

# Self-Assembly of Reverse Micelles in Water/Surfactant/Carbon Dioxide Systems by Molecular Simulation

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One of the primary reasons that supercritical carbon dioxide has thus far failed to achieve its full potential as an environmentally benign alternative to conventional industrial solvents is that few surfactants are known at present for use in CO<sub>2</sub>. As an initial step toward developing the molecular-level understanding needed to design new surfactants, we report the first molecular simulations of the self-assembly of dichain surfactants in supercritical carbon dioxide into stable, spherical aggregates. These aggregates exhibit the expected characteristics of reverse micelles with aqueous cores, consistent with earlier experimental findings, demonstrating the potential of molecular simulation for modeling such complex systems.

Molecular simulation techniques have been successfully applied, in the past decade or so, to study the self-assembly of amphiphilic molecules (molecules with a hydrophilic headgroup attached to a hydrophobic chain or tail) into aggregates such as micelles, vesicles, bilayers, etc.<sup>1–5</sup> These studies used simple molecular models and/or continuum solvent but were still successful in complementing the experimental investigations of oil-in-water micellar systems by leading to the understanding of the morphologies and dynamics of such aggregates. The result of this two-pronged approach (experiments and simulation) is a sound knowledge base of micellar systems in aqueous media. Another class of aggregates is reverse (or inverted) micelles (RMs) in which the roles of the polar and nonpolar parts of the amphiphiles have been reversed and the aqueous microphase is dispersed in a nonpolar solvent. A number of experimental investigations (refs 6–8 and the references therein) have shown the formation of RMs of various surfactants in supercritical solvents such as short chain alkanes and noble gases. Following promising early reports by Hoefling et al.<sup>9</sup> suggesting the formation of a micro-emulsion in a surfactant/water/carbon dioxide system using surfactant molecules with perfluoropolyether (PFPE) tails, considerable interest was generated within the scientific community regarding the formation of RMs in CO<sub>2</sub> as a nonpolar solvent. CO<sub>2</sub> is a nontoxic, chemically inert, nonflammable fluid and as such is a safe alternative to potentially hazardous industrial solvents. A number of recent experimental efforts have focused on discovering suitable surfactants that are capable of stabilizing the

water/CO<sub>2</sub> interface. The most successful surfactant molecules, identified by these experimental investigations,<sup>10–18</sup> contain fluorinated chains as their CO<sub>2</sub>-philic part and various headgroups to support aqueous or polymeric cores. For example, DeSimone and co-workers<sup>10,11</sup> have developed and extensively studied surfactants with CO<sub>2</sub>-philic perfluorooctylacrylate (PFOA) tails and polymeric heads, which thus form a polymeric core and have application in emulsion polymerization. Recently, another class of surfactants known as dichain or hybrid surfactants (surfactants with two tails, one alkane and the other perfluoroalkane) have been synthesized and shown<sup>15,16</sup> to form RMs with aqueous cores in supercritical CO<sub>2</sub>. Johnston and co-workers<sup>16</sup> have shown that RMs of dichain surfactants are capable of solubilizing significant amounts of water (approximately 2 wt %) in the RMs core which is about an order of magnitude greater than is possible without surfactants. Although, these studies have partially succeeded in identifying some desirable elements of an effective surfactant molecule, they shed limited light on the underlying principles that make these surfactants successful while others are not. Understanding these principles is needed to guide future efforts to design new and improved surfactant molecules suitable for widespread industrial applications of CO<sub>2</sub>. Molecular simulation techniques can play an important role in developing this much-needed knowledge base.

Here we report the first successful molecular dynamics (MD) simulation of the dichain surfactant to study the

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dynamics and structural features of the RMs with aqueous cores formed from these surfactant molecules in supercritical CO<sub>2</sub>. In contrast to the prior molecular simulation studies of aqueous micellar systems, this work uses detailed molecular models for all the chemical species present in the system. Our ultimate objective in this work is to make a direct connection between molecular simulation and experiments and to use the concerted effort of both approaches to gain a detailed molecular-level understanding of the characteristics that lead to the formation of stable RMs in supercritical CO<sub>2</sub>. The dichain surfactant molecule [(C<sub>7</sub>F<sub>15</sub>)(C<sub>7</sub>H<sub>15</sub>)CHSO<sub>4</sub><sup>-</sup>Na<sup>+</sup>] used in this study has two seven-carbon tails attached to a sulfate headgroup with a sodium counterion and has been the subject of recent experimental investigations by Eastoe and co-workers<sup>15</sup> and Johnston and co-workers.<sup>16</sup> For the initial study reported here, we chose this particular surfactant molecule because of the relatively small size of the molecule and simplicity in molecular modeling; however, we are currently developing and testing models in our research group to represent PFOA and PFPE surfactant molecules as well. In the following sections, we describe the new model we have developed for the dichain surfactant, the intermolecular potential models, and the simulation methodology. This is followed by discussion of simulation results.

