

Mixtures of Sodium Dodecyl Sulfate/Dodecanol at the Air/Water Interface by Computer Simulations

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Molecular dynamics simulations of monolayers of surfactant mixtures at the air/water interface were performed where the binary mixture was composed of sodium dodecyl sulfate (SDS) and dodecanol molecules. At the same ratio of SDS and dodecanol molecules, two monolayer mixtures were prepared. In the first monolayer, all the dodecanol molecules were placed together in the center of the simulation box, whereas in the second monolayer, those molecules were uniformly distributed in the surface area in such a way that they were far from each other. Simulations of both systems indicate that the dodecanol tails in the first monolayer are straighter and more ordered than those in the second monolayer. From the present results, we observed new insights of how the different molecules should array or distribute at the interface in real systems. Finally, studies of the interfacial water around the different surfactants were also analyzed, showing that they are closer to the polar headgroups of dodecanol than to the SDS headgroups.

Introduction

In the past few years, several investigations of surfactant molecules at liquid/vapor and liquid/liquid interfaces have been reported not only for their scientific interest but also for their industrial application. These studies have been conducted using different experimental techniques including fluorescence, resonance Raman scattering, neutron reflection, second harmonic generation, vibrational sum-frequency spectroscopy, Brewster angle microscopy, atomic force microscopy, and using a time-resolved quasielastic laser.^{1–8} Most of these studies have been carried out in systems of only one kind of surfactant molecule. However, most of the actual problems, such as commercial products, consist of a mixture of surfactants that 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 dishwashing liquids, and washing powders. Therefore, studies of surfactant mixtures also have been conducted using different experimental techniques such as calorimetry, X-ray, neutron scattering, and surface tension measurements among others.^{9–24}

Special attention has been paid in studying the structure and composition of surfactant mixtures (extension of the chains, thickness of the monolayer mixture, etc.) at the interfaces.^{20–24} For instance, Lu et al.²² observed differences in the position of the molecules along the interface by neutron reflection experiments of dodecanol and sodium dodecyl sulfate at the air/water interface. SDS seemed to penetrate more into the solvent than the dodecanol. From another series of experiments of anionic–nonionic (C₁₆TAB/C₁₂E₆) surfactants, Penfold et al.²¹ found an increasing change in the position of the nonionic molecules at the interface relative to the solvent with increasing solubility of the nonionic molecules. Moreover, surface tension experiments have shown that mixtures with similar hydrophobic tail length but with different headgroups may show different properties that can affect the structure of the monolayer at the interface (i.e., the behavior of the different surfactants might be attributed to the different polar groups of the molecules).

On the other hand, computer simulations became an important tool for the study of such complex interfacial systems.^{25–35} Those investigations allow us to obtain more information about dynamical and structural properties

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Table 1. SDS and Dodecanol Intermolecular Potential Parameters

Site	q (charge)	σ (Å)	ϵ (kcal/mol)
Sodium Dodecyl Sulfate			
S	1.284	3.550	0.250
O(SO ₃)	-0.654	3.150	0.200
O(ester)	-0.459	3.000	0.170
CH ₂ (attached to O)	0.137	3.905	0.118
CH ₂	0.000	3.905	0.118
CH ₃	0.000	3.905	0.175
Na ⁺	1.000	2.275	0.115
Dodecanol			
H	0.439	0.000	0.000
O	-0.721	3.150	0.150
CH ₂ (attached to O)	0.282	3.905	0.118

of interfacial problems from a molecular level, which are not easy to obtain from real experiments.

In the present work, we studied the effect of the charge distribution on surfactant monolayer mixtures of anionic and nonionic molecules at the air/water interface (i.e., we investigated how the charge distribution of the polar heads might affect the monolayer structure and the behavior of the different surfactants at the interface). Finally, studies of the orientation and order of the molecule chains in the mixture are also analyzed.

For the anionic surfactant, we used one of the most common surfactants, sodium dodecyl sulfate (SDS), whereas for the nonionic molecule, we used the dodecanol molecule. The system was chosen since it has been previously studied by several authors,^{10–14,21–24} and some experimental data are available that will allow us comparisons, in some cases, with the present results.

