Computer Studies on the Effects of Long Chain Alcohols on Sodium Dodecyl Sulfate (SDS) Molecules in SDS/Dodecanol and SDS/Hexadecanol Monolayers at the Air/Water Interface

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Molecular dynamics simulations of sodium dodecyl sulfate (SDS)/dodecanol and SDS/hexadecanol monolayers at the air/water interface were investigated where the monolayer mixtures were prepared by two different configurations. In the first configuration, all of the dodecanol (or hexadecanol) molecules were placed together and also the SDS molecules were placed together in the surface area. In the second configuration, the dodecanol (or hexadecanol) molecules were uniformly distributed with the SDS molecules, forming a homogeneous mixture. The results showed that the alcohol tails are more ordered and thicker than the SDS tails in monolayers where the alcohol molecules are close to each other and separated from the SDS. However, the reverse trend is observed in monolayers where the SDS and alcohol molecules are well mixed; that is, the alcohol tails seem to have less order. Studies of how the SDS tails are affected by the presence of long chain alcohols are also discussed. Basically, by increasing the alcohol chain length, the order and the thickness of the SDS tails increased when those molecules were placed all together in a region of the surface area. When both surfactants were well mixed, the order and thickness of the SDS chains decreased as the alcohol chain length increased. Comparisons of the present results with actual experiments of similar systems were performed, and they showed similar tendencies.

1. Introduction

The behavior of surfactant molecules at different interfaces has been extensively studied for the last years not only for the scientific interest but also for the applicability in the industry. Therefore, several experimental techniques have been conducted to study systems of one kind of a surfactant molecule such as fluorescence, resonance Raman scattering, neutron reflection, second harmonic generation, vibrational sum-frequency spectroscopy, Brewster angle microscopy, atomic force microscopy, and time-resolved quasi-elastic laser.[1−6] However, most of the interesting problems, with applications in commercial products, consist of a mixture of surfactant molecules which have richer properties than individual ones. For instance, nonionic surfactants are generally used together with anionic surfactants as active ingredients in products such as shampoo, hand dish washing liquids, and washing powders. Therefore, it is not a surprise to find also several studies in the literature on surfactant mixtures using several experimental techniques such as calorimetry, X-ray, neutron scattering, and surface tension measurements among others.[7−16]

Of particular interest is the study of the structure and composition of the surfactant mixtures such as the extension of the chains or the thickness of the monolayer mixture at interfaces.[14−16] For instance, using neutron reflection experiments,[16] some authors have performed studies to investigate differences in the position of the components of the sodium dodecyl sulfate/dodecanol mixture at the air/water interface. Other experiments of anionic/nonionic mixtures have described an increasing change in position of the nonionic molecules at the interface relative to the solvent with increasing solubility

of the nonionic molecules.[15] Moreover, surface tension experiments have shown that mixtures with similar hydrophobic tail lengths but different headgroups may show different properties which can affect the structure of the monolayer at the interface. Those results suggest that the behavior of different surfactants at interfaces might be attributed to the different polar groups of the molecules.

However, the role of the chain length of the molecules in surfactant mixtures is discussed only briefly by some authors. For instance, in the early experimental work of Patist et al.,[17] they present studies of sodium dodecyl sulfate with long chain alcohols, showing how the compatibility between the chain length plays an important role in the stabilization of sodium dodecyl sulfate (SDS) micelles.

On the other hand, due to the substantial increase in the computational power, computer simulations became an important tool for the study of such complex interfacial systems.[18−26] Using this computational methodology, it is possible to extract more information about dynamical and structural properties from a molecular level which sometimes are not easy to obtain from real experiments.

Therefore, in the present work, we performed a series of computational experiments to investigate the effects of the length of the tails of different surfactants on the structure of monolayer mixtures. In particular, we focused on monolayer mixtures of anionic/nonionic surfactants; moreover, we investigated how two different nonionic molecules which have the same headgroups but different tail lengths affect the behavior of the anionic surfactant or in general the role of the chains of the nonpolar surfactants in the position of the surfactant molecules at the interface. Particularly, the SDS/dodecanol mixture was chosen, since dodecanol seems to be the most common contaminant of SDS caused by the synthesis which makes this system interesting

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to study. The other monolayer was the SDS/hexadecanol mixture. In fact, previous works of SDS/dodecanol monolayers have been published in the literature and some experimental[8−11,15,16] and computational[26] data are available. Although those results were performed at a low concentration of the nonionic surfactant in this work, we also wanted to study the effects of having a significantly higher nonionic surfactant concentration in the mixture. Therefore, when it was possible, some comparisons of actual experiments with the present results were conducted.

2. Computational Method and Model

Simulations of two anionic/nonionic monolayer mixtures were performed using the molecular dynamics (MD) method. For the anionic surfactant, we used the well-known SDS molecule model composed of a headgroup (SO_4) attached to a hydrocarbon chain of 12 united carbon atoms. For the first nonionic surfactant, we used the dodecanol molecule which has the same tail length as the SDS molecule, and for the second nonionic surfactant, we used the hexadecanol which has the same hydroxyl group of dodecanol but a longer tail. For both nonionic molecules, the same united carbon model of the SDS for the hydrocarbon tails was employed and the simulation parameters for the SDS and dodecanol were the same as those used in previous works[18,26] (the hexadecanol molecule has basically the same structure as the dodecanol with a longer hydrocarbon tail), whereas for water molecules we used the SPC (simple point charge) model.

