Surfactant Aggregation at a Hydrophobic Surface

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Molecular dynamics (MD) simulations have been carried out to investigate the morphology of monolayers of the cationic surfactant cetyltrimethylammonium bromide ($C_{16}TAB$) at the interface between a hydrophobic substrate and an aqueous solution. The simulation system consisted of two flat hydrophobic surfaces separated by a distance of 70 Å along z (direction normal to the interface). Initially, one surface was covered with a uniform monolayer of 94 erect surfactant molecules, with surface area of 45 Å^2/molecule. The other surface was covered with two hemicylindrical aggregates, each containing 64 surfactant molecules. A 1 ns trajectory was then generated at constant volume and temperature ($T = 300$ K). The hemicylinder aggregates relaxed to a semielliptical rather than semicircular cross section but were observed to be otherwise stable during the simulation run. The monolayer arrangement was, however, unstable and evolved into hemicylindrical type aggregates. The present simulation provides support for the interpretation of recent atomic force microscopy (AFM) measurements, which claim $C_{16}TAB$ forms stable hemicylindrical aggregates at the interface between an aqueous solution and hydrophobic surfaces, such as graphite.

1. Introduction

Amphiphilic molecules are known to self-assemble in aqueous solution into a variety of liquid crystalline structures, such as quasi-spherical micelles, rod-shaped micelles, bilayers, etc.[1−8] While structural probes have been used to explore the behavior of surfactants films at the air/water interface,[9−11] it is not clear how surfactant self-assembly is influenced by the presence of a solid boundary surface. A proper understanding of the aggregation of surfactants at a solid−liquid interface is a key issue toward modeling industrial processes, such as detergency, crude oil refining, purification, lubrication, etc.[12,13]

Different experimental techniques such as adsorption isotherms,[14] neutron reflection,[15] fluorescence probe analysis,[16] and surface force apparatus (SFA)[17] have been used over last three decades to study the adsorption process of surfactants at liquid−solid interfaces. Most of these techniques provide a quantitative measure of surfactant adsorption, but little information has been obtained about the topology of the adsorbed surfactants. Recently, Manne and co-workers[18−24] have reported a series of atomic force microscopy (AFM) measurements to study the organization of a variety of surfactants, both ionic as well as nonionic, adsorbed from aqueous solution on different types of solid surfaces. As far as the adsorption of ionic surfactants on hydrophobic surfaces is concerned, there is a general agreement between all these experiments provided that the concentration of the surfactant is low (well below the cmc). It is clear that, at low concentration, the hydrophobic interaction between the surfactant molecules and the surface plays the dominant role and an adsorbed layer is formed with the surfactant tails oriented

parallel to the plane of the substrate.[22] However, there has been sharp difference in opinion about the structure of the aggregates at high surfactant concentration. It has been proposed earlier by Zettlemoyer[23] that with increasing surfactant density the orientation of the molecules changes from parallel to perpendicular resulting in the formation of monolayers, bilayers, etc., at the surface. Recent AFM measurements of cationic surfactants containing trimethylammonium headgroups ($C_{16}TAB$ and $C_{14}TAB$), adsorbed on graphite at a concentration above the cmc,[18,19] showed a high degree of curvature and periodicity in the images, which were not consistent with earlier models of flat monolayers and bilayers. The AFM images of CTABs on graphite showed straight parallel stripes separated by approximately twice the surfactant chain length, which is consistent with hemicylindrical type of aggregates. It has also been observed that the same surfactant forms different types of patterns on different surfaces, indicating that the nature of the surface has a strong influence in determining the topology of the aggregates. For example, AFM images indicated formation of full cylinders of $C_{14}TAB$ on mica and spherical micelles on amorphous silica.[19] It was also predicted that nonionic surfactants such as poly(oxyethylene)dodecyl ether ($C_{12}E_n$) form similar hemicylindrical patterns on a graphite interface,[21] whereas different surfactants seemed to form different types of aggregates (either full or half cylinders) on metal surfaces such as gold.[20] These experiments, therefore, predict that surfactants form "novel" structures at the water−solid interfaces that are quite similar to those in bulk aqueous solution.

