Molecular Simulation of a Dichain Surfactant/Water/Carbon Dioxide System. I. Structural Properties of Aggregates

S. Salaniwal,† S. T. Cui,‡ H. D. Cochrane,§ and P. T. Cummings*,‡§

Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996-2200, and Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6224

Received April 12, 2000. In Final Form: October 11, 2000

Molecular dynamics simulation of a dichain surfactant + water + carbon dioxide (solvent) system is performed to study the structural properties of reversed micelle-like surfactant aggregates formed in the system. The simulations use a detailed and realistic molecular model for the surfactant molecule and explicit representation of the water and solvent molecules to enable quantitative comparisons with a prior experimental (small-angle neutron scattering) study. The results of the simulation are found to be in reasonable agreement with experimental values. The simulations show that the size and shape of the surfactant aggregates depends on their water-to-surfactant ratio. A higher water-to-surfactant ratio results in larger and more spherical aggregates. The two distinct tails of the surfactant molecule exhibit different conformations in carbon dioxide indicating contrasting CO₂-philic behavior. The perfluoroalkane tails assume more extended conformation than the alkane tails. The microstructure of the aqueous core reveals that the water molecules in the interfacial region are strongly oriented in response to the electric fields of the anionic headgroups and sodium counterions, while water near the center of the core approaches bulklike properties with the presence of a hydrogen-bonded network.

Introduction

Over the past few years, molecular simulation techniques have been increasingly applied to investigate the morphology, dynamics, and rheology of surfactant aggregates (micelles) formed in aqueous systems.1–14 The advantage of these techniques lies in their ability to use simple molecular models for surfactant molecules (e.g., bead-spring model used by Smit et al.)7,9 and other simplifications, such as constrained aggregate3–5 or lattice-based simulations,13,14 to obtain a description of the size, shape, surface roughness, and the internal structure of micelles. In fact, in some instances,1,9 these studies have even helped clarify interpretations of prior experimental results. In certain conditions where experiments are impractical or impossible (e.g., high temperatures and pressures), molecular simulation techniques can be successfully applied to obtain the much-needed information about the various properties of surfactant aggregates. Surprisingly, very few simulation studies15,16 have addressed the phenomenon of surfactant aggregation in nonpolar solvents. The phenomenon of surfactant aggregation in nonpolar solvents (e.g., benzene, toluene, cyclohexane, carbon tetrachloride, etc.) results in the formation of aggregates known as reversed (or inverted) micelles (RMs). Structurally, these aggregates are characterized by the presence of a hydrophilic (often aqueous) core that is surrounded by a hydrophobic corona made up of surfactant tail groups. In essence, the structure of RMs is simply reversed from their aqueous counterparts because of the reversal in the roles of the hydrophilic and hydrophobic moieties of the surfactant molecules. These aggregates find numerous applications in fields such as...
Lubrication, emulsion polymerization reactions, drug delivery, and enhanced oil recovery, to name a few.

Recently, some experimental studies\(^{18-24}\) have investigated the feasibility of using carbon dioxide (CO\(_2\)) as a nonpolar solvent medium for the formation of RMs. Carbon dioxide is a nonpolar compound that is chemically inert (nontoxic, nonflammable) and an environmentally benign alternative to potentially hazardous industrial solvents currently in use. Also, its easy availability and low cost make it a cheap raw material. Thus, formation of surfactant aggregates in CO\(_2\) offers the possibility of (nontoxic, nonflammable) and an environmentally benign dioxide is a nonpolar compound that is a chemically inert surfactants that are suitable for industrial applications. Actants are termed "CO\(_2\)-philic" surfactants because they of forming stable RMs in CO\(_2\) because of their negligible solubility. This is attributed to the fact that most of these surfactants are suited for aqueous solvents while CO\(_2\) is relatively nonpolar (CO\(_2\) has a weak quadrupole) because of its low polarizibility and dielectric constant. This has motivated a number of experimental efforts\(^{26-29}\) focused on discovering suitable surfactant molecules. These surfactants are termed "CO\(_2\)-philic" surfactants because they should exhibit favorable interactions with CO\(_2\) to enable dispersion of the aggregates. Although these studies have been partially successful in identifying a few CO\(_2\)-philic surfactant molecules, little is known about the factors determining CO\(_2\)-philicity. Knowledge of these underlying principles can be quite helpful in guiding future efforts in discovering or designing new and improved CO\(_2\)-philic surfactants that are suitable for industrial applications.

Molecular simulation techniques can play an important role in developing this much-needed knowledge base.

