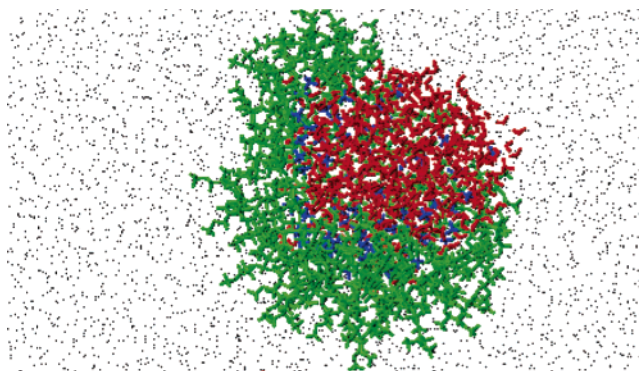

Figure 2. Equilibrated configuration of the PE system. The color scheme is the same as in Figure 1, except the surfactant anions are PE anions. The region of direct contact between water and carbon dioxide is in the upper-right corner of the aggregate.

on systems containing (a) 66 surfactant and 1108 water molecules, (b) 66 surfactant and 270 water molecules, and (c) 66 surfactant and 139 water molecules. In all cases we also observed self-assembly, and in cases (a) and (b) the micellar shape was spherical. In case (c) the micelle had a wormlike shape. Although in case (a) the micelle remained spherical and the surfactants were uniformly distributed over the surface of the sphere, we observed a larger contact between water and $scCO_2$ due to a large surface area of the water core.

We also performed a set of simulations with the PE surfactant. Again, the potential parameters describing the PE molecule were the same as those used by Senapati and Berkowitz. In the simulation containing 66 PE surfactants and 554 water molecules, we observed self-assembly into a micellar-type aggregate but with one side of this aggregate having a direct water/$scCO_2$ contact (See Figure 2). Such a contact increases the surface tension and, therefore, the free energy of the micelle, indicating that in our system the PE surfactant is not effective for creation of a microemulsion. To see if we could create a RM containing a uniform distribution of PE surfactants, we decreased the number of water molecules in few other simulations with PE. In each of these cases we observed aggregates containing regions of direct contact between water and CO_2, like

those observed in Figure 2. When the number of water molecules became small, the aggregate had a wormlike shape.

In summary, we showed for the first time that, simulating a system containing three components such as water, $scCO_2$, and polyether surfactants on a relatively detailed atomic level, one can observe a self-assembly of molecules after relatively short periods of time. When the surfactant is fluorinated (PFPE), the self-assembled aggregate represents a nicely shaped RM. In this case stable RMs are observed for a wide range of W_0. When a hydrogenated analogue of the PFPE surfactant is used, an aggregate represents a micellar-like assembly with a nonuniform distribution of surfactant molecules, thus creating a large contact area between water and CO_2, indicating that the hydrogenated analogue of PFPE is not a good agent for creating microemulsions in w/c systems. If, in general, RMs are quickly assembled in computer simulations, then, with detailed descriptions of molecules, one can study these micelles in detail in their most stable states.

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