In the system under investigation there are three chemical components, viz., CO<sub>2</sub> (solvent), water, and surfactant molecules. Of the many models for CO<sub>2</sub> and water available in the literature, we chose to use relatively simple models that have been shown to yield accurate results in the past. The model for CO<sub>2</sub> used here, developed by Harris and Yung,<sup>19</sup> is a potential model with three atomic sites. Each site consists of Lennard-Jones (LJ) interaction and a central point charge. The water molecules were represented based on the SPC/E potential model<sup>20</sup> with one LJ site centered on oxygen and three point charges. The Harris-Yung and SPC/E models reproduce well the experimental critical points of CO<sub>2</sub> and water, respectively. We constructed the model of the surfactant molecule by assembling existing models for each of the four parts of the molecule (sodium ion, sulfate headgroup, alkane tail, and perfluoroalkane tail), with each part to be modeled explicitly. The tail groups (alkane and perfluoroalkane) of the surfactant are modeled according to Cui et al.<sup>21,22</sup> for perfluoroalkane tail and to Siepmann et al.<sup>23</sup> for the alkane tail. This involves representing the CF<sub>3</sub>, CF<sub>2</sub>, CH<sub>3</sub>, and CH<sub>2</sub> groups as united atoms with LJ interactions only (no electrostatic interactions or polarizability). Intramolecular interactions within the tails include bond-bending and angle-torsion potentials. The model for the sulfate headgroup was that proposed by Cannon et al.<sup>24</sup> This is a fully atomistic model with a tetrahedral structure, with sulfur at the center and the oxygen at the apexes. The sulfur and the oxygen sites have charges for Coloumbic interactions in addition to LJ interactions. The model for the sodium ion<sup>25</sup> is a single LJ site with a unit positive charge.

The choice of the system size was governed by a balance between two competing considerations: modeling the system as realistically as possible but at the same time keeping it computationally tractable for exploratory calculations. The second consideration was important since this was the first attempt at simulating such a system. These considerations led us to a system size of 30 surfactant molecules, 132 water molecules, and 2452 CO<sub>2</sub> molecules. The state point of our simulation is  $T = 310$  K and solvent (CO<sub>2</sub>) density = 0.482 g/cm<sup>3</sup>. The critical temperature and critical density for CO<sub>2</sub> are 304 K and 0.468 g/cm<sup>3</sup>; thus CO<sub>2</sub> is in the supercritical region of the phase diagram. Compared to experimental measurements, this is a high concentration (by a factor of approximately 5) of water and surfactant molecules. The simulation technique employed is constrained MD using the Rattle algorithm<sup>26,27</sup> to maintain fixed bond lengths.

Figure 1 shows snapshots of our system, obtained from the MD simulation, at various instants of time during the course of the simulation (CO<sub>2</sub> molecules are not shown for clarity). The starting configuration ( $t = 0$ , not shown) of our simulation was a single spherical core consisting of all the water molecules surrounded by the surfactant molecules in an all-trans (fully extended) conformation. The hydrophilic headgroups of the surfactant molecules were immersed in the aqueous core. This initial condition is one of many possible configurations, which can be used to startup the simulation, and was chosen solely for the sake of convenience. Figure 1a shows the surfactant and water molecules in a dispersed state throughout the simulation box at 29.6 ps. The rapid evolution of the initial condition into this dispersed state implies a highly unstable initial condition. At this instant (29.6 ps) the system has no correlation with the initial state and thus we believe that the initial condition chosen does not affect the long-time dynamics of the system, and we have confirmed this with an independent simulation beginning from a completely dispersed initial condition. Figure 1b (time = 169.2 ps) shows the agglomeration of the earlier dispersed surfactant and water molecules into aggregates in which water molecules are surrounded by a single layer of surfactants. This picture of the aggregates formed closely resembles the picture of RMs described in the literature. Thus, our system of dichain surfactants in supercritical CO<sub>2</sub> rapidly self-assembles into aggregates which have the appearance of RMs but may be a long-lived transition state to an even fewer number of RMs. Parts c and d of Figure 1 show the system configurations at 888.0 and 1036.0 ps, respectively, and clearly show the formation of three roughly spherical and similar sized aggregates at these state conditions. In essence, the system goes from a highly dispersed state of surfactants into stable micelle-like aggregates in a span of about 1 ns. This is quite an interesting result in sharp contrast to the micelle formation dynamics in aqueous media, which occur on a scale of milliseconds. This rapid aggregation in supercritical CO<sub>2</sub> may be attributable to the enhanced mass transfer characteristics (particularly diffusion) of the surfactant and water molecules in supercritical CO<sub>2</sub> compared to those in liquid solvents. The SANS study of Eastoe et al.,<sup>15</sup> although performed at different state conditions, showed the formation of spherical RMs of dichain surfactants with aqueous cores in supercritical CO<sub>2</sub>, qualitatively consistent with our simulation. Simulations at the experimental state conditions are more than five times as large and will be reported on in a future

