

Molecular Simulation of a Dichain Surfactant/Water/Carbon Dioxide System. 2. Self-Assembly and Aggregation Dynamics

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

We report on the aggregation dynamics of the dichain surfactant $[(C_7F_{15})(C_7H_{15})CHSO_4^-Na^+]$ + water + carbon dioxide (solvent) system described in our preceding paper. Our results indicate that the aggregation process follows a two-step mechanism: hydration of anionic headgroups and Na^+ counterions followed by aggregation of hydrated surfactant molecules. The kinetics of aggregation is consistent with the Smolouchowski theory of diffusion-limited aggregation, though on a much faster time scale compared to aggregation observed in aqueous surfactant systems. This is attributed to the fact that the intermolecular interactions responsible for aggregation in the system under investigation are electrostatic in nature and the carbon dioxide permits faster diffusion of surfactant molecules than water. The surfactant tails forming the corona of the aggregates provide steric stabilization of the aggregates thereby reducing the rate of aggregation.

Introduction

In the first paper of this series, we presented molecular dynamics simulation of a dichain surfactant $[(C_7F_{15})(C_7H_{15})CHSO_4^-Na^+]$ + water + carbon dioxide (solvent) system and estimated the structural properties (size and shape) of reversed micelle (RM)-like aggregates formed in the system. As shown by Johnston and co-workers,¹ the dichain surfactant is one of the few known CO_2 -philic surfactants that form stable RMs in CO_2 with appreciable (1.98 wt %) water-solubilizing capacity. The detailed atomistic models used in this work were intended to yield a realistic simulation, and the reasonably good agreement of the structural properties with those measured experimentally by Eastoe et al.² via small-angle neutron scattering (SANS), indicated that our surfactant model and the simulation technique are suitable for obtaining information regarding aggregation of dichain surfactant and water molecules in CO_2 . A detailed description of the potential models for all the three chemical species present in the system (dichain surfactant, water, and carbon dioxide) and the simulation methodology are provided in our earlier paper.³ In this paper, we explore the dynamics of aggregation observed in this surfactant system via molecular dynamics simulation in an effort to shed some light on the dominant interactions present in the system that are responsible for self-assembly of surfactant molecules into RM-like aggregates. Specifically, the

mechanism and kinetics of aggregation are investigated. It is expected that this study should motivate further experimental or simulation efforts in this direction.

Results and Discussion

Molecular dynamics (MD) simulations were performed on two different system sizes (referred to as the small system and the large system). The small system, as the name suggests, is a reasonably small system (~ 8300 total interaction sites) and was chosen for exploratory calculations.⁴ The molar ratio of water to surfactant molecules ($W_0 \sim 4$) in this system was essentially governed by computational simplicity. The solvent conditions used in this system correspond to $T = 310$ K and $\rho_{\text{solvent}} = 0.482$ g/cm³. On the other hand, the large system ($\sim 42\,000$ interaction sites) corresponds to the size of a single "average-sized" reversed micellar aggregate at the overall composition ($W_0 \sim 35$) studied by Eastoe et al.² The solvent conditions for this system correspond to $T = 298$ K and $\rho_{\text{solvent}} = 0.85$ g/cm³. The difference in the two systems reflects the effect of factors such as surfactant concentration, water-to-surfactant ratio, and solvent properties on surfactant aggregation.

The simulations were performed with two different starting configurations, viz., an aggregated starting configuration and a scattered starting configuration, for each of the two system sizes to test if different starting configurations had any effect on aggregation dynamics. In the aggregated starting configuration, all the water molecules were placed within a spherical core at the center of the simulation box with the surfactant molecules (in fully extended conformation) surrounding the core. In the scattered starting configuration, all the water molecules were scattered within the simulation box. These starting configurations are simply two of the infinite possible configurations and were chosen because they were easy

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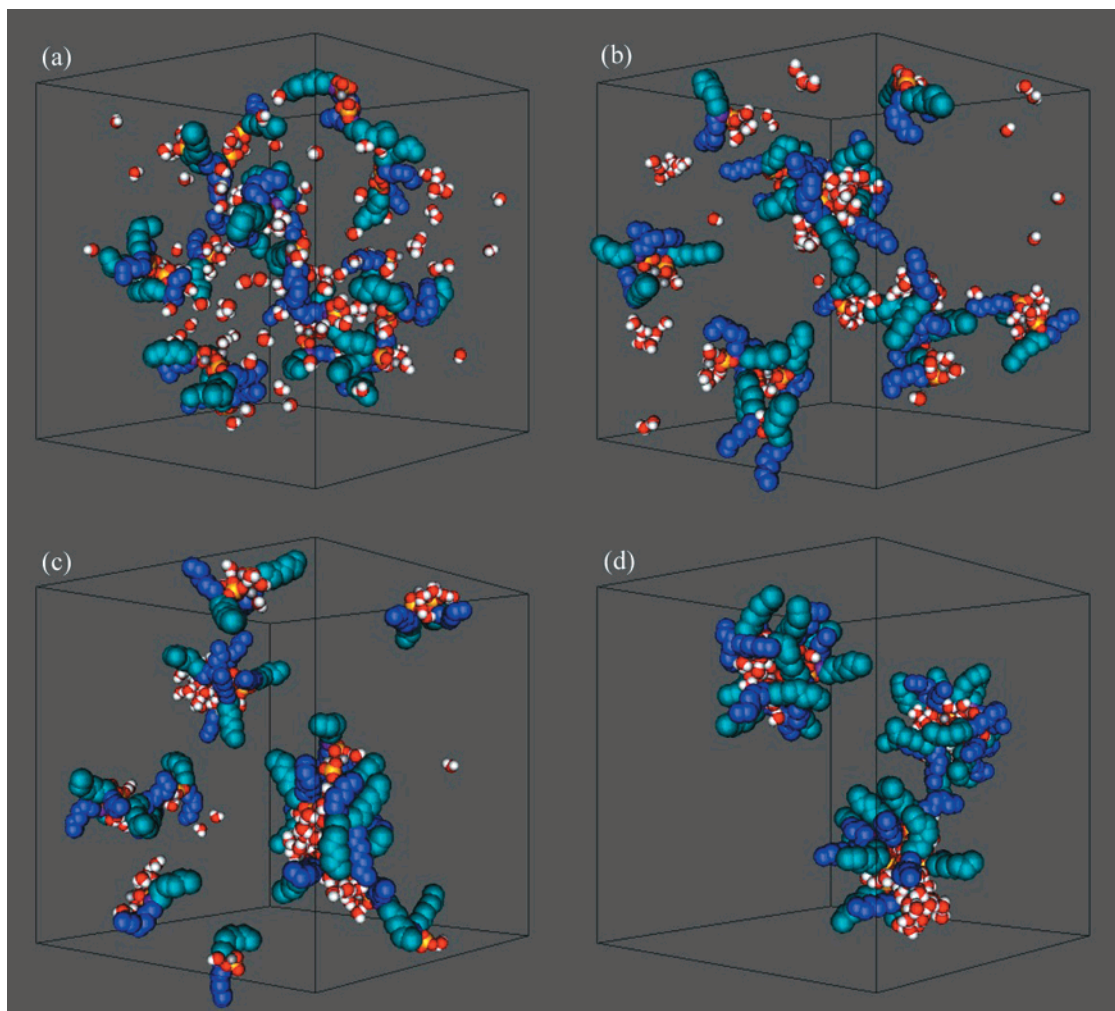