All simulations were carried out using the Berendsen pressure algorithm with a time step of 0.002 ps using the DL-POLY package.[27] However, for these simulations, the calculation of the pressure was modified to change the $X-Y$ box dimensions only to have a $NP_{xy}T$ algorithm. Bond lengths were constrained using the SHAKE algorithm with a tolerance of 10^{-4}, and all simulations were performed at $T = 296$ K. The long range electrostatic potential was handled with the particle mesh Ewald method with a precision of 10^{-4}, and the van der Waals interactions were cut off at 10 Å.

The initial configuration was constructed from 81 SDS molecules in an all-trans configuration placed perpendicular to the $X-Y$ plane in a square area. Then, 49 SDS molecules were replaced with 49 dodecanol molecules also in an all-trans configuration, leaving only 32 SDS molecules. The number of dodecanol molecules was selected in order to have nearly 50−50 % in molecular weight.

To investigate how the different surfactant molecules arrange in mixtures of actual experiments, two mixtures of the same system were prepared. In the first case, all of the dodecanol molecules were placed together and also all of the SDS molecules were placed close to each other, and we called this monolayer MND1. This system would help us to see if a probable configuration of the monolayer is to form domains of surfactants as some experiments suggest. For the second system, the dodecanol molecules were placed randomly at the interface, avoiding the case of having together two molecules of the same surfactant close in the mixture; that is, SDS and dodecanol were well mixed. We called the monolayer MND2.

The same procedure was conducted for the SDS/hexadecanol monolayer mixture; that is, a system with 49 hexadecanol and 32 SDS molecules was prepared in the two different forms as described above. The first monolayer (MNH1) has all of the hexadecanol molecules placed together, whereas in the second monolayer (MNH2) the hexadecanol molecules were placed uniformly in the surface area well mixed with the SDS molecules.
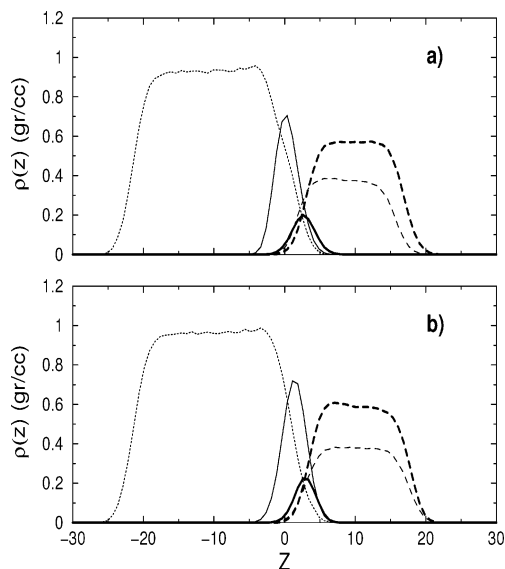

Figure 1. Density profiles for the SDS/dodecanol monolayer at the air/water interface. The top picture corresponds to the MND1 monolayer, whereas the bottom picture represents the MND2 monolayer. Water is depicted by the dotted line, the SDS headgroups by the light solid line, and the SDS tails by the light dashed line. The dodecanol polar groups are given by the dark solid line and the dodecanol tails by the dark dashed line.

In all of the simulations, a water/vapor interface was imposed at one opposite end of the simulation box ($z < 0$), whereas, in the other side of the box ($z > 0$) where the tails were located, there was a large empty space; that is, the z-dimension of the box was set to 150 Å.

Once each monolayer was prepared, 1185 water molecules were added surrounding the headgroups and 32 sodium anions (Na^+) were randomly inserted in the interfacial region. Periodic boundary conditions were applied, and with the headgroup of the molecules initially pinned, a short MD simulation at $T = 296$ K was performed. Then, each system was equilibrated for 100 ps, and finally, they were run up to 6.5 ns, collecting data for the last 2 ns for analysis. The configurational energy was monitored as a function of time to determine when the system reached equilibrium.

3. Results

In this section, we present the calculations performed on the monolayer mixtures. Analysis of the structure and orientation of the two distinct surfactant molecules in the different monolayers is discussed.

3.1. Density Profile. In Figures 1 and 2, the profiles of the monolayer mixtures are shown, that is, the z-dependent density profiles for water, headgroups, and hydrocarbon tails of each surfactant molecule. To make the plots clear, the distributions of the SDS and the dodecanol (and the hexadecanol) molecules were plotted separately. The SDS headgroup density profile includes the SO_4^- group and the Na^+ counterion. In Figure 1, the plots for MND1 (Figure 1a) and MND2 (Figure 1b) are shown with the headgroup and tail profiles plotted separately. An interesting feature is the flat region of the chain profiles, since in previous simulations of the same system at low dodecanol concentration it did not appear, suggesting that both surfactant tails want to be more straight at high nonionic concentration. In both figures, basically the same trend is depicted; however, the SDS tail profile seems to be slightly wider in MND2 than that in MND1, indicating that the SDS
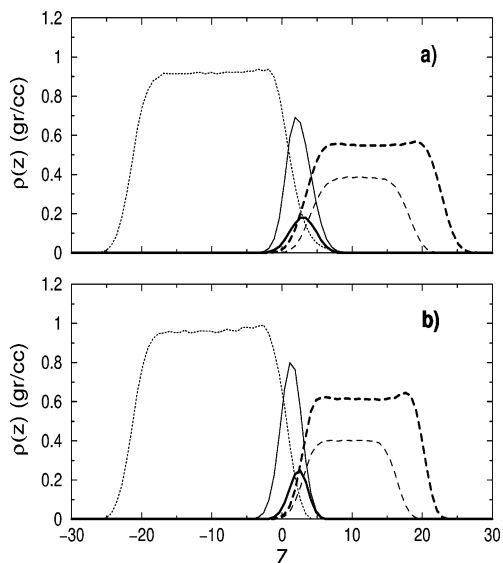
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Figure 2. Density profiles for the SDS/hexadecanol monolayer at the air/water interface. The top picture corresponds to the MNH1 monolayer, whereas the bottom picture represents the MNH2 monolayer. Water is depicted by the dotted line, the SDS headgroups by the light solid line, and the SDS tails by the light dashed line. The hexadecanol polar groups are given by the dark solid line and the hexadecanol tails by the dark dashed line.

chains are thicker when SDS molecules are randomly placed with dodecanol than when they are all together.