As an initial step in this direction, we performed molecular dynamics (MD) simulation of a dichain surfactant + water + carbon dioxide (solvent) system. The dichain surfactant molecule ([CF\(_{15}\)CH\(_2\)F\(_{15}\)]\(\text{Na}^+\)) (also known as a hybrid surfactant molecule) is one of the few CO\(_2\)-philic surfactant molecules that has been shown\(^{29}\) to form RMs with aqueous cores in CO\(_2\). Recently, Eastoe et al.\(^{35}\) performed a small-angle neutron scattering (SANS) study on the dichain surfactant system and obtained information regarding the structural properties (size and shape) of the RMs formed. In the simulations presented here, this particular surfactant molecule was chosen for two main reasons. First, in terms of the molecular complexity this is a relatively small molecule compared to other known CO\(_2\)-philic surfactant molecules. Thus, from a computational perspective, it is relatively easy to model this surfactant to a sufficient degree of detail and study the aggregation behavior for a relatively large system size. Second, the structural properties of the surfactant aggregates estimated from simulations can be quantitatively compared to the experimental results of Eastoe et al.\(^{35}\) In our previous paper,\(^{36}\) we presented preliminary results showing the spontaneous aggregation of the dichain surfactant and water molecules into RM-like aggregates in this ternary system. The results presented here are for a much larger (exploratory) system that was used to test the feasibility of these simulations. In this paper, we present additional simulations on a much larger system intended to reproduce the experimental system.\(^{35}\) We also describe the detailed molecular models for the dichain surfactant molecule, water, and carbon dioxide adopted for this study and the simulation methodology used to simulate this complex physical system. Quantitative comparisons of the simulation results with the experimental results of Eastoe et al.\(^{35}\) are presented. Also, microscopic structural details of the aqueous core are presented.

POTENTIAL MODELS

Since one of the objectives of the present work is to make quantitative comparisons with the experimental work of Eastoe et al.,\(^{35}\) a high degree of realism is desirable to accurately represent all the intermolecular interactions present in the system. Thus, the simulations presented in this work involve detailed and realistic molecular models for all the three chemical species (dichain surfactant, water, and carbon dioxide) present in the system. Although this makes the system computationally complex and demanding, it minimizes any artificiality that might be included in the system and affect the dynamics of surfactant aggregation and/or the morphology of the aggregates formed. With these factors in consideration, the potential model for the hybrid surfactant molecule used in this simulation study was constructed by assembling existing models for each of the four functionally distinct parts of the molecule, i.e., the alkane tail, perfluoroalkane tail, sulfate headgroup, and the sodium counterion. This allows the surfactant model to capture most of the essential characteristics of the real dichain surfactant molecule.


For interactions between unlike sites (on the same or different molecules) we have used the conventional Lorentz–Berthelot combining rules without any fitted binary parameter.

**Alkane Tail.** The potential model for the alkane tail of the surfactant molecule is the united atom model for alkanes proposed by Siepmann and co-workers\(^{37}\) (SKS model). This model accurately predicts the experimentally measured phase envelopes of n-alkanes. More importantly, as shown by Cui et al.,\(^{38}\) the SKS model predicts the solubility of n-alkanes in CO\(_2\) that is also consistent with experimentally determined values. In this potential model, each of the methylene (CH\(_2\)) and methyl (CH\(_3\)) functional groups is represented by a single spherical interaction site (united atom) with its interaction center located at the center of the carbon atom. The interaction sites are connected via rigid bonds of length 1.54 Å. Interaction sites on different surfactant molecules and those on the same molecule separated by more than three bonds interact via the well-known 12-6 Lennard-Jones (LJ) potential given by

\[
U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{1}
\]

where \(\epsilon_{ij}\) is the well depth and \(\sigma_{ij}\) is the zero point of the potential between site \(i\) and site \(j\). The LJ size parameters for the methyl and methylene functional groups are same (\(\sigma_{CH3} = \sigma_{CH2} = 3.93\) Å) while the well-depth energy parameters are \(\epsilon_{CH2}/k_B = 114\) K and \(\epsilon_{CH3}/k_B = 47\) K, respectively. The intramolecular interactions include the bond-angle bending potential to account for the bond vibrational motion, and torsional angle potential to account for the spatial orientation of the tails. The bond angle bending potential is described by a harmonic function of the form

\[
U_{\text{bending}}(\theta_i) = \frac{1}{2} k_{\theta} (\theta_i - \theta_{\text{eq}})^2 \tag{2}
\]

where \(\theta_{\text{eq}}\) is the equilibrium angle between successive bonds and \(k_{\theta}\) is the force constant and is a measure of the rigidity of the bond angle. The torsional angle potential for the alkane tail is given by\(^{49}\)

\[
U_{\text{torsion}}(\phi) = \sum_{i=0}^{3} a_i \cos((i+1)\phi) \tag{3}
\]

where \(\phi\) is the dihedral angle that is defined as the angle between the normal to the two planes, each of which is formed by three successive interaction sites. Table 1 lists the potential parameters for the alkane model.