Figure 1. Snapshots of the simulation taken at (a) 5.5, (b) 44.6, (c) 148.3, and (d) 1036.0 ps showing the mechanism of surfactant aggregation for the small system with aggregated starting configuration. The color scheme of the various species is as follows: light blue for perfluoroalkane tail, dark blue for alkane tail, yellow for sulfur, red for oxygen, white for hydrogen, and gray for sodium. CO_2 molecules are not shown for visual clarity.

to generate. The details of the two different system sizes and starting configurations are provided in our previous paper.³

Aggregation Mechanism. An important aspect of the dynamics of surfactant self-assembly is the mechanism through which randomly dispersed surfactant molecules spontaneously form stable and highly organized molecular aggregates. Understanding the mechanism of surfactant aggregation is also important in identifying the interactions between component molecules that are responsible for holding the surfactant molecules together in an aggregate. The mechanism of the formation of oil-in-water micelles is quite well understood (both theoretically and experimentally) and has been used to develop mathematical models that provide an estimate of the critical micelle concentration of these systems.^{5,6} On the other hand, even standard experimental methods such as temperature and pressure jump and stopped flow techniques, which have been quite successful for aqueous surfactant systems, have not been used and may not be feasible for surfactant aggregates in nonpolar solvents because these techniques are strongly dependent on the electrical conductivity of the solvent medium. The MD

simulation technique is able to follow the molecular trajectory directly and thus can be quite useful in understanding the mechanism of surfactant aggregation in nonpolar solvents, provided the aggregation takes place on a time scale accessible to simulation.

Figure 1 shows the snapshots of the small system (with aggregated starting configuration) at the various important stages of the aggregation process highlighting the mechanism of surfactant self-assembly. Although, these snapshots correspond to the system evolution from the aggregated starting configuration, as shown later a similar mechanism was observed for the system evolution from the scattered starting configuration of this system as well. In all these snapshots the solvent molecules are intentionally not shown for reasons of visual clarity. Figure 1a shows the system configuration at 5.5 ps, which is quite early in the aggregation process. All the dichain surfactant and water molecules appear somewhat randomly dispersed within the simulation box with no evidence of surfactant aggregation. The only noticeable fact is that the Na^+ ions and the anionic surfactant molecules exist as contact ion pairs. Also, the system configuration at this instant appears to have little correlation with the aggregated starting configuration, suggesting that perhaps the starting configuration has little effect on the long-time dynamics of this system. Figure 1b shows the system configuration at 44.6 ps. At this stage a significant

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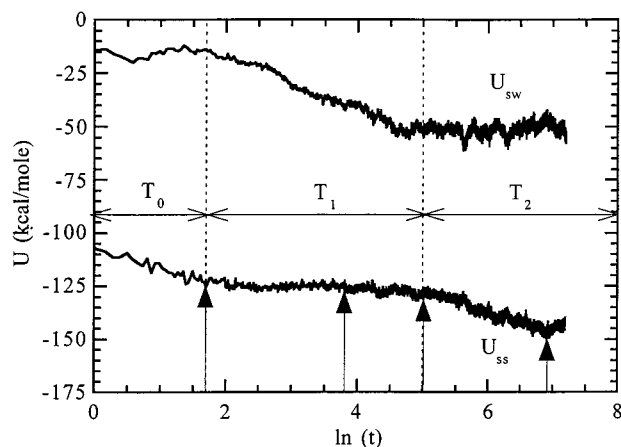


Figure 2. Time evolution of the surfactant–surfactant (U_{ss}) and surfactant–water (U_{sw}) interaction energies showing the two-step mechanism in the small system with aggregated starting configuration. Arrows indicate the times corresponding to the snapshots in Figure 1.

number of water molecules have associated themselves with the ionic species present in the system; i.e., the water molecules tend to hydrate the anionic headgroup and Na^+ counterion of the surfactant molecules. Although preliminary evidence of surfactant aggregation is noticeable by the presence of small clusters of hydrated surfactant molecules, still no appreciable aggregation is evident in the system. The system configuration in Figure 1c corresponds to 148.3 ps and shows that nearly all the water molecules have associated themselves with the surfactant molecules. Also, small surfactant aggregates have developed in the system indicating the beginning of surfactant aggregation. However, no RM-like (an aqueous core surrounded by surfactant molecules with their headgroups immersed in the aqueous core and the tails forming a corona) aggregates are noticeable in the system. However, after a sufficiently long time (1036.0 ps) the system consists of three roughly similar-sized surfactant aggregates that have the appearance of RMs, as shown in Figure 1d. The water molecules in these aggregates appear to form an aqueous core that is well shielded from the surrounding solvent by a layer of surfactant molecules with their headgroups pointing toward the aqueous core and tails extending into the solvent. This morphology of the aggregates formed closely resembles the description of RMs⁷ thereby indicating the formation of reversed micelle-like aggregates in this system.

The aggregation process described above can be further clarified by following the energetics of the system. Figure 2 shows the time evolution of surfactant–surfactant (U_{ss}) and surfactant–water (U_{sw}) interaction energies observed in the small system. The term surfactant here denotes contributions from the anionic surfactant molecule as well as the sodium counterion (cation). The figure shows two distinct steps in the evolution of U_{ss} and U_{sw} . The first step, which corresponds to the time interval $T_1 \equiv 1.7 < \ln(t) \leq 5.0$ ($5.5 < t \leq 148.3$ ps), shows a decrease in U_{sw} from a value of -20 kcal/mol to about -50 kcal/mol while U_{ss} remains nearly constant. This decrease in U_{sw} is attributed to hydration of anionic surfactant– Na^+ ion pairs by the water molecules present in the system, as shown in panels b and c of Figure 1. The value of U_{ss} remains nearly constant because there is no appreciable surfactant aggregation during this step. The time interval