Computer simulation studies can provide a microscopic level picture of such phenomena. But, because of the long time scale involved, no computer simulation study has attempted so far to study interfacial aggregation using models of sufficient detail. In recent years, with the increasing power of computers and

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TABLE 1: 9-3 Lennard-Jones Potential Parameters for Surface–Site Interactions

site	CH$_3$	CH$_2$	N(CH$_3$)	CH$_3$(N)	CH$_2$(N)	O$_{H_2O}$	Br
σ_{9-3}, Å	2.856	2.856	2.516	2.871	2.871	2.474	3.203
ϵ_{9-3}, K	281.538	180.526	243.523	224.904	224.904	232.860	177.188

the development of sophisticated simulation methodologies[24] it has become possible to study self-assembly of surfactants using realistic models,[25] which until recently was considered to be practically impossible. In this Letter, we employ molecular dynamics (MD) simulation to study the aggregation of the cationic surfactant cetyltrimethylammonium bromide (C$_{16}$TAB) at an interface between water and a flat hydrophobic substrate. Anticipating our results, we will see that a monolayer arrangement of C$_{16}$TAB on a hydrophobic surface is unstable and transforms into a parallel hemicylindrical type of aggregates. This observation supports the model proposed from AFM studies, namely, that CTABs self-assemble into hemicylinders on hydrophobic surfaces such as graphite.[18,19]

2. System Setup and Simulation Details

There are different ways that one can set up the system with proper periodic boundary conditions while minimizing any artifact on the structure of either the surfactants or water due to the presence of the interface.[26–28] A commonly used practice in simulations of monolayers of surfactant/water systems is to take a thick slab of aqueous solution with the top and bottom covered with surfactant monolayers, the thickness of the slab being large enough so that the two monolayers have practically no influence on each other.[27,29] Another difficulty in simulating such systems is the proper handling of the long-range electrostatic interactions. In principle, one could employ a "two-dimensional" Ewald summation method such as that developed by Hautman and Klein.[30] But an efficient use of this method requires that the dimension in the nonperiodic direction be much smaller than the periodic directions, a criterion that is not satisfied in the present work. Therefore, we decided to use a system confined between two flat hydrophobic surfaces separated by a distance of 70 Å along z (direction normal to the interfaces) and employ three-dimensional periodic boundary conditions and an Ewald summation with the largest cell dimension along z. This ensures that the interactions between periodic images are insignificant in the z-direction. The overall simulation box dimension was 92 × 46 × 200 Å^3.

At the begining of the simulation, the surface at $z = +35$ Å (surface I) was covered with a uniform monolayer of 94 surfactant ions, with a low surface area per molecule of 45 Å^2.[31] The other surface at $z = -35$ Å (surface II) was covered with two hemicylindrical aggregates, each containing 64 surfactant ions. The two hemicylinders were then arranged parallel to each other such that their principal axes of symmetry were parallel to the y-axis and spaced 46 Å apart in the x-direction (approximately twice the length of the surfactant chain) in accordance with the AFM measurements.[18,19] A slab of water approximately 25 Å thick was then introduced between the two surfaces so that the headgroups are in contact with water. The thickness of water slab was sufficient to ensure that there is a thin layer of bulk solution near the center of the simulation cell. Then, 222 of the water molecules were randomly replaced by bromide ions. The resulting system contained 222 surfactant cations, 222 bromide counterions, and 4372 water molecules.