**Perfluoroalkane Tail.** The potential model for the perfluoroalkane tail used in this study is that proposed by Siepmann and co-workers\(^{37}\). The molecule has a rigid tetrahedral structure (O=S=O bond angle of 109.4°) with the sulfur atom at the axis and the oxygen atoms at the four apexes. The bond between the sulfur and oxygen atoms is fixed at 1.489 Å. To account for electrostatic interactions, the sulfur atom carries a charge of \(+2e\) while three oxygen atoms each carry a charge of \(-1e\). The fourth oxygen atom does not carry any negative charge as it is attached to the CH group, which in turn is attached to the two tails. A sum of Coulombic (for electrostatic interactions) and LJ terms describes the intermolecular interactions

\[
U(r_{ij}) = \sum_{i} \sum_{j} \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{5}
\]

where \(q_i\) represents the Coulombic charge on the atom \(i\). A single LJ sphere with a unit positive charge represents each sodium ion. Table 2 lists the potential parameters for sulfur and oxygen atoms and sodium ion used in this study. According to this model, each surfactant molecule consists of 21 interaction sites including one for the Na\(^+\) ion.


Table 2. Potential Parameters for the Sulfur and Oxygen Atoms of the Headgroup and the Sodium Counterion

<table>
<thead>
<tr>
<th>atom type</th>
<th>(\sigma) (Å)</th>
<th>(\epsilon/k) (K)</th>
<th>(q) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfur</td>
<td>3.55</td>
<td>126</td>
<td>+2</td>
</tr>
<tr>
<td>oxygen</td>
<td>3.15</td>
<td>126</td>
<td>−1</td>
</tr>
<tr>
<td>sodium</td>
<td>2.667</td>
<td>37.65</td>
<td>+1</td>
</tr>
</tbody>
</table>

Table 3. Potential Parameters for the Carbon Dioxide Potential Model

<table>
<thead>
<tr>
<th>atom type</th>
<th>(\sigma) (Å)</th>
<th>(\epsilon/k) (K)</th>
<th>(q) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon</td>
<td>2.757</td>
<td>28.129</td>
<td>+0.6512</td>
</tr>
<tr>
<td>oxygen</td>
<td>3.033</td>
<td>80.507</td>
<td>−0.3256</td>
</tr>
</tbody>
</table>

Table 4. Potential Parameters for the SPC/E Potential Model for Water

<table>
<thead>
<tr>
<th>atom type</th>
<th>(\sigma) (Å)</th>
<th>(\epsilon/k) (K)</th>
<th>(q) (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrogen</td>
<td>0.0</td>
<td>0.0</td>
<td>+0.4238</td>
</tr>
<tr>
<td>oxygen</td>
<td>3.166</td>
<td>78.2</td>
<td>−0.8476</td>
</tr>
</tbody>
</table>

**Carbon Dioxide.** The carbon dioxide (solvent) molecules are represented by a simple site-based potential model proposed by Harris and Yung,\(^{(42)}\) which has been shown to accurately reproduce the experimental vapor–liquid coexistence curve and critical point. The model consists of three LJ interaction sites with a Coulombic charge centered on each atom. The molecule has a rigid linear (O–C–O bond angle = 180°) geometry with the C–O bond length of 1.149 Å. The carbon atom carries a charge of +0.6512e while the two oxygen atoms carry a charge of −0.3256e each to make the molecule electrically neutral. Table 3 lists the parameters of the potential model.

**Water.** For water molecules, the extended simple point charge (SPC/E) potential model of Berendsen et al.\(^{(43)}\) is used in this study. The model has a single LJ site for the oxygen atom that also carries a charge of −0.8476e. The two hydrogen atoms are simply represented by point charges, each carrying a charge of +0.4238e. Rigid molecular geometry is assumed with the O–H bond length of unity and H–O–H bond angle equal to the tetrahedral angle (109.4°). Table 4 lists the potential parameters for this model.

**Simulation Methodology**

Molecular dynamics simulations of two different system sizes were performed. The first system (referred to as the small system) consists of 30 dichain surfactant, 132 water, and 2452 CO\(_2\) molecules. This system (with approximately 8300 interaction sites) was chosen for exploratory calculations (with computational economy in mind) and to provide qualitative insight into the dynamics of aggregation and the morphology of the aggregates. Some preliminary results on this system were reported previously.\(^{(36)}\)

The state conditions used with this system were, \(T = 310\) K and \(\rho_{\text{solv}} = 0.482\) g/cm\(^3\). These conditions were chosen to ensure that CO\(_2\) was in the supercritical state. The critical point of CO\(_2\) is \(T_c = 304.3\) K, \(P_c = 73.8\) bar, and \(\rho_c = 0.468\) g/cm\(^3\). The second system (referred to as the large system) has 33 surfactant, 1175 water, and 12,800 CO\(_2\) molecules at \(T = 298\) K and \(\rho_{\text{solv}} = 0.848\) g/cm\(^3\). This system mimics the surfactant and water concentrations, temperature, and density used by Eastoe et al.\(^{(35)}\) in their SANS study of this ternary system. The system size corresponds to one “average-sized” aggregate observed by Eastoe et al.\(^{(35)}\) In this system, the CO\(_2\) is in the high-temperature liquid state at 500 bar. The equations of motion for each interaction site were solved using the Rattle algorithm\(^{(44)}\) to constrain the rigid bond lengths in molecules. The time step used to solve the equations of motion was 1.483 fs.