Computational Methods and Models

Simulations of the SDS/dodecanol mixtures at low dodecanol concentrations were performed using the molecular dynamics (MD) method. For the anionic system, we used a SDS model of 12 united carbon atoms in the hydrocarbon chain attached to a SO₄ headgroup with its atoms explicitly modeled. The simulation parameters for SDS were the same as in previous works.^{32,34} The nonionic surfactant was constructed with the same structure of the dodecanol molecule by using the same united carbon model of the SDS hydrocarbon tail. All the simulation parameters are shown in Table 1. For water molecules, we used the SPC model.

All simulations were carried out in the NVT ensemble with a time step of 0.002 ps using the DL-POLY package.³⁶ Bond lengths were constrained using the SHAKE algorithm with a tolerance of 10⁻⁴, and the temperature was controlled using the Hoover-Nose thermostat with a relaxation time of 0.2 ps³⁷ at $T = 300$ K. The long-range electrostatic interactions were 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.

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The initial configuration was prepared similarly as in ref 34. First, a monolayer of 36 SDS molecules in an all-trans configuration was constructed and placed in a box with dimensions $x = y = 40.249$ Å (i.e., we have an area per headgroup of 45 Å²/molecule). This value was chosen since it is equal to the critical micelle concentration area for the SDS molecules at the water/vapor interface, as found in neutron reflection experiments.²³ The z -dimension of the box was set to 150 Å, and for convenience of the simulations, a water/vapor interface in one opposite end of the box ($z < 0$) was present. In the other side of the box ($z > 0$), where the tails were located, there was a large empty space. Then, four SDS molecules were replaced for four dodecanol molecules. With this small number of dodecanol molecules as compared with those of SDS, the area per headgroup should not change significantly. This can be observed from the surface concentration calculated with the number of molecules in the monolayer and using the following relation to estimate the area per headgroup:

$$A = \frac{1}{\Gamma N_a} \quad (1)$$

where Γ is the surface concentration (in mol cm⁻²) and N_a is Avogadro's number (see, e.g., ref 22). The amount of moles in the surface area (SDS and dodecanol) was calculated from the number of molecules and the molecular weight of SDS and dodecanol. Then, the surface concentration obtained was $\approx 3.7 \times 10^{-10}$ mol cm⁻² given an area per headgroup of ≈ 45 Å²/molecule. This value is in agreement with the neutron experiments of Lu et al.²² where they measured surface areas of the same system at different concentrations of SDS and dodecanol. They found, for instance, surface concentrations of 3.6 – 3.8×10^{-10} mol cm⁻² with areas per headgroup of 43–46 Å²/molecule.

To understand the behavior (arrangements) of the different surfactants in the mixture, two systems were prepared (i.e., two monolayer systems with 32 SDS and four dodecanol molecules were constructed). In the first monolayer, which is called MN1, the four dodecanol molecules were placed together in the middle of the simulation box. In the second monolayer (MN2), the four dodecanol molecules were randomly placed in the mixture far apart from each other.

Once the monolayer was prepared, 1185 water molecules were added surrounding the headgroups, and 32 sodium anions were randomly inserted in the interfacial region. With the headgroup of the molecules initially pinned, a short MD simulation at $T = 300$ K was performed. Then, both systems were equilibrated for 100 ps, each one was run up to 5.5 ns, and we collected data from the last 2 ns for analysis. The configurational energy was monitored as a function of time to determine when the system reached equilibrium.

Results

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

Density Profile. The first analysis was performed for the density profiles. In Figure 1, the profiles of the monolayer mixtures are shown (i.e., the z -dependent density profiles for water, headgroups, and hydrocarbon tails of each surfactant molecules). To make a distinction between the distribution of the SDS and the dodecanol molecules, they were plotted separately. The SDS headgroup density profile includes the SO₄⁻ group and the Na⁺ counterion. Basically, the same features are observed for monolayers MN1 and MN2 (i.e., there are not significant differences in the profiles of the two monolayers). Both surfactant headgroups are well-solvated by water as can be observed in Figure 1. Since the dodecanol headgroups have less atoms than SDS, the profiles of these groups were not observed in this scale; therefore, for clarity of the pictures, the dodecanol headgroup profiles were plotted 10 times larger than their actual size.