The intermolecular potential model was based on pairwise additive site–site Lennard-Jones and electrostatic contributions. We used a flexible water model with the intermolecular Lennard-Jones potential parameters and the charges of the

SPC/E water model[32] and the intramolecular parameters from the work of Toukan and Rahman.[33] The CH$_3$ and CH$_2$ groups of the surfactants were modeled as united atoms (i.e., these groups were represented by single interaction sites). The hydrocarbon chains were made flexible by including bond stretching and bending interactions, and the potential parameters were taken from the literature.[34] The tetramethylammonium ions were modeled using the CHARMM PARAM19 parameters,[35] with modified Lennard-Jones parameters and charges taken from the work of Jorgensen and Gao.[36] The parameters for bromide ions were taken from the work of Lybrand et al.[37] The Lennard-Jones cross interactions were calculated using Lorentz–Berthelot combination rules.[38] The interactions with the hydrophobic surface were modeled using 9–3 Lennard-Jones potentials similar to those used earlier in surface studies,[28,39,40] which are appropriate for molecular interactions with a homogeneous solid surface.[41] The water–wall interaction parameters were taken from the work of Lee et al.[39] These parameters were used to express the surfactant–wall interactions, so that they are consistent with information already implicit in the respective intermolecular Lennard-Jones parameters. The different surface–site interaction parameters are listed in Table 1.

To reduce the computational expense, the initial equilibration was carried out with a system half the size, containing one, instead of two, hemicylinders on surface II. The number of surfactants in the monolayer (surface I) and water molecules and bromide ions were adjusted accordingly. This smaller system was heated, from 100 to 300 K, with an increment of 10 K at every 10 ps interval. This system was then simulated for 250 ps at 300 K. At this point, the system size was doubled. After a short relaxation period (~10 ps), the run was continued at 300 K for a total duration of 1 ns. The calculations were performed in NVT ($T = 300$ K) ensemble using the Nosé–Hoover chain thermostat extended system canonical dynamics method.[42] The use of the recently developed reversible multiple time step algorithm RESPA[24] allowed us to use a time step of 6 fs. This was achieved with a three-stage force decomposition into intramolecular and short range, and long-range intermolecular forces. The minimum image convention[38] was employed to calculate both the van der Waals interactions and the real part of the Ewald sum with spherical truncations of 7 Å for the short-range and 10 Å for the long-range part of the RESPA decomposition. A Nosé–Hoover chain length of 3 with thermostat frequency of 1 ps was assigned to every atom.[43]

3. Results and Discussion

Figure 1 shows snapshots (cross-sectional view perpendicular to the interface) of the configuration of the system near the beginning (a) and at the end (b) of the simulation run. The most significant feature of these snapshots is the change in the topology of the surfactant aggregate from the initial uniform monolayer of erect molecules on surface I (shown at the top of the figure) into a curved hemicylindrical type of aggregate, indicating that the monolayer arrangement of C$_{16}$TAB on hydrophobic surface is unstable. On the other hand, although the cross section of the hemicylindrical aggregates on surface II (shown at the bottom of the figure) relaxed to semielliptical rather than semicircular, both aggregates remained stable over the nanosecond time scale of the simulation run. These
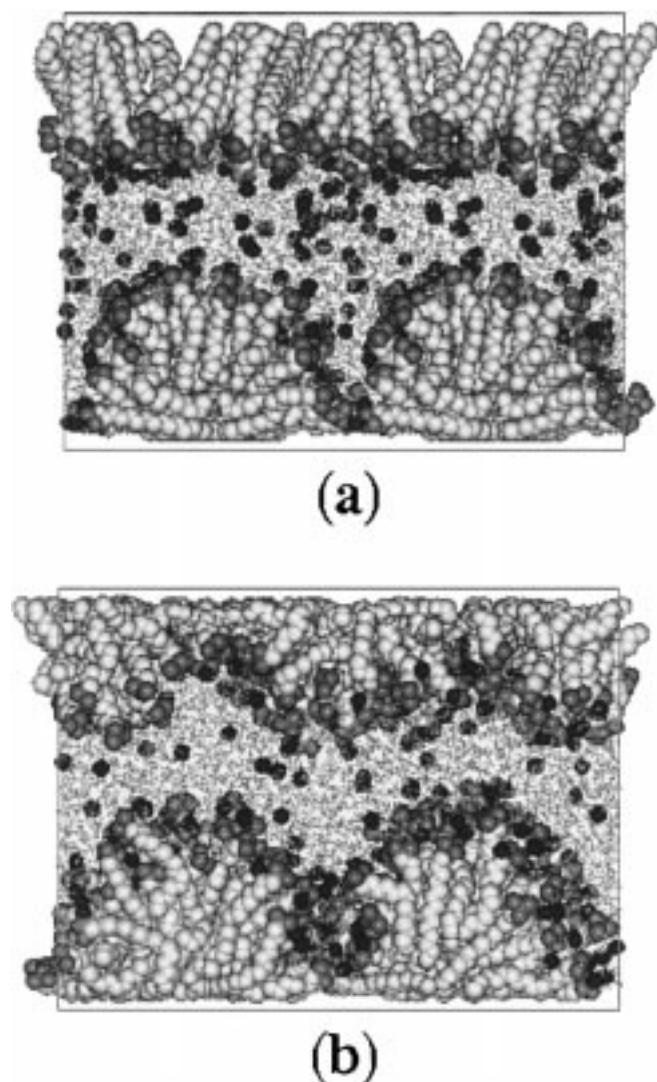
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(a)