As discussed in the following paper of this series, aggregation of reverse micelles with aqueous cores in carbon dioxide from this system, with the scattered starting configuration, is rapid, on the order of 0.2 \(\mu\)s, compared with the 1–10 \(\mu\)s for a typical oil-in-water micelle, because of the strong Coulombic forces present in the system studied here in comparison with the much weaker hydrophobic forces in the oil-in-water system.

The simulations were performed with two independent initial conditions, viz., (a) an aggregated starting configuration and (b) a scattered starting configuration, shown in Figures 1 and 2 for the small system and the large system, respectively. In the aggregated starting config-
uration, all the water molecules were placed within a spherical core at the center of a cubic simulation box. The surfactant molecules with fully extended tails were placed on the surface of the core with their headgroups pointing toward the center. Structurally, this configuration resembles a reversed micellar aggregate and hence the term aggregated starting configuration. In contrast, the scattered starting configuration has all the water molecules scattered within the simulation box. These initial conditions are two of the infinite configurations that can be used as starting conditions and were chosen solely for the sake of convenience.

Results and Discussion

Figure 3 shows the snapshots of the small system (from aggregated starting configuration), large system (from aggregated starting configuration), and large system (scattered starting configuration) at 1.036, 1.0, and 2.0 ns. In all these snapshots, the CO₂ molecules are intentionally hidden so that the surfactant aggregates can be seen clearly. All the figures show the presence of surfactant aggregates in the system that have the appearance of RMs, i.e., aggregates consisting of aqueous cores surrounded by surfactant molecules with their headgroups immersed in the core and the tails form a corona. Figure 3a shows the system consists of three roughly similar-sized aggregates with their aqueous cores well shielded from the surrounding solvent. The surfactant aggregates formed in the small system with scattered starting configuration (not shown) were also similar to those shown in Figure 3a. Parts b and c of Figure 3 show that the aggregates formed in the large systems have their aqueous cores considerably exposed to the surrounding solvent. This difference between the small and the large system could be attributed to the higher water-to-surfactant molar ratio, $W_o$, in the large system ($W_o \sim 35$...
for the large system; cf. $W_0 \sim 4$ for the small system). Figure 3b shows that during the time interval of 1.0 ns, the aggregated starting configuration of the large system evolves into a configuration with a large aggregate consisting of most of the surfactant and water molecules (the few remaining surfactant and water molecules were distributed between three smaller aggregates). On the other hand, the scattered starting configuration of the large system evolves into a configuration consisting of five small-sized surfactant aggregates. Since the overall composition of the large system corresponds to one average-sized aggregate observed by Eastoe et al., the expected final state in the large system is a single surfactant aggregate consisting of all the surfactant and water molecules. Thus, it can be argued that Figure 3b is much closer to the expected final state compared to Figure 3c. On the basis of these times corresponding to these configurations, it can also be stated that the aggregated starting configuration of the large system approaches the expected final state in a shorter time compared to the scattered starting configuration. In our next paper, we demonstrate that the scattered starting configuration of the large system follows a realistic trajectory and should also reach the expected final state in ~200 ns. In essence, using the aggregated starting configuration as the initial condition for the large system simply reduces the time needed to approach the expected final state thereby allowing the study of structural properties of surfactant aggregates in a reasonable amount of computer time. Thus, the structural properties of the largest aggregate in Figure 3b can be quantitatively compared to the experimental results of Eastoe et al. 

**Aggregate Size and Shape.** The general structural properties of the RM-like aggregates formed in the simulations presented above can be characterized by the shape and size of their aqueous cores. A good measure of the size is the radius of gyration ($R_g$), which is a measure of the distribution of the mass of atomic groups or molecules that constitute the aqueous core relative to its center of mass. Since the core is essentially made up of water molecules, sodium ions, and anionic headgroups, the mass of only these groups (tail groups are not considered) is considered in the estimation of $R_g$. The $R_g$ of the aqueous core (to be compared with the core radius fitted to the SANS data) can be calculated by the equation

$$R_g^2 = \sum_i m_i (r_i - r_o)^2 / \sum_i m_i$$

(6)