To measure the width of the tail profiles, the following function was fitted

$$\Omega = \Omega_0\left(\tanh\left(\frac{Z - Z_1}{w}\right) - \tanh\left(\frac{Z - Z_2}{w}\right)\right) \qquad (1)$$

Here, Z is the position of the different molecule groups along the interface and the difference $\Delta Z = Z_1 - Z_2$ gives us the width of the profile. In this case, both tail density profiles in MND2 are slightly wider than those in MND1. For the SDS tail profiles, $\Delta Z = 13.8$ Å in MND1 and $\Delta Z = 14.6$ Å in MND2, whereas, for the dodecanol tail profiles, $\Delta Z = 13.9$ Å in MND1 and $\Delta Z = 14.3$ Å in MND2. Those results indicate that the tails of both surfactants are more bent in MND1 than in MND2, as stated before.

The analysis of the headgroups was calculated by fitting a Gaussian of the profiles using the following distribution:

$$\rho = \rho_0 \exp\left(\frac{-4(Z - Z_0)^2}{\sigma^2}\right) \qquad (2)$$

For MND1, the SDS headgroup profile is centered at $Z_0 = 0.26$ Å, whereas the dodecanol headgroup is at $Z_0 = 2.68$ Å; that is, there is a distance difference of about $\Delta = 2.42$ Å. For MND2, the headgroup profiles are located at $Z_0 = 1.40$ Å and $Z_0 = 2.93$ Å for the SDS and dodecanol profiles, respectively. Here, the distance difference is $\Delta = 1.53$ Å. Although the distance difference (Δ) for MND1 and MND2 monolayers is small, we clearly observe that the SDS headgroups are deeper into the solvent region; that is, the SDS heads seem to penetrate more into the water phase than the dodecanol headgroups. The same tendency has been observed in neutron reflection experiments of the same system at low dodecanol concentration, where it was observed that the SDS volume fraction profile was displaced toward the water from the dodecanol profile.[15,16]
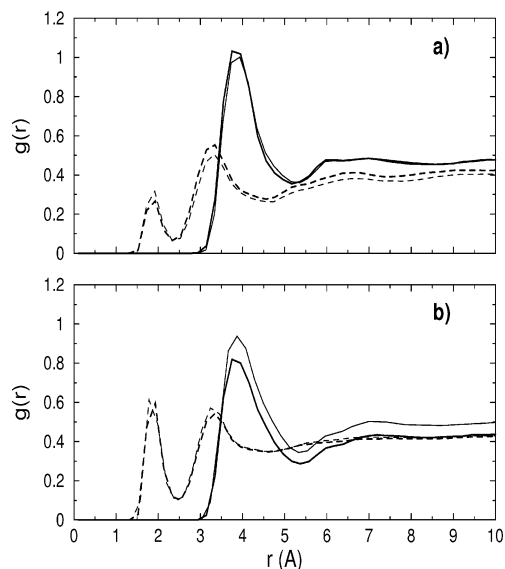

Figure 3. Radial distribution functions, $g(r)$, in the SDS/alcohol mixtures. Panel a shows $g(r)$ when both surfactants are well mixed, MND2 and MNH2. The light solid and dashed lines represent $g_{sd2}(r_{S-OW})$ and $g_{hd2}(r_{H-OW})$, respectively, for the MND2 (SDS/dodecanol) monolayer. The dark solid and dashed lines represent $g_{sh2}(r_{S-OW})$ and $g_{hh2}(r_{H-OW})$, respectively, for the MNH2 (SDS/hexadodecanol) monolayer. In panel b, the $g(r)$'s of MND1 (SDS/dodecanol) and MNH1 (SDS/hexadecanol) when both surfactants (SDS and dodecanol or hexadecanol) are separated are shown. The light solid and dashed lines represent $g_{sd1}(r_{S-OW})$ and $g_{hd1}(r_{H-OW})$, respectively, for the MND1 monolayer. The dark solid and dashed lines represent $g_{sh1}(r_{S-OW})$ and $g_{hh1}(r_{H-OW})$, respectively, for the MNH1 monolayer. The meaning of each $g(r)$ is given in the text.