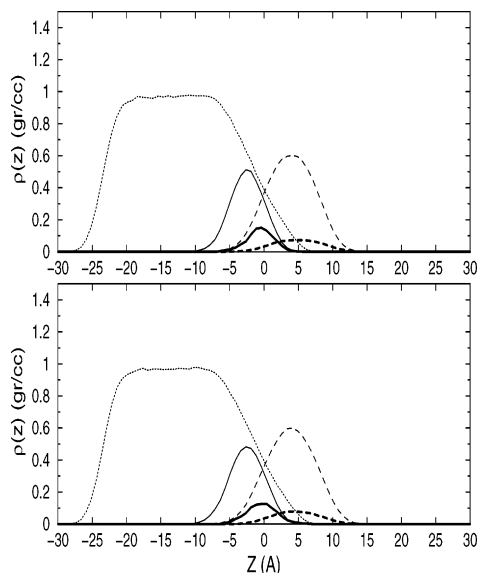


Figure 1. Density profiles for the SDS/dodecanol monolayer at the air/water interface. The top picture corresponds to the MN1 monolayer, whereas the bottom picture represents the MN2 monolayer. Water is depicted by the dotted line, the SDS headgroups by the light solid line, and the SDS tails by the light dashed line. The dodecanol polar groups are given by the dark solid line and the dodecanol tails by the dark dashed line.

An interesting feature is the average position of the molecules that was calculated by fitting a Gaussian (eq 2) of the profiles of the headgroups and the tails.

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

From these results, it is observed that the SDS heads penetrate more into the water phase than the dodecanol headgroups. For MN1 (top of Figure 1), the SDS headgroup profile is located at $Z_0 = -2.4$ Å, whereas the dodecanol headgroup is at $Z_0 = -0.5$ Å (i.e., there is a distance difference of about $\Delta = 1.9$ Å). For MN2 (bottom of Figure 1), the headgroup profiles are located at $Z_0 = -2.4$ Å and $Z_0 = -0.4$ Å for SDS and dodecanol, respectively. Here, the difference is $\Delta = 2.0$ Å. Although the distance difference (Δ) of MN1 and MN2 monolayers is small, we clearly observe that the position of the SDS headgroup is shifted to the solvent region. The same tendency has been observed in neutron reflection experiments of the same system where it is observed that the SDS volume fraction profile is displaced toward the water from the dodecanol profile.^{21,22} In those experiments, the authors found a difference in the position of the SDS and dodecanol relative larger in contrast with the values found here, and they observed that the dodecanol is 3.5 Å from SDS. However, the difference can be due to the different amount of SDS and dodecanol used in those experiments, 6.7 mM and 0.5 wt % of dodecanol (i.e., a different area per headgroup).

The profiles of the tails for the SDS molecules look alike in MN1 and MN2 (from the fitting Gaussian). However, the tail profiles for dodecanol in MN1 are slightly wider than in MN2, suggesting that the tails in MN1 are straighter.

Hydrocarbon Tails, Length, and Tilt Angle. The total length of the tails, δ_t , was measured as the distance from the first carbon to the last carbon in the chain. The projection of the chains along the normal to the interface, which is called the thickness of the monolayer in the experiments, δ_z , was also calculated. To study the dif-

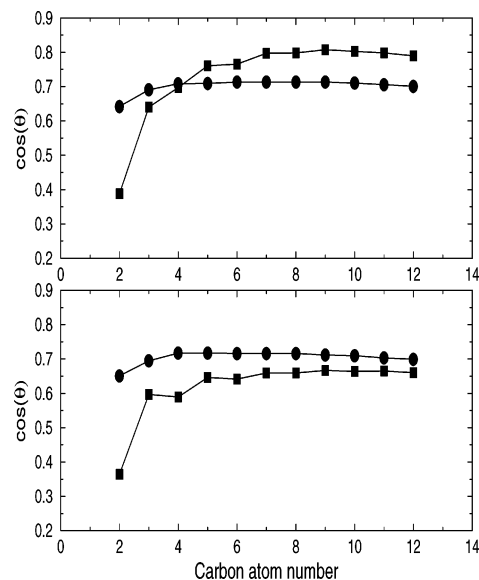


Figure 2. Cosine of the angle between the C_1-C_n ($n = 2, 3, \dots, 12$) vector and the vector normal to the interface of the surfactant molecules in the SDS/dodecanol monolayer mixture. Top and bottom pictures show $\cos \theta$ of the tails in the MN1 and the MN2 monolayers, respectively. Circles are for the SDS molecules, and squares are for the dodecanol molecules.