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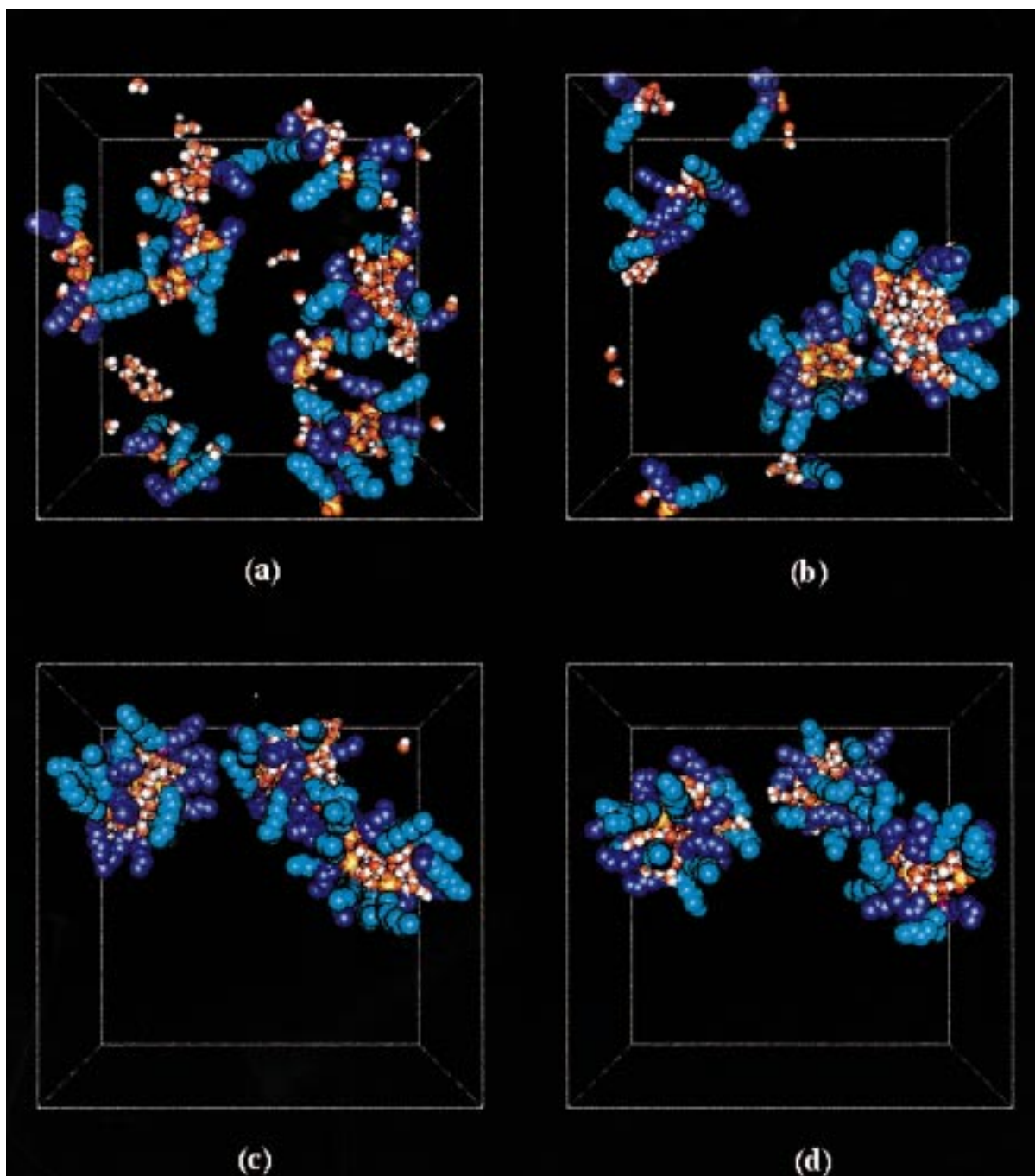
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**Figure 1.** Snapshots of the simulation taken at (a) 29.6 ps, (b) 169.2 ps, (c) 888.0 ps, and (d) 1036.0 ps. The color scheme of the various species is as follows: light blue for perfluoroalkane tail, dark blue for alkane tail, yellow for sulfur, red for oxygen, gray for sodium ion, and white for hydrogen. CO<sub>2</sub> molecules are not shown for clarity. The simulation was performed at constant NVT conditions.