In Figure 2, the SDS/hexadecanol monolayers are shown. In this case, the headgroup profiles of the SDS and hexadecanol are wider when the molecules are grouped (Figure 2a) with molecules of the same kind than when the molecules are well mixed (Figure 2b). The positions of the headgroup profiles are $Z_0 = 2.33$ Å for SDS and $Z_0 = 2.99$ Å for hexadecanol in MNH1, with the distance difference being $\Delta = 0.66$ Å. For MNH2, the headgroup profiles are located at $Z_0 = 1.31$ Å and $Z_0 = 2.36$ Å for the SDS and hexadecanol profiles, respectively, and the distance difference is $\Delta = 1.06$ Å. It seems that, once again, the SDS headgroups are deeper into the solvent than the hexadecanol headgroups. On the other hand, while the tail density profiles of the SDS molecules look alike in both monolayers (MNH1 and MNH2), the hexadecanol tail profile in MNH1 is slightly wider than that in MNH2, suggesting that those chains are straighter in MNH1 than in MNH2. For this monolayer, we have $\Delta Z = 14.0$ Å in MNH1 and $\Delta Z = 13.45$ Å in MNH2 for the SDS tail profiles, respectively, whereas, for the hexadecanol profiles, $\Delta Z = 19.7$ Å in MNH1 and $\Delta Z = 17.7$ Å in MNH2.

3.2. Surfactant Structure at the Interface. How the headgroups arrange at the interface can be analyzed in terms of the pair distribution function, $g(r)$. The $g(r)$ value can give us information about the water molecules located at the interface and their distribution around the headgroups of the different surfactants in the mixtures. Since we are interested in how the SDS tails change with different cosurfactants which have the same headgroups but different tails, we plotted in the same panel the case when the anionic molecule interacts either with dodecanol or with hexadecanol. In Figure 3a, the $g(r)$ values for MND2 and MNH2 are shown. $g_{sd2}(r_{S-OW})$ is the pair distribution function of the sulfur atoms, of the SDS in MND2, with the water oxygens, and $g_{sh2}(r_{S-OW})$ is the one of the sulfur

atoms, of the SDS in MNH2, with the water oxygens. $g_{hd2}(r_{H-OW})$ is the pair distribution function of the hydrogen atoms, of the OH headgroup in dodecanol−MND2, with the water oxygens, and $g_{hh2}(r_{H-OW})$ is the distribution function of the hydrogen atoms, in hexadecanol−MNH2, with the water oxygens. Since the dodecanol and hexadecanol headgroups are identical, basically the same plots are depicted for $g_{sd2}(r_{S-OW})$ and $g_{sh2}(r_{S-OW})$ and also for $g_{hd2}(r_{H-OW})$ and $g_{hh2}(r_{H-OW})$. The first peak of $g_{sd2}(r_{S-OW})$ and $g_{sh2}(r_{S-OW})$ is around 4.0 Å where the first solvation shell is defined which is a similar value found in previous studies of SDS at the water/CCl4 interface[18] and in previous simulations of SDS/dodecanol at low dodecanol concentration.[26]

The $g(r)$'s indicate a large number of water molecules around the SDS headgroups; however, hydrogen bonds between the OH groups of dodecanol (or hexadecanol) with the oxygens of water make these two groups get closer, as $g_{hd2}(r_{H-OW})$ and $g_{hh2}(r_{H-OW})$ indicate. Moreover, $g_{hd2}(r_{H-OW})$ and $g_{hh2}(r_{H-OW})$ present more structure with two well-defined peaks around 1.9 and 3.1 Å where the first and the second solvation shells are defined.

When the dodecanol (or hexadecanol) molecules were placed all close together in the monolayer MND1 (or MNH1), we also observed similar shapes of $g(r)$ (Figure 3b) to those in Figure 3a. Although the peaks are nearly at the same position as those in Figure 3a, their heights are slightly different. The same notation is used for the $g(r)$'s; however, these functions are given for MND1 and MNH1, as stated by the subnumber 1, instead of 2, in the $g(r)$'s. $g_{sd1}(r_{S-OW})$ and $g_{sh1}(r_{S-OW})$ have small peaks compared with $g_{sd2}(r_{S-OW})$ and $g_{sh2}(r_{S-OW})$ ($g_{sh1}(r_{S-OW})$ is even smaller than $g_{sh2}(r_{S-OW})$). It seems that there are less waters around SDS, in MND1 and MNH1, compared with MND2 and MNH2.

The first peak of $g_{hd1}(r_{H-OW})$ and $g_{hh1}(r_{H-OW})$ becomes higher, having nearly the same height as the second peak, suggesting that there are more water molecules close to the hydrogens in dodecanol (or hexadecanol) in these monolayers. It seems that these monolayer configurations help the water molecules approach more the dodecanol (or hexadecanol) headgroups, leaving less water close to the SDS headgroups.

It is worth mentioning that the monolayers are inhomogeneous and nonsymmetric systems in the z-direction, since the water is placed only in the negative z-axis. Therefore, this is the reason the $g(r)$'s of the surfactant−water do not go to unity and they seem to take lower values as compared to typical $g(r)$'s of bulk systems.

In Figure 4, the plots of the number of water molecules around the sulfur atoms in SDS and the hydrogens in the OH headgroups of dodecanol (or hexadecanol) are shown. From those pictures, we observed how the number of water molecules around the dodecanol (hexadecanol) headgroups (0−2.5 Å) increased in the first solvation shell in MND1 (Figure 4c) and MNH1 (Figure 4d) monolayers compared with those in MND2 (Figure 4a) and MNH2 (Figure 4b), respectively. At the same time, it seems that water molecules around the SDS headgroups (0−5.2 Å) decreased in the first solvation shell in MND1 (Figure 4c) and MNH1 (Figure 4d) compared with those in MND2 (Figure 4a) and MNH2 (Figure 4b), respectively. These results are complementary to those observed in the above $g(r)$ calculations.