(b)

Figure 1. Snapshots of the configuration of the system near the beginning (a) and at the end (b) of the simulation run. Surfaces I and II, separated by a distance of 70 Å, are at the top and bottom of the figures, respectively. Surface I was initially covered with a uniform monolayer of erect molecules and surface II with two hemicylindrical aggregates (see text). The headgroup nitrogen and methyl groups, hydrocarbon chains, and bromide counterions are drawn as colored spheres, while the water molecules are drawn as sticks.

observations contradict the early models of adsorption of ionic surfactants at the hydrophobic surface–aqueous solution interface,[23,44] which proposed that the surfactant ions should be oriented perpendicular to the interface. The present findings are consistent with the interpretation of recent atomic force microscopy (AFM) measurements, which suggested formation of hemicylindrical aggregates of CTABs at the interface between a hydrophobic substrate (such as graphite) and water.[18,19]

The time evolution of the number density profiles of different components of the system in the direction normal to the interface (z) are displayed in Figure 2. The general features of the plot are in reasonable agreement with the standard picture of surfactant aggregation at an aqueous interface.[29] Note the increase of hydrocarbon density with time near surface I ($z = +35$ Å, the monolayer side). Eventually, this profile becomes almost similar to that at surface II ($z = -35$ Å, the hemicylinder side), reflecting the transformation of a rather unstable monolayer arrangement to more stable hemicylinders (see Figure 1b). The density profiles are not symmetric about the center of the system (e.g., the larger width of the hydrocarbon density
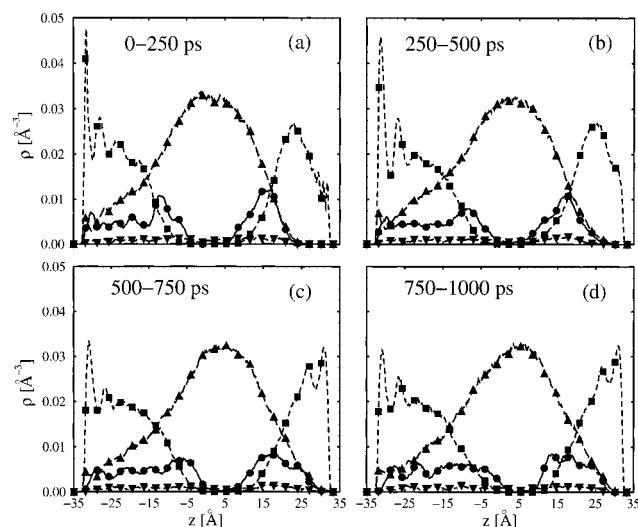