publication when they have been completed. Figure 2, which plots the number of aggregates existing during the course of the simulation, clearly depicts the rapid micellization followed by a relatively long period of stabilization of the aggregates. To show more clearly that the aggregates formed in our simulation are indeed RMs, we also performed another simulation of water (no surfactant molecules present) in CO<sub>2</sub> at the same temperature and solvent density. We observed the formation of a single cluster of almost all the water molecules in equilibrium with a small fraction of water molecules dispersed in CO<sub>2</sub>. This represents a droplet of water in equilibrium with some water dissolved in CO<sub>2</sub> (water has limited solubility in CO<sub>2</sub>). The concentration of dispersed water molecules in our water/CO<sub>2</sub> simulation was  $0.3 \pm 0.1$  mol %, which

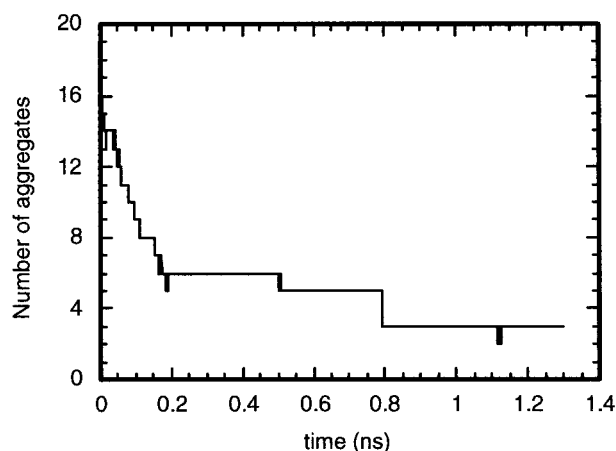
is in good agreement with the saturation concentration of water in CO<sub>2</sub> measured by Jackson et al.<sup>29</sup> In light of these two simulations, it can be inferred that dichain surfactants help to disperse water in supercritical CO<sub>2</sub> to form microdroplets and thus the aggregates formed in our simulation may indeed be RMs.

Having established that our molecular model of a dichain surfactant molecule does exhibit the formation of

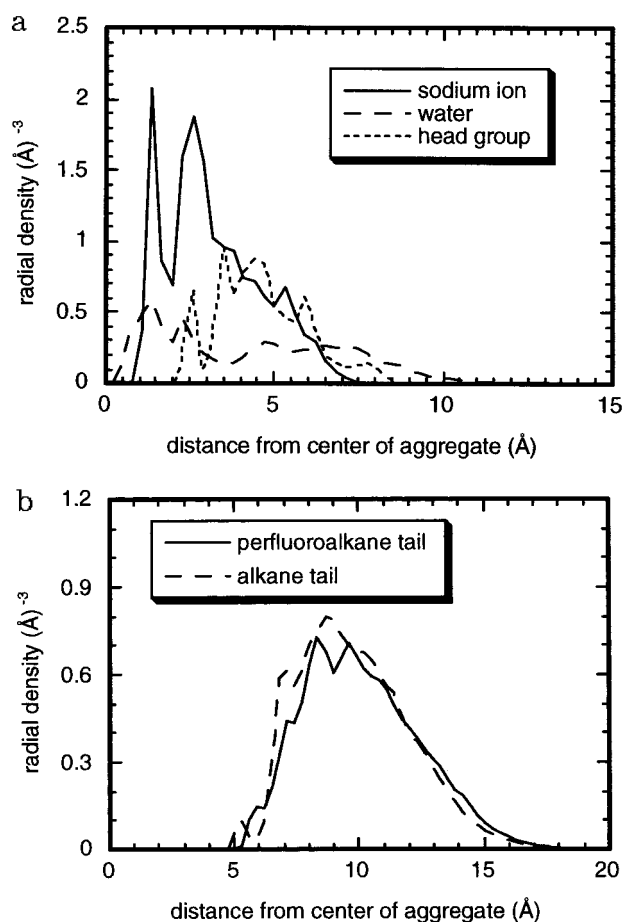
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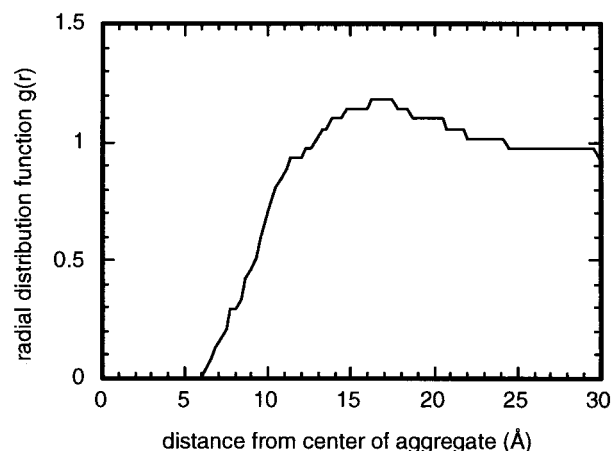