To understand how water responds to the charged surface, the orientation of the water molecules next to the surfactants at the interface was also analyzed. Then, the probability distribution $P(\cos\theta)$ was calculated, where θ is the angle of the vector going
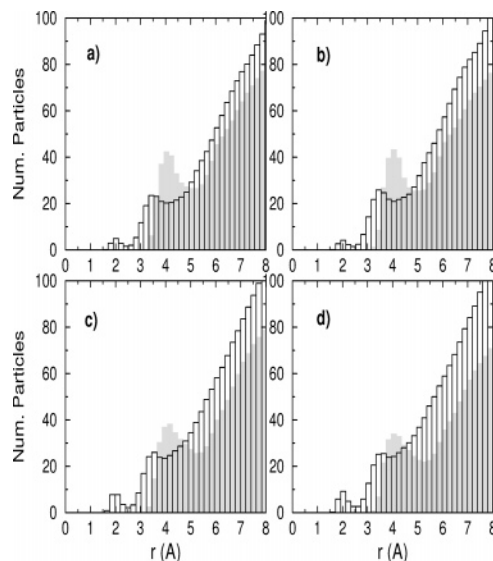

Figure 4. Number of water molecules (as a function of the distance) around the sulfur atoms in the SDS headgroups (grey histogram) and around the hydrogens in the dodecanol (or hexadecanol) headgroups (black line histogram). Monolayers where both surfactants are well mixed (a) MND2 (SDS/dodecanol) and (b) MNH2 (SDS/hexadecanol). Monolayers where both surfactants are separated (c) MND1 (SDS/dodecanol) and (d) MNH1 (SDS/hexadecanol). The meaning of the distance r is the same as that in the $g(r)$ functions of Figure 3.

from one water oxygen to the sulfur atom of a SDS molecule (or hydrogen, OH, of the dodecanol or hexadecanol) and the water dipole vector of the same water molecule. Moreover, $P(\cos\theta)$ was determined in the two solvation shells around the headgroups defined by the distance of the first and second peaks in $g(r_{S-OW})$ and $g(r_{H-OW})$ for each monolayer mixture.

All of the distributions in monolayers MND1, MND2, MNH1, and MNH2 are shown in Figure 5. The top and bottom figures are the $P(\cos\theta)$ of SDS (left) and dodecanol or hexadecanol (right) for (MND2 and MNH2) and (MND1 and MNH1), respectively.

Regardless of the monolayer, the water distributions around the SDS headgroups look alike (Figure 5a and c). In the first solvation shell, the water dipole has the highest probability, pointing approximately 51° away from the water-oxygen-to-sulfur vector (solid lines in Figure 5a and c). This value is in agreement with previous simulations of SDS at the water/oil interface.[18,25] Since for these systems there is not a well-defined second solvation shell (see $g(r)$ in Figure 3), we calculated an angular distribution of water molecules in the interval from 5.2 to 7.8 Å in $g_{sd2}(r_{S-OW})$, $g_{hd2}(r_{H-OW})$, $g_{sd1}(r_{S-OW})$, and $g_{sh1}(r_{S-OW})$. The apparent large distance of the second solvation shell (to observe water molecules) from the SDS headgroups and the flat region of $g(r)$ at that distance suggest that the water molecules have nearly a bulk behavior. Therefore, the water molecules should be more uniformly oriented around the SDS headgroups, as indicated by the lack of structure in the orientational distributions (dashed lines) of Figure 5a and c.

On the other hand, the angular distribution of water around the dodecanol (or hexadecanol) headgroups presents different shapes with respect to those next to the SDS molecules. In this case, the water dipoles, in the first solvation shell, point to the opposite directions of the oxygen(H20)-to-hydrogen(OH) vector (solid lines in Figure 5b and d), whereas, in the second solvation shell, the water dipoles were more uniformly oriented (dashed lines in Figure 5b and d), although there is a tendency to orient the water dipoles to the H20−OH vector. Moreover, in MND1

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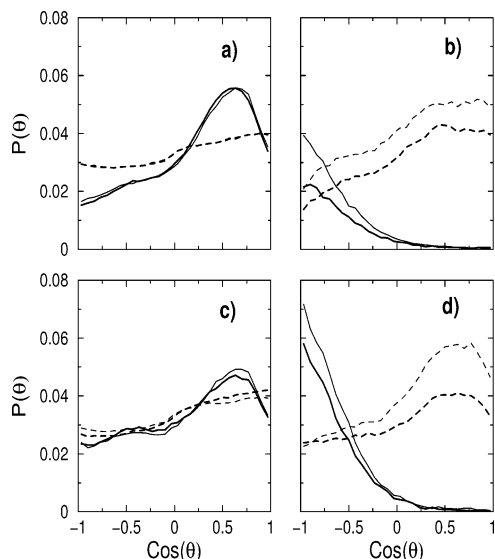*J. Phys. Chem. B, Vol. 110, No. 26, 2006* **13155**

Figure 5. Orientational distribution function, $P(\cos\theta)$, of water in the first and second solvation shells. The light solid and dashed lines represent $P(\cos\theta)$ of water around the sulfur atoms (in SDS) in the first and second solvation shells, respectively, in MND2 (left top, a) and in MND1 (left bottom, c). The dark solid and dashed lines represent $P(\cos\theta)$ of water around the sulfur atoms (in SDS) in the first and second solvation shells, respectively, in MNH2 (left top, a) and in MNH1 (left bottom, c). The light solid and dashed lines represent $P(\cos\theta)$ of water around the hydroxyl groups of dodecanol in the first and second solvation shells, respectively, in MND2 (right top, b) and in MND1 (right bottom, d). The dark solid and dashed lines represent $P(\cos\theta)$ of water around the hydroxyl groups of hexadecanol in the first and second solvation shells, respectively, in MNH2 (right top, b) and in MNH1 (right bottom, d).

and MNH1, a maximum is observed also nearly at $\approx51°$. It is also observed in this case that the probabilities are in general slightly higher in the SDS/dodecanol mixture than in the SDS/hexadecanol mixture.