where $m_i$ is the mass of atom located at a radial distance $r_i$ from the center of mass of the aggregate core $r_o$. The shape of the aqueous core can be quantified using two different parameters, namely, the ratio of the largest to the smallest principal moments of inertia ($I_{\text{max}}/I_{\text{min}}$) and the eccentricity ($\eta$). The eccentricity is calculated by the equation

$$\eta = 1 - I_{\text{min}} / I_{\text{avg}}$$

(7)

where $I_{\text{avg}}$ is the average of all the three components of the principal moment of inertia. Both these parameters provide a measure of the deviation from a perfectly spherical object ($I_{\text{max}}/I_{\text{min}} = 1, \eta = 0$). The uncertainty in the values of these parameters reflects the effect of the spatial or temporal fluctuations in the shape of the aqueous core. Together these two parameters can reveal details of the actual shape (spherical, cylindrical, or disklike) of the aggregates.

Table 5 provides the structural properties of the largest aggregate in Figure 3b along with the experimental values measured by Eastoe et al. via SANS experiments. The radius of gyration ($R_g$) of the aggregate formed in this simulation study is 15.4 ± 0.3 Å. This is in reasonable agreement with the experimentally reported value of 20.5 ± 1.0 Å, given that the time for which the simulation has been carried may be considerably shorter than that required to achieve a final equilibrium state. The shape parameters for the aggregate are $I_{\text{max}}/I_{\text{min}} = 1.2 ± 0.1$ and $\eta = 0.1 ± 0.05$ (no experimental data available), which indicates that the aggregate is nearly spherical with small fluctuations. This is expected because of the high $W_0$ in this aggregate. The high value of $W_0$ provides the aggregate with an aqueous core of considerable volume (and surface area) thereby facilitating a low packing density of surfactant molecules around the aqueous core. To characterize the shape of the aggregates formed in the experimental investigation, Eastoe et al. determined the surface area of the aqueous core per surfactant molecules ($A_o$), given by the equation

$$A_o = 4\pi R_g^2 N_s$$

(8)

where $N_s$ is the aggregation number (number of surfactant molecules in the aggregate). In essence, this quantity is a measure of the packing density of the surfactant molecules in the aggregate and, thus, can be related to the shape of its aqueous core. The value of $A_o$ for the aggregate estimated from the simulation is 115 Å$^2$, which is in approximate agreement with the experimentally reported value of 140 Å$^2$.

The structural characteristics of the large aggregate in Figure 3b merit some additional discussion. First, the question must be addressed, “Is this aggregate structurally similar to the reverse micelles observed in the SANS experiments?” The only way to answer this is as follows: (a) The models used have been tested and have yielded results in reasonable agreement with the relevant experimental data in the literature, and (b) as shown in Table 5, the simulation results are in reasonable agreement with all of the experimentally measured structural properties of reverse micelles. A second issue then arises, the large aggregate in Figure 3b does not look like the common picture of a reverse micelle; a large portion of the aqueous core is directly exposed to the CO$_2$, and the surfactant molecules are not uniformly distributed on the interface. In fact, the experimental result ($A_o = 140 Å^2$) indicates that even more of the aqueous core should be exposed, and even though on average the surfactant distribution on the interface should be uniform, this does not imply that the instantaneous distribution should be

---


Table 5. Structural Properties of the Largest Aggregate Formed in the Large Simulation System (Aggregated Starting Configuration)

<table>
<thead>
<tr>
<th>Property</th>
<th>this work</th>
<th>SANS experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>916 ± 10</td>
<td></td>
</tr>
<tr>
<td>surfactant</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>$W_0$</td>
<td>35.2</td>
<td>35</td>
</tr>
<tr>
<td>$R_g$ (Å)</td>
<td>15.4 ± 0.2</td>
<td>20.5 ± 1.0</td>
</tr>
<tr>
<td>$I_{\text{max}}/I_{\text{min}}$</td>
<td>1.3 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.12 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>$A_o$ (Å$^2$)</td>
<td>115 ± 3</td>
<td>140</td>
</tr>
</tbody>
</table>

---

Table 6. Structural Properties of Surfactant Aggregates Formed in the Small System (Aggregated Starting Configuration)

<table>
<thead>
<tr>
<th></th>
<th>aggregate no. 1</th>
<th>aggregate no. 2</th>
<th>aggregate no. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>26</td>
<td>57</td>
<td>49</td>
</tr>
<tr>
<td>surfactant</td>
<td>10</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>(W_0)</td>
<td>2.6</td>
<td>6.3</td>
<td>4.4</td>
</tr>
<tr>
<td>(R_3 (\text{Å}))</td>
<td>6.2 ± 0.1</td>
<td>7.2 ± 0.2</td>
<td>6.9 ± 0.1</td>
</tr>
<tr>
<td>(l_{\text{max}}/l_{\text{min}})</td>
<td>1.8 ± 0.1</td>
<td>1.7 ± 0.3</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>(\eta)</td>
<td>0.28 ± 0.02</td>
<td>0.27 ± 0.08</td>
<td>0.13 ± 0.03</td>
</tr>
</tbody>
</table>

uniform. Perhaps the common picture of a reverse micelle should be reconsidered.