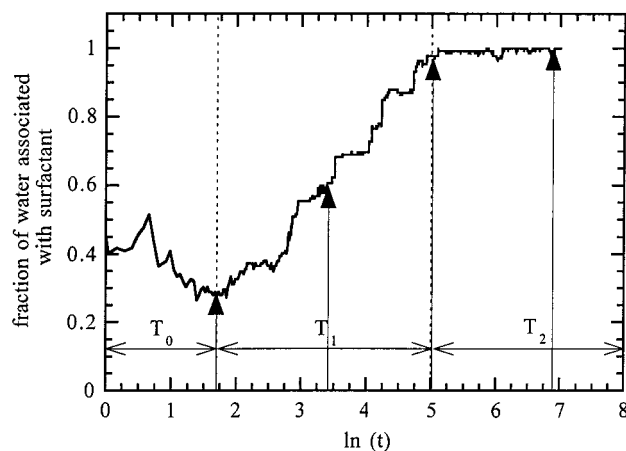


Figure 3. Time evolution of the fraction of water molecules present in the small system (aggregated starting configuration) that are associated with the surfactant molecules. Arrows indicate the times corresponding to the snapshots in Figure 1.

preceding T_1 ($T_0 \equiv \ln(t) \leq 1.7 \Rightarrow t \leq 5.5$ ps) simply involves the formation of ion pairs (Figure 1a) from the starting configuration and does not contribute to the aggregation process. During the second step of the aggregation process ($T_2 \equiv \ln(t) > 5.0 \Rightarrow t > 148.3$ ps), the trends in the evolution of U_{ss} and U_{sw} change with U_{ss} showing a gradual decrease (considering the fact that the horizontal axis in Figure 2 is logarithmic time) while U_{sw} remains nearly constant. The gradual decrease in U_{ss} is due to the intermolecular interaction of hydrated surfactant molecules resulting in the formation of surfactant aggregates. As the hydrated surfactant molecules assemble to form RM-like aggregates with their headgroups forming the core, their tail groups experience strong steric resistances to packing. As a result the surfactant molecules within the aggregate rearrange to achieve a lower energy configuration. Thus U_{ss} decreases gradually until it reaches a minimum where the interaction energy simply fluctuates around a constant value. The interaction between water and surfactant molecules remains unchanged during this step of the aggregation process since there is negligible change in the hydration characteristics due to the low W_0 (~ 4) in this system.

Thus, the aggregation process in the small system (with aggregated starting configuration) described above appears to follow a two-step aggregation mechanism. The first step (T_1) involves a rapid (within the first 150 ps) hydration of anionic headgroups and the sodium counterions that exist as ion pairs prior to hydration. There is no appreciable surfactant aggregation during this step. Figure 3, which shows a plot of the fraction of total water molecules associated with surfactant molecules versus time for this system, clearly depicts that the first step primarily involved ion hydration. The figure shows that almost all the water molecules present in the system become associated with the sodium ion–anionic surfactant ion pair during the first step and remain associated subsequently. In contrast, the second step (T_2) of the aggregation process is a much slower step involving gradual aggregation of the hydrated surfactant molecules via hydrogen bond formation³ into stable RM-like aggregates.

For the small system with scattered starting configuration, Figure 4 shows the energy profiles of U_{ss} and U_{sw} . The figure clearly shows two distinct steps (T_1 and T_2) in the aggregation process quite similar to those observed for the small system with aggregated starting configuration. The first step (T_1) involves a decrease in U_{sw} while U_{ss} remains nearly constant, while the second step (T_2)

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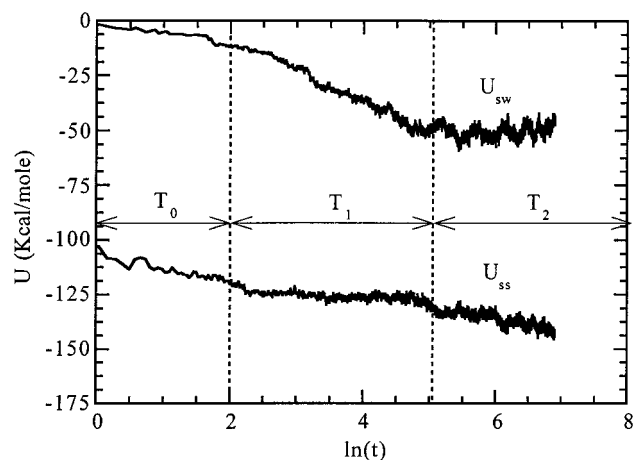


Figure 4. Time evolution of the surfactant–surfactant (U_{ss}) and surfactant–water (U_{sw}) interaction energies showing the two-step mechanism in the small system with scattered starting configuration.

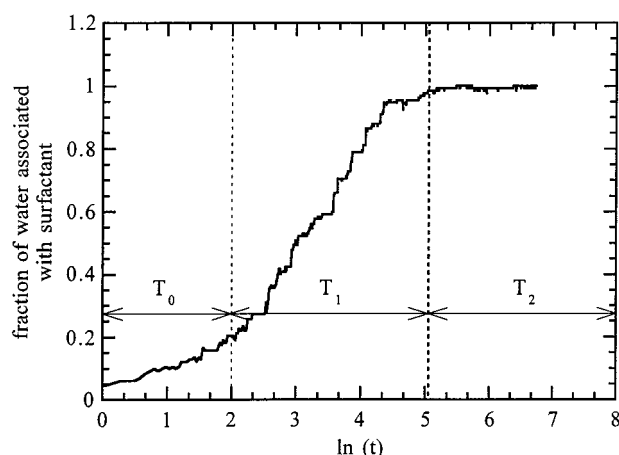


Figure 5. Time evolution of the fraction of water molecules present in the small system (scattered starting configuration) that are associated with the surfactant molecules.

involves a gradual decrease in U_{ss} while U_{sw} remains nearly constant. Thus, as stated earlier, this system also exhibits the two-step aggregation mechanism (ion hydration followed by surfactant aggregation) described earlier. Figure 5 shows the plot of the fraction of total water molecules associated with surfactant molecules versus time for this system (small system with scattered starting configuration). The figure shows that the fraction of water molecules associated with surfactant molecules approaches unity within a time interval of ~ 150 ps. Again, this is similar to that observed for the small system with aggregated starting configuration (Figure 3). Thus, it can be concluded that both the starting configurations for the small system exhibit similar aggregation mechanism leading to the formation of RM-like aggregates.