We also measured the average orientation of the water dipoles at the interface for all of the monolayers, and an angle of $\approx78°$ (in all systems) was found, pointing to the positive z-axis with respect to the normal to the interface.

3.3. Hydrocarbon Tails, Length, and Tilt Angle. The thickness of the monolayer as measured in experiments is calculated in the simulations by the projection of the chains along the normal to the interface δ_z. For the monolayer MND1, the average thickness for the SDS and dodecanol is 12.4 and 12.5 Å, respectively; that is, both tails have mainly the same extension. For MND2, the SDS tails are slightly longer ($\delta_z = 13.2$ Å) than those of the dodecanol ($\delta_z = 12.8$ Å). Calculating the total length of the tails, δ_t, it is also possible to make a rough estimate of the chain tilt from the ratio between δ_z and δ_t, $\cos\theta = \delta_z/\delta_t$. For the SDS/dodecanol monolayer, the tilt angles are $\theta = 20.7°$ and $\theta = 21.4°$ for SDS and dodecanol tails in MND1, respectively, whereas, in MND2, the tilt angles are $\theta = 11.8°$ and $\theta = 14.8°$ for SDS and dodecanol tails, respectively. An interesting feature is that both molecule tails bend more when the two surfactants are separated at the interface than when they are uniformly mixed.

Experiments of neutron reflection of SDS/dodecanol at the air/water interface conducted by Lu et al. showed that the dodecanol is thicker than the anionic surfactant,[16] and they also observed that the tilt angle of the SDS chain is higher than that of the dodecanol.

For the MNH1, we have $\delta_z = 12.8$ Å for SDS and $\delta_z = 18.1$ Å for hexadecanol, whereas, for the MNH2, $\delta_z = 12.3$ and 16.2
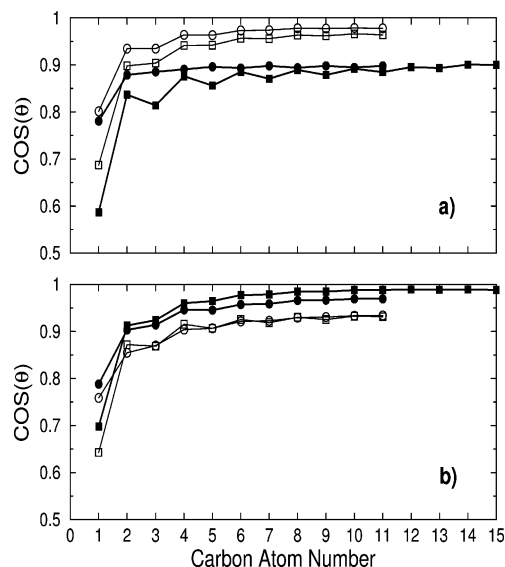

Figure 6. Cosine of the angle between the C_1-C_n ($n = 2, 3, ..., 12, ..., 16$) vector and the vector normal to the interface of the surfactant molecules. The top picture shows $\cos\theta$ of the tails in MND2 and MNH2. The light lines with empty circles and square symbols are for the SDS and dodecanol molecules in MND2, respectively. The dark lines with full circles and square symbols are for the SDS and hexadecanol molecules in MNH2, respectively. The bottom picture shows $\cos\theta$ of the tails in MND1 and MNH1. The light lines with empty circles and square symbols are for the SDS and dodecanol molecules in MND1, respectively. The dark lines with full circles and square symbols are for the SDS and hexadecanol molecules in MNH1, respectively.

Å for SDS and hexadecanol tails, respectively. Here, hexadecanol tails are thicker than SDS tails, as expected. The tilt angles in MNH1 are $\theta = 13.9°$ and $\theta = 8.8°$ for the SDS and the hexadecanol tails, respectively. For MNH2, $\theta = 26.1°$ and $\theta = 25.9°$ for the SDS and hexadecanol tails, respectively. In this case, the SDS/hexadecanol systems have a reverse trend with respect to the SDS/dodecanol monolayers: the tails of both surfactants are more bent when the molecules are well mixed than when the SDS and hexadecanol are separated. All of these values are in agreement with those tendencies observed in Figures 1 and 2 of the density profiles.

More information about the inclination of the tails can be calculated from the average angle between the C_1-C_n vector (C_1, first carbon; C_n, the nth carbon in the tail; $n = 2, 3, ..., 12, ..., 16$) and the vector normal to the interface.

In Figure 6a, the results for the SDS/dodecanol and the SDS/hexadecanol monolayers when both surfactants are completely mixed (MND2 and MNH2) are shown. From these graphs, we observed that at the beginning of the chain the dodecanol bends more than the SDS tails. Nevertheless, all of the tails reach a plateau at the end, suggesting that the last carbons in each tail have the same inclination. In MND2, the dodecanol tails are more bent than those of the SDS and the same tendency is depicted from MNH2; the hexadecanol is slightly more bent than the SDS.

When all of the SDS molecules are together at the interface, a reverse trend is observed in MND1 and MNH1 (Figure 6b). In MND1, the dodecanol tails are straighter than the SDS tails, although the cosine values are quite similar for both surfactant chains. In the monolayer MNH1, the same tendency is depicted; that is, the hexadecanol tails are also slightly straighter than the SDS tails.