For surfactant aggregates formed in the small system (Figure 3a), the structural properties are influenced by the low water-to-surfactant ratio \((W_0 \sim 4)\) in this system. Table 6 lists the \(R_3\), \(l_{\text{max}}/l_{\text{min}}\), and \(\eta\) values for the three aggregates shown in Figure 3a. The \(R_3\) values for all the three aggregates lie within the range of 6.2–7.2 Å indicating nearly equal-sized aggregates. The \(l_{\text{max}}/l_{\text{min}}\) values for all the three aggregates are significantly greater than unity and the \(\eta\) values are significantly greater than zero. Thus, the aggregates formed are highly nonspherical compared to those formed in the large system. Clearly, the low \(W_0\) in this system results in aggregates with much smaller aqueous cores (smaller \(R_3\)) thereby resulting in significantly higher packing density of surfactant molecules. Another factor that may also contribute to the high nonsphericity in these aggregates is the ineffective dielectric screening of ionic headgroups. The simulations showed that most of the water molecules (∼94%) in the small system lie within the hydration shell of anionic headgroups and Na\(^+\) ions (in contrast to ∼62% for the large system) and thus very few water molecules were available to provide the dielectric screening of ionic charges. As a result, the interactions between ionic charges lead to the distortion of the interface. Similar results regarding the nonsphericity of aggregates with low water-to-surfactant ratio \((W_0 = 2)\) were obtained by Brown and Clarke\(^1\) for a model reversed micelle. Interestingly, the standard deviations in the values of \(l_{\text{max}}/l_{\text{min}}\) and \(\eta\) for the aggregates of Figure 3a, as shown in Table 6, are quite low. As mentioned earlier, these deviations are a measure of the fluctuations in the shape of the aggregates. The low value of these deviations suggests that the temporal fluctuations in the shape of these aggregates are quite low. The fluctuations observed in the time evolution of \(l_{\text{max}}/l_{\text{min}}\) and \(\eta\) are more prominent in aggregate no. 2 than in the other aggregates. This can be attributed to a slightly higher water-to-surfactant ratio in this particular aggregate \((W_0 \sim 6)\) compared to the other two aggregates.

**Aggregate Microstructure.** Having established that the structure of the largest aggregate formed in the large system (Figure 3a) with aggregated starting configuration is in reasonable agreement with the experimental findings, it is logical to explore the microstructure of this aggregate. Molecular simulations provide a powerful tool to obtain this information. A primary measure of the microscopic structure is the singlet distribution function (singlet radial density) profiles of the various atomic groups or molecules constituting the aggregate. As the name suggests, the singlet distribution function is a time-averaged measure of the distribution of an atom or molecule from a reference point. It is calculated by the equation

\[
\rho(r) = \langle N(r) \rangle/4\pi r^2 \Delta r
\]

where \(\langle N(r) \rangle\) is the time average of the number of an atom or molecule that is found in a shell of thickness \(\Delta r\) at a radial distance \(r\) from a reference point. The center of mass of the aqueous core represents a suitable reference point.

Figure 4 shows the microscopical details of the largest aggregate formed in the large system with aggregated starting configuration (Figure 3b). Figure 4a shows the density profile of water and CO\(_2\) (solvent) molecules. The density of water in the aqueous core is ∼1.0 g/cm\(^3\) indicating the presence of bulklike water. A broad (∼10–15 Å) interfacial region is observed, where the water density decreases while the CO\(_2\) density increases as the distance from the center of mass of the increases. The solvent density approaches its bulk density of ∼0.85 g/cm\(^3\) outside the interfacial region. Negligible penetration of the solvent molecule into the aqueous core of the aggregate is observed. This is consistent with the high ionic strength, I ∼1.5, due to the ionic headgroups and the counterions in the small aqueous core. Figure 4b plots \(\rho(r)\) as a function of the radial distance \(r\) for the various groups of the surfactant molecules. The distribution of the headgroups shows a peak at ∼17.2 Å indicating the presence of headgroups at the surface of the aqueous core. The distribution for the Na\(^+\) ions is quite similar to that for the headgroups implying that the Na\(^+\) ions also reside at the surface of the aqueous core and may be ion-paired to the anionic headgroups. The density distribution of the two tails suggests that the tails form the corona of the aggregate. The distribution of the perfluoroalkane tail is shifted slightly away from the center of mass and is an indication of its CO\(_2\)-philic behavior.