The composition of the large system is significantly different from that of the small system, with lower surfactant concentration, high water-to-surfactant molar ratio ($W_0 \sim 35$), and higher solvent density. Thus, it should be insightful to investigate if these factors play any role in the aggregation process for this system. Figures 6 and 7 show the snapshots of the evolution of the large system with aggregated and scattered starting configurations, respectively. Figure 6 shows the aggregation process observed in the large system with aggregated starting configuration at 5, 20, 100, and 1000 ps, respectively. Figure 6a shows that the starting configuration expands

almost instantaneously (~ 5 ps). However, in contrast to the small system (Figure 1a), the high water-to-surfactant molar ratio in this system prevents dispersion of surfactant and water molecules as monomers and dimers. Most of the surfactant molecules appear to be connected to each other via water bridges. The system then rapidly re-aggregates (within ~ 100 ps) to form four surfactant aggregates, as shown in Figure 6c. One large aggregate consists of most of the surfactant and water molecules while the remaining surfactant and water molecules are distributed among the three smaller aggregates. No further aggregation is observed in this system even up to ~ 1.0 ns, as shown in Figure 6d.

For the large system with scattered starting configuration, parts a–d of Figures 7 show the snapshots of the system at 100, 200, 500, and 2000 ps, respectively. During the first 200 ps (parts a and b of Figure 7), most of the surfactant molecules appear to be randomly distributed with their anionic headgroups (and Na^+ counterions) hydrated by the water molecules present in the system. Nearly, all the water molecules present in the system appear to be directly or indirectly associated with surfactant molecules within this time interval. No appreciable surfactant aggregation is evident in the system at this stage. Figure 7c shows the presence of small surfactant aggregates (mostly consisting of two to three surfactant molecules per aggregate) indicating the propensity of the system for surfactant aggregation. Finally, Figure 7d (at 2000 ps) shows the presence of five surfactant aggregates in the system.

Figure 8 shows the plot of fraction of water molecules associated with surfactant molecules for the large system with both the starting configurations. During the interval $T_1 \equiv \ln(t) \leq 6.0$ ($t \leq 403.4$ ps), the curve for the large system with scattered starting configuration shows an almost linear increase in the fraction of associated water molecules. This behavior is quite similar to those observed for the two small systems (Figures 3 and 5), implying that this system also follows the two-step aggregation mechanism (ion-hydration followed by surfactant aggregation). Further evidence of this is shown in Figure 9, which shows the energetics of this system. As expected, the evolution of U_{ss} and U_{sw} shows two distinct steps indicating the two-step aggregation process. The relatively larger time scales of aggregation steps in this large system compared to the small systems can be attributed to the higher solvent density in the large system. Figure 10 shows the mean-squared displacement (MSD) of surfactant molecules during the first 80.0 ps (during which most of the surfactant molecules are in the dispersed state) for the small system (aggregated starting configuration) and the large system (scattered starting configuration). The slope of the MSD versus time curve is a measure of the diffusivity (mobility) of the surfactant molecules. As expected, the curve for the small system has a higher slope than that for the large system, implying that the surfactant molecules in the small system have higher diffusivity than in the large system. This clearly suggests that solvent conditions also play an important role in the dynamics of surfactant aggregation in CO_2 .

As shown in Figure 8 for the large system with aggregated starting configuration, the fraction of associated water molecules initially decreases, reaches a minimum of ~ 0.8 at $\ln(t) = 1.5$ ($t = 4.5$ ps), and finally increases gradually as time increases. This behavior is not only different from the large system with scattered starting configuration but also different from the small systems. Clearly, this system does not follow the two-step aggregation mechanism; instead, the evolution of this

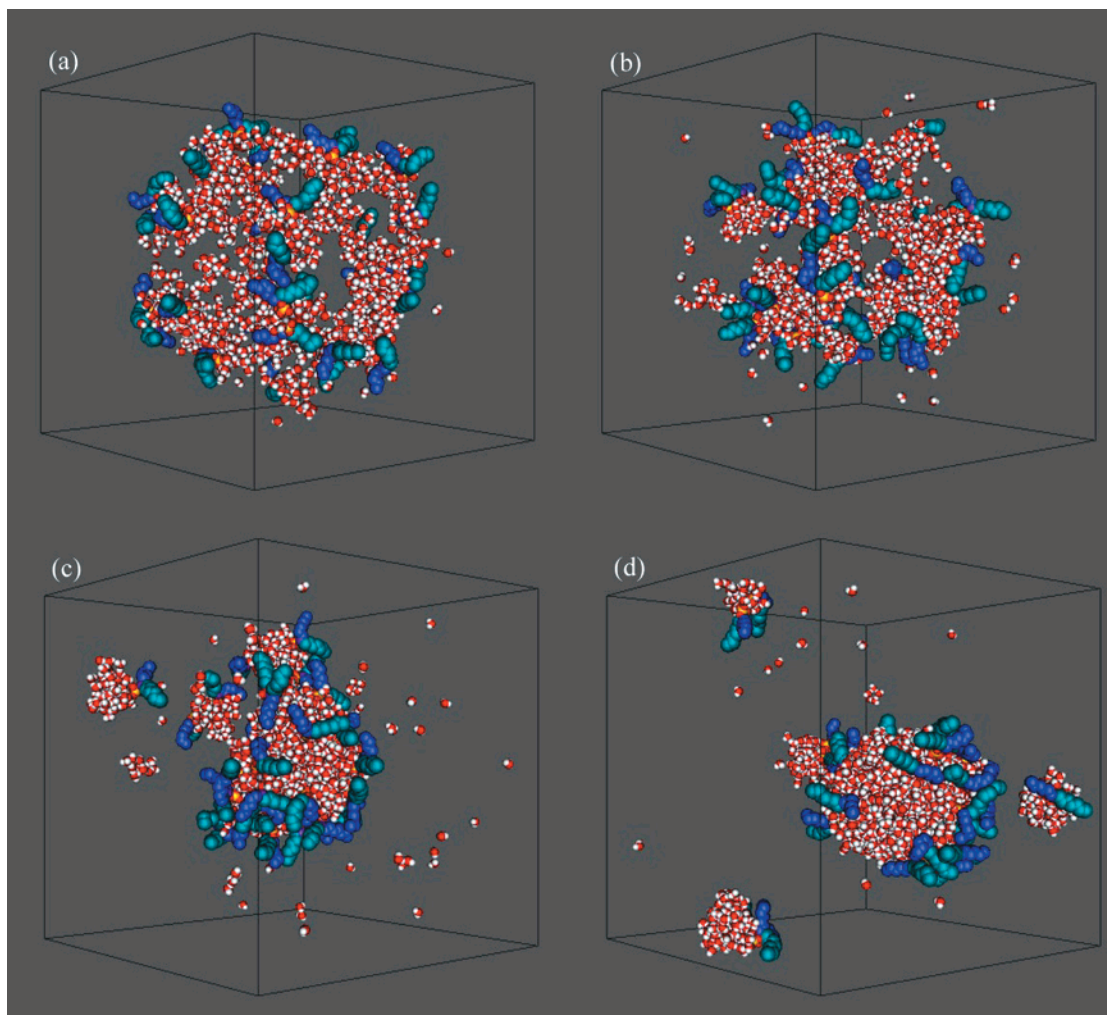


Figure 6. Snapshots of the simulation taken at (a) 5, (b) 20, (c) 100, and (d) 1000 ps showing the mechanism of surfactant aggregation for the small system with aggregated starting configuration. The color scheme of the various species is the same as that given in Figure 1.