**Figure 2.** Evolution of the number of aggregates (or RMs) during the course of simulation. An aggregate is defined according to the cluster definition of Sevick et al. *J. Chem. Phys.* **1988**, 88 (2), 1198.



**Figure 3.** (a) Radial density profile of water molecules, sodium ions, and sulfate headgroups from the aggregate center of mass after the system has equilibrated to three stable RMs. (b) Radial density profile of the alkane and perfluoroalkane tails from the aggregate center of mass.

relatively stable RM-like aggregates in supercritical  $\text{CO}_2$ , we turn our attention to the observed structural features of these aggregates. Figure 3a plots the radial density profile of the three hydrophilic components of the system, i.e., the water molecules, the sulfate headgroup, the sodium ions, from the center of mass of the aggregates. The figure shows that the core of the RMs is essentially made of water molecules. The sodium ions also lie within the core of the RMs while the headgroups are confined to



**Figure 4.** Radial distribution function of the solvent ( $\text{CO}_2$ ) from the aggregate center of mass.

the surface of the core. However, there is significant penetration of some of the headgroups into the core as shown by a peak in the radial density of headgroups at small distances. Figure 3b shows the radial density profile of the alkane and perfluoroalkane tails. Both tails form the corona of the RMs with no penetration into the core. Similar behavior is found in conventional RM simulations. For example, for an ionic surfactant in nonpolar solvents (octane, carbon tetrachloride), Tobias and Klein<sup>30</sup> found that tails extend into the solvent with no penetration into the core. Also noticeable in Figure 3b is the fact that the distribution of radial density of alkane tails occurs at a somewhat smaller distance than that for perfluoroalkane tail. This difference is the manifestation of the different solubility characteristics of the two tails in the solvent. A more direct measure of this different affinity for the  $\text{CO}_2$  by two different tails is obtained by comparing the equilibrium fraction of trans bonds in the tails. The alkane tails had an average of  $74 \pm 4\%$  trans bonds (cf. 89% in vacuum) while the perfluoroalkane tails had  $91 \pm 2\%$  (cf. 81% in vacuum). This implies that the alkane tails assume more contracted conformation in  $\text{CO}_2$  indicating  $\text{CO}_2$ -phobic interaction while the perfluoroalkane tails assume more extended conformation indicating  $\text{CO}_2$ -philic interaction. In fact, we believe it is this contrasting behavior of the two tails which stabilizes the interface. Figure 4 shows the structure of the nonpolar solvent ( $\text{CO}_2$ ) around the aggregate center of mass by plotting the radial distribution function versus the distance from the center. This figure shows negligible penetration of the solvent into the core (as expected) and a positive gradient in the corona of the aggregate.

In conclusion, we have performed the first molecular dynamics simulation of the formation of stable, spherical aggregates that exhibit the expected characteristics of RMs involving dichain surfactants in supercritical  $\text{CO}_2$ . If the RM-like aggregates are indeed stable RMs (which can only be demonstrated via a grand canonical Monte Carlo simulation that is beyond the scope of the present study), our results imply that reverse micellization in supercritical  $\text{CO}_2$  occurs on a much faster time scale than that for micelles in liquid solvents. The structural features of the aggregates formed agree qualitatively with available scattering studies and quantitative comparison at the same state conditions is the focus of current ongoing study. We are further continuing this work to identify molecular characteristics and interactions to aid in designing new

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and improved surfactants; such new surfactants promise to have immense potential in process industries.

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