Figure 5 shows the microscopical details of the aggregates formed in the small system (Figure 3a). The figures show that the core of the aggregates is essentially made up of
water molecules and the sodium ions. The headgroups lie at the surface of the aqueous cores while the tails form the corona surrounding the cores. The nonzero radial density of the headgroups within the core ($r < 6.2$ Å) is not due to the penetration of the headgroups but simply an artifact of the highly nonspherical shape of these aggregates (Table 6). Also, the presence of numerous peaks and troughs in the radial density distribution of the sodium ions and anionic headgroups is a manifestation of the rigid structure of the aqueous core. The rigid structure of the aqueous core also manifests itself in the considerably high water density observed in Figure 5a. The radial density distributions of the two tails are quite similar except for a slight shift away from the center of mass observed for the perfluoroalkane tail. As mentioned earlier, this is due to the CO$_2$-philic nature of this tail.

**Tail Conformation.** A good measure of the CO$_2$-philic behavior of the two different tail groups is the degree to which these tails are fully extended. Figure 6 plots the fraction of torsional angles in each tail that are in trans conformation (fully stretched) as a function of time for the small system with aggregated starting configuration. Similar results were obtained for the large systems as well. The perfluoroalkane tails have an average of 90 ± 2% trans conformation compared to 74 ± 5% for the alkane tails. This implies that the perfluoroalkane tails are approximately 16% more extended than the alkane tails. Interestingly, the behavior of the two tails is quite opposite in vacuo. The perfluoroalkane tail has a trans conformation of 80% in vacuo compared to 89% for the alkane tail. Thus, in the presence of carbon dioxide as a solvent medium, the perfluoroalkane tails assume more extended conformations in vacuo, and the alkane tails assume more collapsed conformations in vacuo. This is an indication of the fact that the perfluoroalkane tails are more CO$_2$-philic than the alkane tails.

More detailed information on the spatial conformation of the two tails can be obtained by calculating the distribution of the radial position of each segment (functional group) of the tails from the CH group, as shown in Figure 7. The common feature of the two tails evident from the figure is the progressive broadening of the distribution for groups farther away from the headgroup. The broadening is relatively larger for the alkane tail compared to that for the perfluoroalkane tail because of the relative stiffness of the perfluoroalkane tail. Also, the distributions of the first two segments are the same for the two tails. The broadening is attributed to the fact that the farther away the segment is from the headgroup the more freedom it has to move. This mobility is due to the ability of torsional angles associated with these segments to switch back and forth between trans and gauche conformations. For the alkane tail the distribution of farther segments exhibits two distinct peaks reflecting a 1 to 3 ratio of gauche to trans conformation of the torsional angles associated with these segments. Thus, the perfluoroalkane tails are more extended and less mobile than the alkane tails.

**Structure of the Aqueous Core.** As shown earlier, the surfactant aggregates formed in this simulation study are characterized by the presence of aqueous cores. These aqueous cores can provide a medium for solubilizing polar...
3.7 Å is a manifestation of the fact that the Na ion correlation, as expected. The location of the first peak at 2.45 Å and a minimum at 3.2 Å. As discussed earlier, the structural characteristics of the aqueous cores is of fundamental importance in understanding the solubilization characteristics and behavior of solutes.

To get an insight into the detailed structural characteristics of the aqueous cores, Figure 8 plots the radial distribution function (rdf) for Na–Na and Na–X pairs (X denotes the anionic headgroups) in the largest aggregate shown in Figure 3b. As discussed earlier, the structural properties of this surfactant aggregate are closest to the RMs observed by Eastoe et al. via SANS experiments. Since the reference ion is located at the interface (Figure 4b), its environment is anisotropic, even at small distances. As a result, the rdf decays to zero with increasing radial distance instead of approaching unity as observed for isotropic systems. Figure 8 shows that Na–X rdf has a prominent first peak at 2.45 Å and a minimum at 3.2 Å. The secondary peaks in the rdf at 3.9 and 4.5 Å are due to the remaining two negatively charged oxygens on the headgroup. There are about ~0.75 Na+ ions within 3.2 Å of each headgroup, implying that most of the Na+ ions are ion paired to the surfactant headgroup. The Na–Na rdf shows a peak at 3.7 Å, a broad minimum at 5.0 Å, and a second peak at 6.3 Å, indicating a weaker ion–ion correlation, as expected. The location of the first peak at 3.7 Å is a manifestation of the fact that the Na+ ions are primarily located at the interfacial region. Figure 9 shows the rdf for the Na–W (W denotes water molecules) and X–W pairs. The rdf for the Na–W shows a distinct hydration shell with a maximum at 2.5 Å. A second hydration peak exists at 4.4 Å. Thus, there exist two distinct hydration shells for the Na+ ion implying a strong structuring of water molecules around the reference ion. The average number of water molecules in the first (primary) hydration ions is ~4. The rdf for the X–W shows a less prominent first peak at 4.1 Å and weak second peak at 6.0 Å. The presence of a less prominent and broad first peak in the X–W rdf may be attributed to the “correlation hole effect” and is related to the tetrahedral geometry of the surfactant headgroups. Since each headgroup has three negatively charged oxygen atoms at a fixed distance from each, a number of possibilities exist in which a particular water molecule can exist around the reference ion. As a result, the ion correlation function involves averaging over distances that involve the van der Waal diameter (σ) as well as the length scale corresponding to fixed interatomic distances. Thus, the peak in the X–W rdf is broader and lower. The average number of water molecules in the first hydration shell of the ionic headgroup is ~9, implying a higher degree of hydration of the headgroup compared to the Na+ ion because it is larger than the Na+ ion and has more charges.