system is influenced by its starting configuration. This is attributed to the fact that the high W_0 of this system results in the aggregated starting configuration having all the surfactant molecules already associated with the water molecules to begin with (Figure 2a of Salaniwal et al.).³ Thus, the ion-hydration step of the aggregation process is not observed with this initial configuration. Also, in contrast to the small system (Figure 1a), the high W_0 in this system results in incomplete dispersion of surfactant and water molecules, as shown in Figure 6a. This results in rapid (~ 100 ps) reaggregation of surfactant and water molecules into RM-like aggregates. Hence, the second aggregation step is also largely absent. As shown earlier,³ the structural properties of the largest aggregate (consisting of most of the surfactant and water molecules) formed in this system are in reasonable agreement with the experimental results of Eastoe et al.² This suggests that although the system fails to exhibit the expected aggregation mechanism, the aggregate formed in this system is consistent with the experimental results. Thus, it can be argued that aggregated starting configuration in the large system simply hastens the approach to the expected final state while the scattered starting configuration follows a more realistic trajectory.

On the basis of the above description, it can be concluded that the aggregation of dichain surfactant and water molecules in CO_2 essentially follows a two-step mechanism. The first step of this mechanism involves hydration

of anionic surfactant and Na^+ counterions, while the second step involves aggregation of hydrated ions to form stable surfactant aggregates. This two-step mechanism (hydration interaction and subsequent hydrogen bond formation linking the surfactant molecules) for surfactant self-assembly has been previously reported by Eicke and co-workers⁸ based on dielectric increment measurements for the system consisting of AOT surfactants (bis-2-ethylhexylsulfosuccinate) in benzene. The AOT surfactant is an anionic surfactant molecule with two tail groups, which is structurally quite similar to the dichain surfactant molecule studied in this work. Thus, it can be concluded that self-assembly of dichain surfactant in CO_2 is similar to that of other ionic surfactants (namely AOT) and is essentially governed by the electrostatic interactions between the surfactant headgroups and water molecules.

In general, the time scales of aggregation in the dichain surfactant system are on the order of 10^{-7} s, a few orders of magnitude smaller than those observed for surfactant aggregation in aqueous media which occurs over a time scale of $\sim 10^{-5}$ – 10^{-6} s.⁹ This may be attributed to the difference in the driving forces for aggregation in two solvent media. The driving forces for aggregation in the

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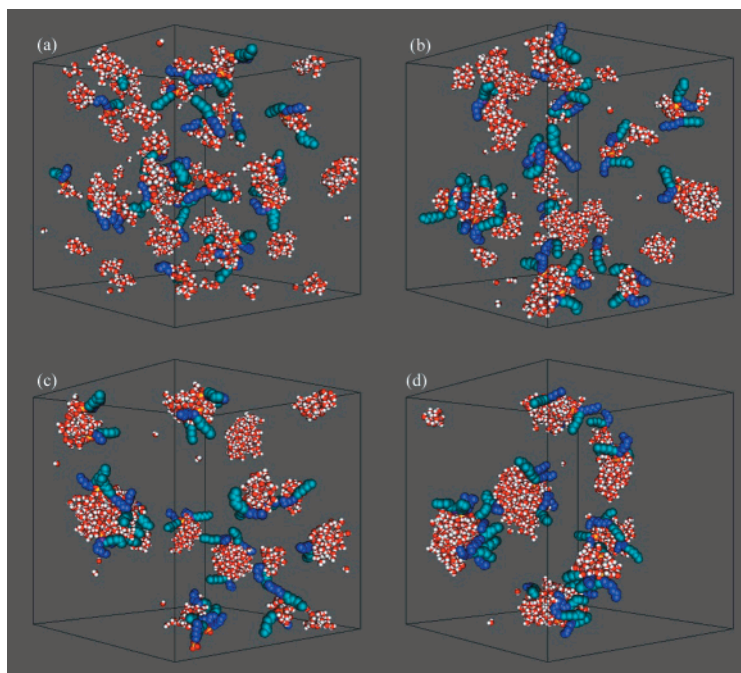


Figure 7. Snapshots of the simulation taken at (a) 100, (b) 200, (c) 500, and (d) 2000 ps showing the mechanism of surfactant aggregation for the small system with aggregated starting configuration. The color scheme of the various species is the same as that given in Figure 1.

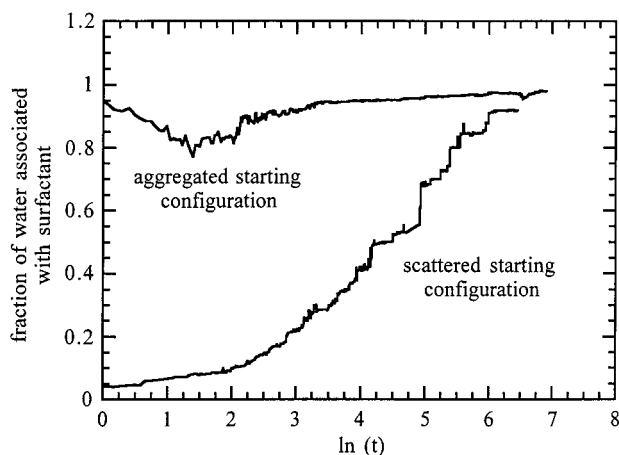


Figure 8. Time evolution of the fraction of water molecules that are associated with the surfactant molecules in the large systems (for both starting configurations).

nonpolar solvents are electrostatic (ion–ion and ion–dipole) in nature, which are much stronger and longer ranged compared to the weak and short-ranged hydrophobic interactions responsible for aggregation in aqueous surfactant systems.¹⁰ As a result, the surfactant and water molecules dispersed in a nonpolar solvent experience much stronger aggregation forces, even at low concentrations. Therefore, surfactants in nonpolar solvents exhibit more rapid aggregation dynamics compared to those observed in aqueous surfactant systems.