Figure 2. Time evolution of the number density profiles of the headgroups (circles), hydrocarbon chains (squares), water molecules (triangles), and bromide counterions (inverted triangles), in the direction (z) normal to the interface. Note the development of the hydrocarbon density on surface I ($z = +35$ Å).

extending from surface II) owing to the higher initial density of surfactants on this surface. The nonzero density of the cationic headgroups, water, and bromide counterions near surface II ($z = -35$ Å) arise because of the hemicylindrical arrangement of the surfactant aggregates (recall Figure 1) and the presence of a narrow strip of water between them. These densities were zero near surface I ($z = +35$ Å) at the beginning because of the presence of a uniform monolayer at this surface. As the monolayer evolves into hemicylinders, narrow gaps form allowing water molecules, headgroups, and counterions to approach the surface, as is clear from the figure.

Figure 3a,b shows the final image of the surfactants on surface II as viewed from the top and bottom of the surface. Note that the two hemicylinders remain roughly parallel to each other, as they were initially, with a roughly uniform distribution of the headgroups (Figure 3a). A view from the bottom (Figure 3b) shows how a layer of the alkane chains remains flat and extended on the surface. The hydrocarbon core of the hemicylinder is shielded from the aqueous solution by the cationic headgroups. Images of the surfactants on surface I are shown in Figure 3c,d. The striking feature of these images is their close similarity to those on the other surface (surface II) despite the fact that the density of surfactants was lower on surface I and the initial arrangement was different (monolayer). During the simulation, the monolayer has evolved into roughly parallel stripes, separated by about twice the length of the surfactant cation (approximately 42 Å). This is in excellent agreement with the topology of $C_{16}TAB$ at the graphite–water interface as observed in AFM measurements.[18] Clearly, there is a hydrocarbon core formed at the center of these roughly hemicylindrical stripes (Figure 3d) shielded from rest of the solution by the headgroups (Figure 3c). There is essentially no difference between the pattern developed on surface I, which was initially covered by a monolayer, with that on surface II, which actually had two hemicylinders adsorbed on it. These patterns provide a microscopic level support to the model proposed by Manne and Gaub[19] concerning the aggregation of the cationic surfactant CTAB from aqueous solution on a hydrophobic substrate, such as graphite.