Another interesting feature in the SDS/dodecanol monolayers is when the SDS molecules are close to each other and apart

from dodecanol (MND1), the tails of both surfactants are more bent than those when the surfactants are randomly mixed in the monolayer (MND2). For the SDS/hexadecanol monolayers, the reverse trend is observed; when the surfactants are well mixed (MNH2), both tails bend more than those when the surfactants are separated (MNH1). It seems that the arrangement of the surfactants helps the chains to become straighter.

These results are in agreement with those calculated from the above previous calculations of the thickness. Moreover, for the SDS/dodecanol monolayers, the same tendencies were observed in simulations of the same system at low dodecanol concentration;[26] however, in the present study, the values of the inclination and the length of the tails are much higher for both surfactants, suggesting that high alcohol concentrations make longer and straighter tails.

Interesting is the behavior of the SDS tails when they are with dodecanol or hexadecanol. If SDS is uniformly mixed either with dodecanol or hexadecanol (MND2 or MNH2), the SDS tails are straighter than those of the dodecanol or hexadecanol, respectively. However, if the dodecanol (or hexadecanol) molecules are placed together (MND1 and MNH1), the SDS tails seem to be more bent, although in MND1 the values of the cosine angles are quite similar for both molecules.

3.4. Order Parameters. In the experiments, a better detailed picture in the interior of the molecules comes from the deuterium NMR spectra where the average inclination of the chains is quantified by an order parameter. The ordering of the tails in phospholipid membranes is usually characterized by the so-called deuterium order parameter, S_{CD}, which shows the average inclination of the C−D bond with respect to the bilayer normal. In those measurements, the hydrogens of the chains are selectively replaced by deuteriums and they are observed with the NMR technique. In computer simulations, where a united CH_n atom model is used, the order parameter is calculated with the following formula:[28]

$$S_{CD} = (^2/_3)S_{xx} + (^1/_3)S_{yy} \qquad (3)$$

$$S_{ij} = (^1/_2)\langle 3 \cos \theta_i \cos \theta_j - \delta_{ij} \rangle \qquad (4)$$

$i, j = x, y, z$ and θ_i is the angle between the ith molecular axis and the normal to the interface (see the details in ref 28).

In Figure 7, the S_{CD} order parameter is calculated for each surfactant in the different monolayers. In Figure 7a, the MND2 and MNH2 monolayers are shown, SDS and dodecanol (or hexadecanol) are mixed, and it is observed that the SDS tails have higher order than the dodecanol or hexadecanol tails in each monolayer, respectively. As a general trend, S_{CD} decreases down the chain, indicating that the last carbons in the chain are distributed in a more isotropical way. However, in the MNH2 monolayer, we observed a plateau region extending for almost all of the carbons in the SDS molecule, whereas, for the hexadecanol molecule, the plateau region extends from carbon 3 to carbon 10. It is also possible to characterize the order in the tails by the quantity $\langle |S_{CD}| \rangle$, which is the average order parameter over all of the carbons in the chain. For MND2, $\langle |S_{CD}| \rangle = 0.44$ and $\langle |S_{CD}| \rangle = 0.42$ for the SDS and dodecanol tails, respectively, and for MNH2, $\langle |S_{CD}| \rangle = 0.35$ and $\langle |S_{CD}| \rangle = 0.33$ for the SDS and hexadecanol tails, respectively. Interesting is the decrease in the S_{CD} order of the SDS tails when they are with hexadecanol compared to when they are with dodecanol surfactants. In fact, both surfactant tails have less order in MNH2 than in MND2.

Different features are observed when both surfactants are separated in the mixture. In MND1 and MNH1, the S_{CD} order
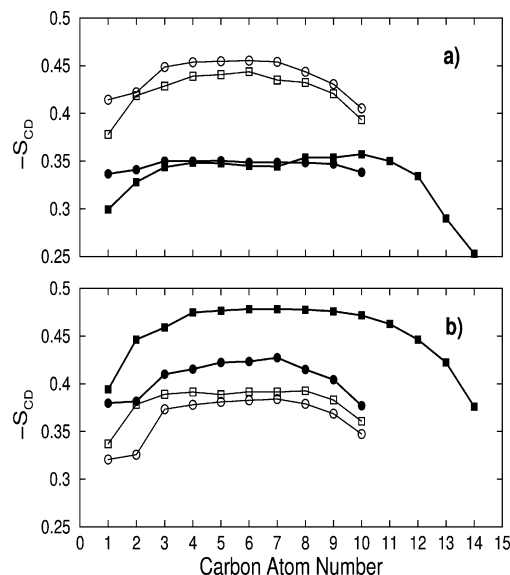

Figure 7. S_{CD} order parameter as a function of the carbon position of the surfactant molecules. The top picture shows S_{CD} of the tails in MND2 and MNH2. The light lines with empty circles and square symbols are for the SDS and dodecanol molecules in MND2, respectively. The dark lines with full circles and square symbols are for the SDS and hexadecanol molecules in MNH2, respectively. The bottom picture shows S_{CD} of the tails in MND1 and MNH1. The light lines with empty circles and square symbols are for the SDS and dodecanol molecules in MND1, respectively. The dark lines with full circles and square symbols are for the SDS and hexadecanol molecules in MNH1, respectively.

parameter is higher for the dodecanol or hexadecanol than that for the SDS, that is, the opposite trend observed in MND2 and MNH2. We have for MND1 $\langle |S_{CD}| \rangle = 0.36$ and $\langle |S_{CD}| \rangle = 0.38$ for the SDS and dodecanol tails, respectively, whereas for MNH1 we have $\langle |S_{CD}| \rangle = 0.41$ and $\langle |S_{CD}| \rangle = 0.45$ for the SDS and hexadecanol tails, respectively. On the other hand, in this case, we observed that the S_{CD} order increased in the SDS tails when the length of the cosurfactant tail (alcohol) increased in the mixtures.