A direct consequence of the aggregation process is the reduced mobility of the surfactant molecules as they form RM-like aggregates. Figure 11 shows the mean-squared displacement of the surfactant molecules during the first 80.0 ps and after ~ 1.0 ns (when stable RM-like aggregates are present in the system) of the aggregation process for the small system. As expected, the surfactant molecules

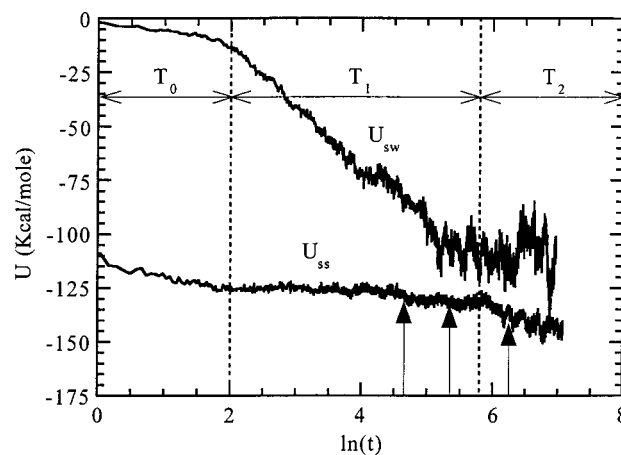


Figure 9. Time evolution of the surfactant–surfactant (U_{ss}) and surfactant–water (U_{sw}) interaction energies showing the two-step mechanism in the large system with scattered starting configuration. Arrows indicate the times corresponding to the snapshots in Figure 7.

have a significantly higher mobility (\propto slope) in the dispersed state, as the molecules are free to move about randomly in the simulation box; however, their mobility is significantly reduced (reduced slope) as these surfactant molecules are gradually incorporated into surfactant aggregates. The low mobility of surfactant molecules has also been observed by Brown et al.¹¹ for a model reversed micellar aggregate.

Another important feature observed in these simulations is the fact that the surfactant aggregates formed in the system scavenge almost all the water from the CO_2 solvent into their cores. Similar observations regarding the scavenging of water by RMs have been previously reported^{12,13} for AOT in decane and dinonylnaphthalene sulfonate in benzene systems. This has been attributed to the high ionic concentration within the aqueous cores

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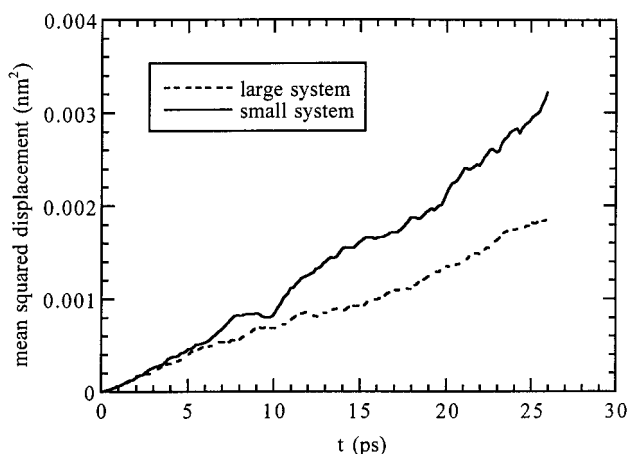


Figure 10. Mean squared displacement of the surfactant during the first 80 ps of the aggregation process for the small system (aggregated starting configuration) and the large system (scattered starting configuration).

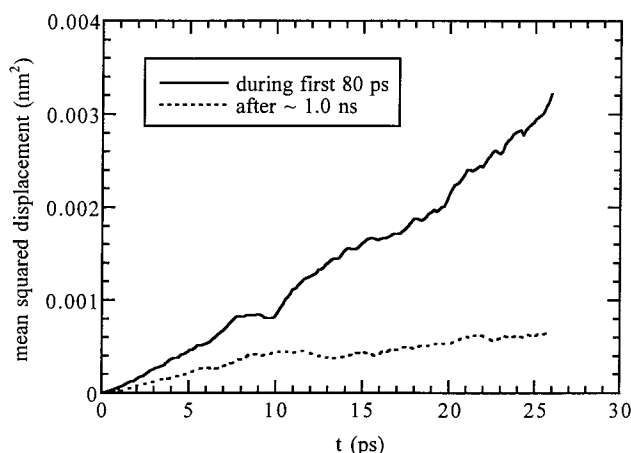


Figure 11. Mean squared displacement of the surfactant during two different time periods of the aggregation process for the small system with aggregated starting configuration.

that causes a substantial reduction in the chemical potential of the water in the core, thereby providing the driving force for the transfer of water molecules from the solvent to the core of the aggregate.

Aggregation Kinetics. The number of simulations and the number of aggregates studied are insufficient to support firm, quantitative conclusions about the aggregation kinetics of the system studied experimentally. However, the reasonable agreement in aggregate structure between simulation and experiment described in the previous paper and the general consistency in aggregation mechanism between small and large systems suggest that the results may yield a representative insight into the kinetic processes of aggregation. The quantitative analysis that follows, then, should be read for the insights it may yield and not necessarily for the quantitative relevance of its results to the experimental system.

To quantify the progress of self-assembly in a surfactant system, the parameter most often used is the rate of aggregation. In the present study, a measure of this rate is estimated by the slope of the plot of $\ln[N(t)]$ versus $\ln(t)$, where $N(t)$ represents the total number of surfactant

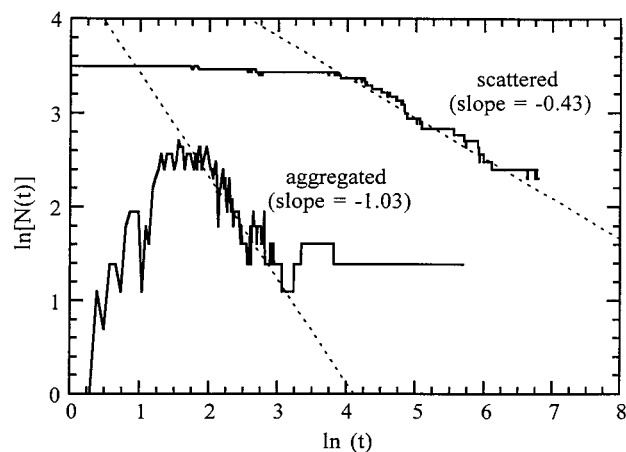


Figure 12. Time evolution of the number of aggregates during the simulation for the surfactant in the large system.

aggregates present in the system at any instant of time. Figure 12 shows the plot for the large system with both starting configurations. In this work, $N(t)$ is calculated based on an efficient cluster-counting algorithm proposed by Sevick et al.¹⁴ according to which any two particles are considered members of the same cluster if they lie within a particular distance of each other. In the present study, the atomic sites of the water molecules, the surfactant headgroups, and the Na^+ ions are considered as part of the same cluster if their center-to-center distance is ≤ 3.3 Å (sites in the tail groups are not considered). Also, according to the definition of a surfactant aggregate adopted in this study, a cluster of molecules classifies as an aggregate only if it contains at least one surfactant molecule. Thus, clusters of only water molecules are not counted in $N(t)$. Strictly speaking, surfactant aggregates with only one or two surfactant molecules are not really micellar aggregates. Instead, they simply represent (premicellar) surfactant aggregates that may eventually aggregate to form stable RM-like aggregates in the system. It should be stated that this definition of an aggregate is somewhat arbitrary and was chosen solely for the sake of convenience. Figure 12 shows that $\ln[N(t)]$ has an inverse linear dependence on $\ln(t)$ with a slope of -0.43 for the scattered starting configuration. If it is assumed that the aggregation curve follows this slope for long times, then the figure suggests that the aggregation process in this system should result in the formation of a single surfactant aggregate consistent with Eastoe et al.² in ~ 200 ns. Unfortunately, the simulation time of ~ 200 ns is beyond the practical limits of this simulation study. Although there is no reason to assume that the linearity of Figure 12 does or does not persist for long times, the run was terminated to avoid the possibility of a massive waste of computational resources.