An important characteristic of the water molecules in the aqueous core is the extent of their hydrogen bonding. In this study, a hydrogen bond is defined to exist if any one of the O–H bonds of a particular water molecule is collinear with an oxygen atom of a neighboring water molecule. To analyze the orientation of the water molecules, angular distribution functions (adf) are used. Figure 10 shows the adf’s of the interparticle dipole vector for water molecules belonging to the primary hydration shell of the Na+ ion and sulfate headgroup. The adf for the Na+ ion is a monotonic decrease along the angular range indicating the alignment of water in such a way that the dipole of water molecules is collinear with the Na+ ions. This is due to the strong electrostatic interaction between Na+ ion and the negatively charged oxygen atom of water molecules. The adf for the headgroup shows a peak at cos φ ~ 0.6 (φ ~ 53°) which is due to the fact that the anionic headgroup interacts with positively charged hydrogen atoms of the water molecules thereby aligning the water dipole at the angle of ~53°. This clearly shows that the strong electric fields from the Na+ ion and the anionic headgroup tend to orient the water dipole vectors in their primary hydration shells. As expected, the orientation effects are relatively stronger for the Na+ ions.
than the headgroups due to the delocalization of negative charges on the anionic headgroup. The adf’s for the interparticle–bond vector angle for water molecules within the bulklike region of the aqueous core showed a peak at \( \cos \phi \approx 0.6 \) (\( \phi \approx 53^\circ \)), Figure 11b shows the adf for the interparticle–dipole vector angle and shows two peaks, one at \( \cos \phi \approx 0.3 \) (\( \phi \approx 107^\circ \)) and the other at \( \cos \phi \approx 1 \) (\( \phi \approx 0^\circ \)). The two peaks correspond to the two bond vectors in a water molecule. The positions of the two peaks clearly indicate the collinearity of OH bond on the water molecules with the oxygen atom of the reference molecule.

Conclusions

Molecular dynamics simulations of two system sizes (small system and large system) are presented. The small system is used for exploratory calculations, while the composition and the solvent condition of the large system mimic the experimental system studied by Eastoe et al., thus enabling quantitative comparison with experiments. The simulations showed that the shape and size of the aggregate formed in the large system (aggregated starting configuration) are in reasonably good agreement with experimental values. In contrast, the properties of the aggregates formed in the small system are influenced by the low water-to-surfactant ratio in this system. The aggregates formed in the small system are quite small and considerably nonspherical compared to those formed in the large system.

In the present study, advantage was taken of the MD simulation technique to explore the microstructure of the aggregates formed. The radial density distribution of the various molecules constituting the aggregate showed that the aqueous core essentially consisted of water molecules and Na\(^+\) ions. The sulfate headgroups are primarily situated at the surface of the aqueous core. The radial density distribution of the two tails indicated the presence of a corona surrounding the aqueous core and thereby effectively shielding it from the nonpolar solvent. Negligible penetration of the solvent molecules in the aqueous core is observed. For the aggregate in the large system, the density of water near the center of the core is \( \approx 1.0 \) g/cm\(^3\), indicating the presence of bulklike water. A fairly broad (10–15 Å) interfacial region is observed. The adf’s of the water molecules in aqueous core revealed that the water molecules in the interfacial region are strongly oriented in response to the electric fields of the anionic headgroups and Na\(^+\) ions, while those near the center of the core exhibit a hydrogen-bonded network. The tail conformations indicate that the perfluoroalkane tails are more extended than the alkane tails, which is opposite to...
that observed in vacuo. Thus, the perfluoroalkane tails exhibit more CO₂-philic behavior than the alkane tails.

Acknowledgment. We are pleased to acknowledge support of this work by the Chemical and Thermal Systems Division of the National Science Foundation under Grant Number CTS-9613555 at the University of Tennessee and by the Chemical Sciences Division of the Department of Energy at Oak Ridge National Laboratory. Oak Ridge National Laboratory is managed by Lockheed Martin Energy Research Corp. for the Department of Energy under Contract Number DE-AC05-96OR2246. We are also pleased to acknowledge the allocation of computational time on the Cray T3E at the National Energy Research Scientific Computing Center at Lawrence Berkeley National Laboratory.

LA000554F