In the SDS/dodecanol monolayer, we also noticed that regardless of the surfactant (SDS or dodecanol) the tails are more ordered when the surfactants are well mixed than when they are separated, that is, $\langle |S_{CD}(\text{MND1})| \rangle$ is lower than $\langle |S_{CD}(\text{MND2})| \rangle$. When the alcohol tails are longer than those of the SDS (SDS/hexadecanol monolayers), the tails are more disordered when the molecules are well mixed than when they are separated; $\langle |S_{CD}(\text{MNH1})| \rangle$ is greater than $\langle |S_{CD}(\text{MNH2})| \rangle$.

4. Discussion and Conclusions

We performed a series of molecular dynamics computer simulations on SDS/dodecanol and SDS/hexadecanol mixtures at the air/water interface at a high concentration of dodecanol and hexadecanol molecules.

In both monolayer mixtures, two systems were prepared at the same dodecanol and hexadecanol concentration. For the SDS/dodecanol monolayer, the first system consisted of all the SDS surfactants placed together and the dodecanol surfactants were also close to each other (MND1). In the second system, the SDS and dodecanol molecules were placed in such a way that all molecules were uniformly mixed in the surface area (MND2). The same preparation was conducted for the SDS/hexadecanol system. The SDS and hexadecanol molecules were separated (MNH1) in different regions of the surface area, and in the other system, all of the SDS and hexadecanol molecules

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were uniformly distributed at the interface (MNH2). In all monolayers, it was observed that the anionic headgroups penetrate deeper into the water phase than the nonionic headgroups. However, from these simulations, some differences can be depicted from the SDS/dodecanol monolayer at high dodecanol concentration with respect to previous simulations at low dodecanol concentration.[26] From these results, we observed that due to the large number of dodecanol molecules less water molecules approach the SDS headgroups (compared with data simulations at low dodecanol concentration), since they also want to form more hydrogen bonds with the hydroxyl groups of dodecanol.

However, the main differences between the monolayers were observed in the arrangement of the tails. The first difference in the SDS/dodecanol system at high alcohol concentration with respect to the low concentration of earlier works is the considerable increase in the order and the thickness of both tails (SDS and dodecanol) shown also in some experiments of the same system.[16] However, more detailed studies of MND1 and MND2 showed that the tails of both surfactants extend more in MND2 than in MND1. Nevertheless, in MND1, the dodecanol chains are slightly straighter than those of SDS, whereas the reverse trend is observed in MND2; that is, the dodecanol chains are more bent than those of SDS. Analyzing the order parameter of the dodecanol and the SDS tails, we found that the values of S_{CD} are higher for both surfactant tails in MND2 than those of MND1. However, the dodecanol tails in MND1 are more ordered than those of SDS, whereas in MND2 the SDS chains are more ordered than the dodecanol chains. These results are in agreement with previous simulations performed at low dodecanol concentration. Moreover, the same tendencies have been shown in experiments of similar systems at 49% dodecanol and 51% SDS.[11] These results suggest that some of the experimental results might be understood by considering that the probable conformation of the monolayer is that when the dodecanol and the SDS are separated (MND1), forming microphases of condensed dodecanol domains at the interface, as observed by Vollhardt et al. in Brewster angle microscopy (BAM) experiments.[10]

Considering that MND1 is the likely conformation of the SDS/dodecanol monolayer compared with some actual experiments, the interesting issue is to understand how the SDS surfactant structure is modified by the chain length of the cosurfactant (alcohol). Therefore, from comparisons of MND1 with MNH1 monolayers, some features are observed; for example, the increase of the alcohol tail length in SDS/alcohol mixtures increased the order and thickness of the SDS tails. Nevertheless, the alcohol tails are straighter and more ordered than those of the SDS. The increase of the order parameter as the length of the alcohol tail increased has also been observed in experiments on phosphotidylcholine monolayers at the air/water interface which have shown that long chain molecules had considerably more order than those with short chains; DPPC tails have more order than the DPMC tails which are more ordered than DLPC tails.[29] Moreover, the same trend was also observed in early computer simulations of the same systems.[30] Therefore, it is reasonable to expect that a domain of hexadecanol molecules presents higher order than a domain of dodecanol molecules. If this is the case, then the high order of the hexadecanol tails somehow is propagated to the SDS tails in the same monolayer, increasing also the order of the SDS chains compared with that of the SDS tails which are with dodecanol.

On the contrary, if the monolayer does not form domains, that is, the surfactant and the cosurfactant are well mixed, having SDS molecules close to dodecanol (MND2) or hexadecanol (MNH2) molecules, the tails have different behavior. The chain length incompatibility between the SDS and the hexadecanol makes the excess hydrocarbon tails, in MNH2, have more thermal motions (as discussed in previous works on the micellar stability of SDS solutions with long chain alcohols[17]), reducing the order and the extension of the tails with respect to those of SDS and dodecanol in MND2 where both surfactants have the same chain length.

Finally, from these computer simulations, we believe that the present results give us new insights to understand the conformation of the SDS with long chain alcohols at interfaces.

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