For the aggregated starting configuration, the shape of the aggregation curve in Figure 12 shows a portion with positive slope followed by a portion with negative slope and finally a portion where $\ln[N(t)]$ remains constant. By fitting a straight line through the portion of the aggregation curve with the negative slope, a value of ~ -1.04 is obtained. The magnitude of this slope is significantly higher than that for the scattered starting configuration (~ -0.43) and is consistent with the understanding that the aggregated starting configuration is much closer to the expected final state (a single surfactant aggregate as

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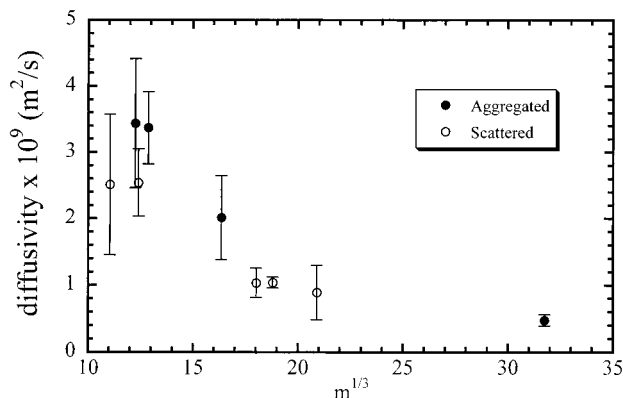


Figure 13. Variation of the diffusivity of surfactant aggregates with $m^{1/3}$ for the large system.

observed by Eastoe et al.)² than the scattered starting configuration and does not follow the two-step aggregation mechanism.

The inverse linear dependence over a limited range of time implies that the aggregation behavior can be well represented by a scaling relation of the form $N(t) \sim t^{-z}$ over this range, where z is the absolute value of the slope of the aggregation curve. This type of aggregation behavior is consistent with the Smolouchowski theory of diffusion-limited aggregation¹⁵ according to which the rate of aggregation in a system of interacting (colliding) particles is dependent on their concentration and diffusivity. The basic assumption involved in this theory is that there exists a constant probability of aggregation upon collisions between aggregates (or surfactants) i.e.

$$\frac{\text{collisions contributing to aggregation}}{\text{total collisions}} \approx \text{constant} \quad (1)$$

The applicability of the Smolouchowski's theory of aggregation to the system under consideration can be explained as follows. During the early stages of aggregation most of the water and surfactant molecules are present mainly as monomers. Thus, the concentration of the colliding particles is high as well as their diffusivity, as shown in Figure 11. As a result the frequency of collisions between the interacting particles is quite high in the early stages of the aggregation process resulting in rapid aggregation. However, as aggregation proceeds the interacting particles are no longer individual surfactant (or water) molecules, rather they are premicellar or micellar aggregates. As the result, the concentration of the aggregating particles decreases and the particles have lower diffusivity because of their larger sizes. Figure 13 shows a plot of the diffusivity of aggregates versus $m^{1/3}$, where m is the mass of the aggregate. The diffusivity was calculated from the mean squared displacement according to the Einstein relation. The quantity $m^{1/3}$ is an approximate measure of the size (diameter) of an aggregate. The figure shows that for the large system with both starting configurations the diffusivity versus $m^{1/3}$ shows a nearly linear dependence with a negative slope. Thus, it can be inferred that the Stokes–Einstein relation ($D = kT/3\pi\eta d$, where D is the diffusivity, T is the temperature, η is the viscosity of the solvent, and d is the radius of the particle) is valid for the surfactant aggregates formed in the system under investigation.

(15) Ziff, R. M.; McGrady, E. D.; Meakin, P. On the validity of Smolouchowski's equation for cluster–cluster aggregation kinetics. *J. Chem. Phys.* **1985**, *82*, 5269–5274.

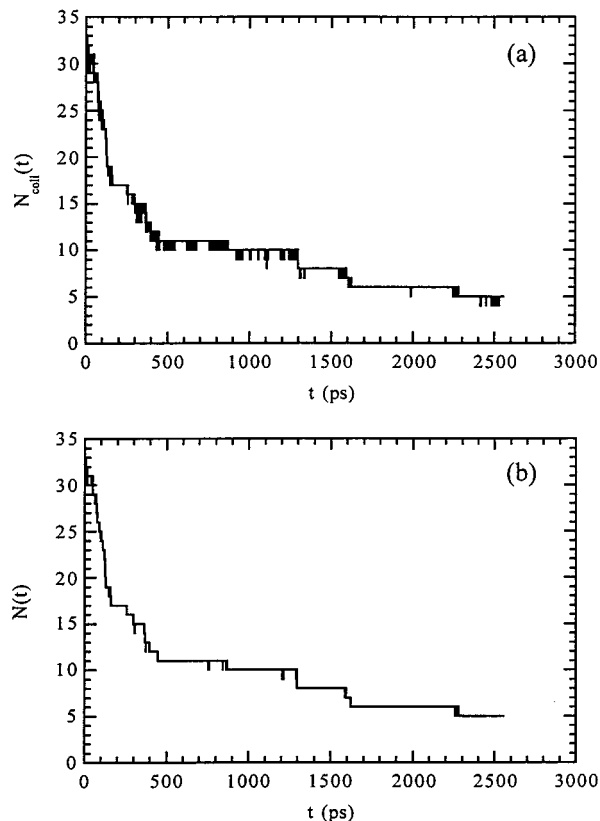


Figure 14. Time evolution of (a) number of collision aggregates and (b) number of aggregates, during the simulation for the surfactant in the large system (scattered starting configuration).