In summary, though numerous attempts have been made over last three decades to characterize the behavior of surfactants
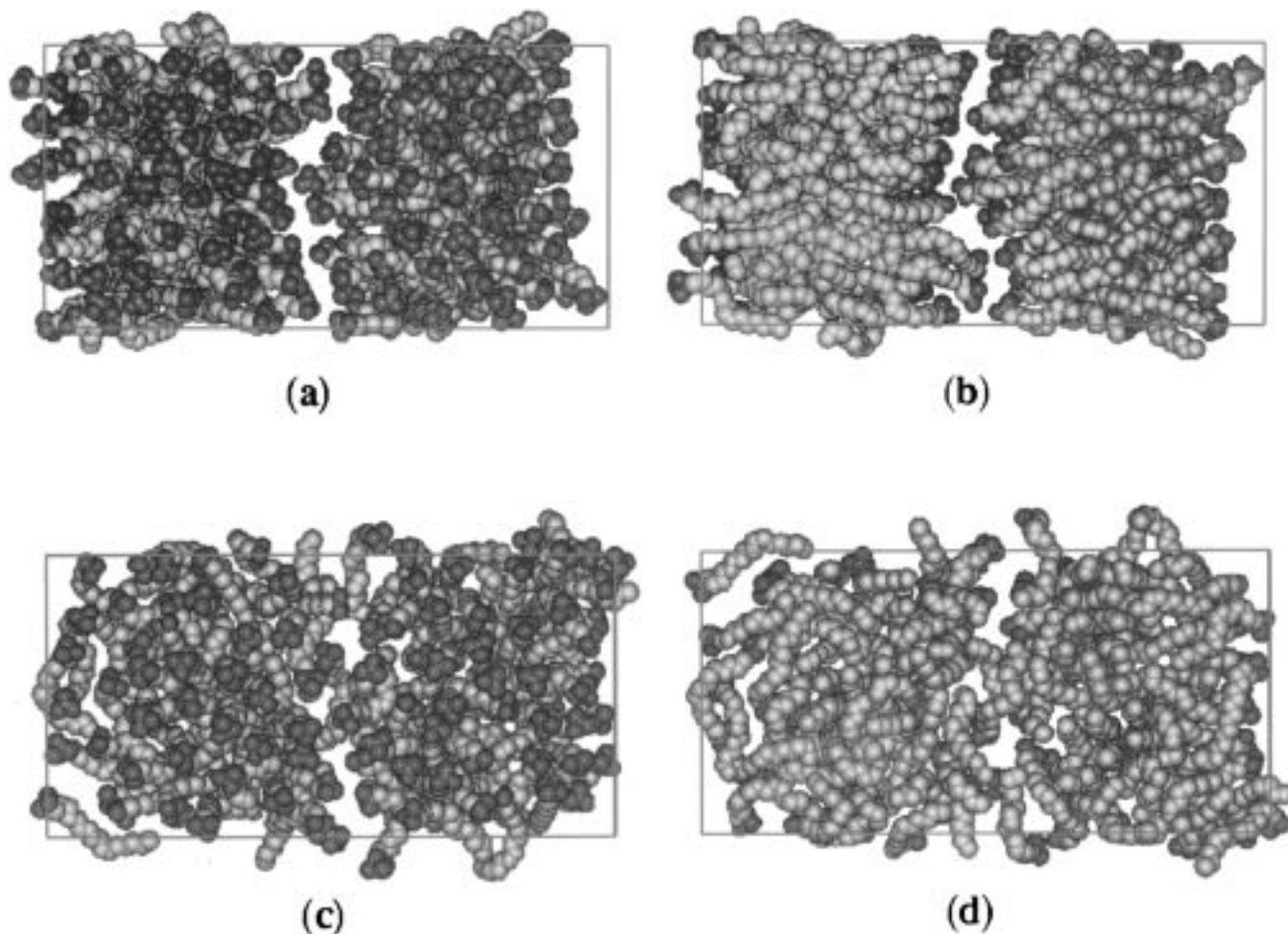
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Figure 3. Images of the final configuration of the surfactants as viewed from above (a, c) and underneath (b, d) the surfaces. Surface II was initially covered with two hemicylinders and surface I with a uniform monolayer. The coloring scheme is same as for Figure 1.

on surfaces, our understanding is still poor and there is not much consensus over this matter. In the recent past AFM measurements over a wide variety of surfactants at the solid−liquid interfaces suggested formation of different types of "novel" aggregates, whose structures depended both on the nature of the interface and on the type of the surfactant. Recent advances in simulation methodology prompted us to attempt to study the interfacial aggregation of surfactants in order to resolve the existing conflicts between different models proposed on the basis of different experiments. In particular, using an atomistic model we carried out a long MD simulation that spanned over 1 ns duration, to study the aggregation of a common cationic surfactant, $C_{16}TAB$, at the interface between a flat hydrophobic surface and water. The most remarkable finding from our simulation was the slow evolution of a uniform erect monolayer arrangement of the surfactants into hemicylindrical type aggregates, which were organized in parallel stripes on the surface. As observed in AFM images, the periodicity is about twice the surfactant chain length. Therefore, our atomistic simulation gives support to the claim that an aqueous solution of cationic surfactants such as $C_{16}TAB$ can form stable hemicylinders, rather than monolayers on a hydrophobic surface. Additional studies are necessary for better understanding of the surfactant self-assembly process. These include exploring the use of "real" surfaces, altering the *z*-separation between the surfaces I and II, and varying the initial arrangements of the surfactants.

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