An important aspect of the aggregation behavior observed in this system is the effect of steric resistances to aggregation offered by the two tails of the dichain surfactant molecule. The steric resistances arise because of the typical structure of the aggregates formed in this system. As stated earlier, the RM-like aggregates formed in this system are characterized by the presence of an aqueous core with the surfactant headgroups at the interface, while the tails surround this aqueous core forming a corona. Since, the aqueous cores of two colliding aggregates should come in contact with each other to form a larger aggregate; successful aggregation of surfactant molecules involves overcoming the steric resistances offered by the respective coronas. As a result only a small fraction of aggregate collisions are expected to be successful in the formation of larger aggregates i.e.

$$\frac{\text{collisions contributing to aggregation}}{\text{total collisions}} \ll 1 \quad (2)$$

This is shown in parts a and b of Figure 14, which plots the time evolution of $N_{\text{coll}}(t)$ and $N(t)$, respectively, where $N_{\text{coll}}(t)$ represents the number of “collision aggregates” at any instant of time. As the name suggests, a “collision aggregate” is an aggregate formed when any two parts of surfactant molecules or aggregates (tail groups included) satisfy the distance criteria (≤ 3.3 Å) mentioned earlier. The figures show that $N_{\text{coll}}(t)$ varies much more frequently with time than $N(t)$ showing many instances of $N_{\text{coll}}(t)$ decreasing by one unit and then immediately returning to its previous value (a collision that did not result in aggregation), indicating that numerous collisions between surfactant molecules or aggregates are required before coalescence occurs. To further investigate the effect of steric resistance offered by the surfactant tails, a simula-

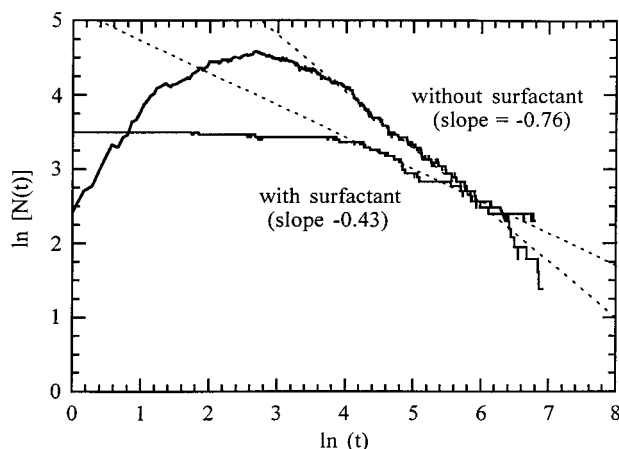


Figure 15. Time evolution of the number of aggregates during the simulation for the large system (scattered starting configuration) with and without surfactant.

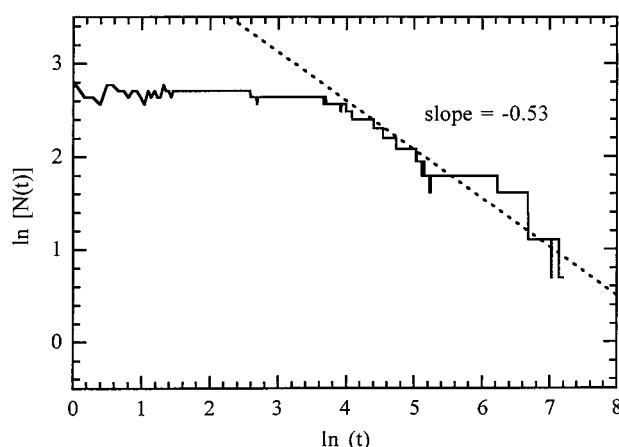


Figure 16. Time evolution of the number of aggregates during the simulation for the surfactant (small system with aggregated starting configuration).

tion of the large system was performed (scattered starting configuration) without the surfactant molecules (water in CO₂ only). Figure 15 shows the coalescence curve for this system along with that for the system with surfactants. The initial increase in N for the water–CO₂ system is a result of the arbitrary initial configuration and is of no significance. The slope of the coalescence curve for the system without surfactants is ~ -0.76 , which is higher than that for the system with surfactants (slope ~ -0.43). Clearly, the lack of steric resistances in the system without surfactant results in an enhanced rate of coalescence in comparison to the system with surfactants. Further analysis of the water–CO₂ system and its comparison with the surfactant system could provide some additional insight into the influence of surfactant molecules on the structure and dynamics of the aggregates and will be probed in continuing work.

Figure 16 shows the aggregation curve for the small system with aggregated starting configuration. As expected, the shape of the curve is similar to that for the large system with scattered starting configuration, however with a slope of -0.53 . The steeper slope for the small system is consistent with the fact that the rate of

aggregation in the small system is enhanced by the high surfactant concentration and the supercritical state of the solvent. A caveat to this conclusion is that the difference between the slopes is small and may be statistically insignificant. As shown by Ziff et al.¹⁵ and Meakin et al.,¹⁶ the quantitative estimates of the slopes can be improved by carrying out numerous ($\sim 10^3$) independent simulations, but this would be vastly impractical in a study like the present one.

Conclusions

The simulations reported in this paper involve MD simulation of a dichain surfactant [(C₇F₁₅)(C₇H₁₅)-CHSO₄⁻Na⁺] + water + carbon dioxide system. The results of the simulation reveal a rapid and spontaneous self-assembly of dichain surfactant and water molecules into aggregates that resemble RMs in appearance. The aggregation process follows a two-step mechanism, similar to those observed experimentally for similar surfactants in other nonpolar solvents. The first step of aggregation involves rapid (~ 150 – 300 ps) hydration of anionic head-groups and Na⁺ ions, while the (slower) second step involves gradual (~ 1 – 2 ns) aggregation of hydrated surfactant molecules into RM-like aggregates. In the large system the second step is further slowed due to higher solvent density in this system. In general, the time scales of the aggregation steps observed in these simulations are a few orders of magnitude smaller than those normally observed in aqueous surfactant systems because of the stronger and long-ranged electrostatic interactions (compared to hydrophobic interactions) responsible for aggregation in the system under investigation.

The progress of surfactant aggregation in these simulations is estimated by the time evolution of the number of surfactant aggregates present in the system, $N(t)$. The results show that when $\ln[N(t)]$ is plotted versus $\ln(t)$, an inverse linear dependence is observed, indicating that the evolution of the number of aggregates is well represented by a power-law function of the form $N(t) \sim t^{-z}$, where z is a measure of the rate of aggregation. This aggregation is consistent with Smolouchowski's theory of diffusion-limited aggregation. The simulations also reveal that in addition to diffusional characteristics, steric resistances also play an important role in determining the rate of aggregation. These resistances are due to the surfactant tails and come into play because of the typical structure of the aggregates formed. The simulations showed that for successful aggregation, the aqueous cores of two colliding aggregates should come into contact with each other. The probability of core contact is reduced considerably by steric resistances of the surfactant tails resulting in slower aggregation.

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.

(16) Meakin, P.; Vicsek, T.; Family, F. Dynamic cluster-size distribution in cluster–cluster aggregation: Effect of cluster diffusivity. *Phys. Rev.* **1985**, *31*, 564–569.