ference between SDS and dodecanol molecules in the mixture, the average length of the tails for each molecule in the monolayer was calculated separately. In monolayer MN1, the average thickness is $\delta_z = 8.1$ Å for SDS and 9.0 Å for the dodecanol chains. In monolayer MN2, the thicknesses are $\delta_z = 8.1$ and 7.6 Å for SDS and the dodecanol chains, respectively. It seems that the dodecanol tails are thicker than the SDS tails when they were closer together (MN1) than when they were separated (MN2). A rough estimate of the chain tilt can be obtained from the ratio between δ_z and δ_t (i.e., $\cos \theta = \delta_z/\delta_t$). For MN1, the average tilt angle indicates that the tails of the SDS molecules ($\theta = 45^\circ$) seem to be more bent than the tails of dodecanol ($\theta = 37^\circ$). For MN2, the opposite trend is observed; here, the SDS tails are straighter ($\theta = 45^\circ$) than the dodecanol tails ($\theta = 49^\circ$).

Experiments of neutron reflection of SDS–dodecanol at the air/water interface conducted by Lu et al. showed that the dodecanol is thicker (15.5 Å) than the anionic surfactant (12.5 Å),²² and from the same experiments, they also observed that the tilt angle of the SDS chain (45°) is higher than that of dodecanol (20°). However, those experiments were conducted at different SDS and dodecanol concentrations, which would explain the difference with our results.

To obtain more information about the inclination of the tails, we calculated the average angle between the C_1-C_n vector (C_1 is first carbon and C_n is the n -carbon in the tail, $n = 2, 3, \dots, 12$) and the normal to the interface. Figure 2 shows the results for MN1 (top) and for MN2 (bottom). From these graphs, we observed that at the beginning of the chain, the dodecanol bends more than the SDS tails. Nevertheless, all the tails reach nearly a plateau at the end, suggesting that the last carbons in each tail have the same inclination. However, an interesting feature is found in the last cosine angles of the dodecanol tails as compared with those of SDS. These values are higher for the dodecanol than for SDS in the MN1 monolayer, indicating that the dodecanol tails are straighter than those of SDS. For the monolayer MN2, the reverse trend is depicted, the dodecanol tails are more bent than those of SDS. These

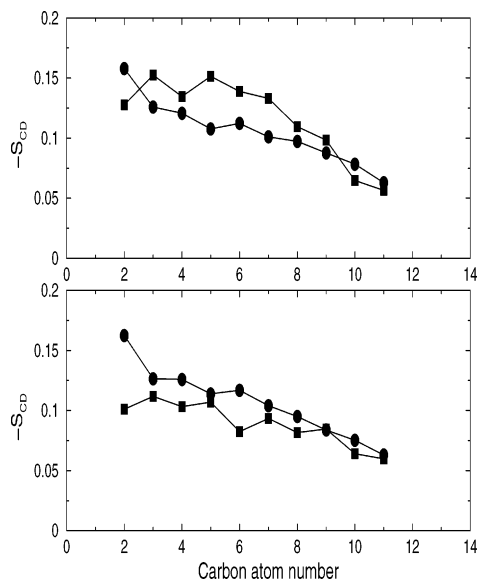


Figure 3. S_{CD} order parameter as a function of the carbon position of the surfactant molecules in the SDS/dodecanol monolayer mixture. The top picture shows the order in the carbons of the SDS and the dodecanol tails in the MN1 monolayer, and the bottom picture shows the order of the carbons of the SDS and the dodecanol tails in the MN2 monolayer. Circles are for the SDS molecules, and squares are for the dodecanol molecules.

results are in agreement with the previous thickness calculations.

Order Parameters and Gauche Defects. 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. For these measurements, the hydrogens of the chains are selectively replaced by deuteriums, and they are observed with the NMR technique. In computer simulations using the united CH_n atom model, the S_{CD} order parameter is calculated with the following formula:³⁸

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

$$S_{ij} = (1/2)\langle 3 \cos \theta_i \cos \theta_j - \delta_{ij} \rangle \quad (4)$$

where $i, j = x, y, z$, and θ_i is the angle between the i th molecular axis and the normal to the interface (see the details in ref 38).

The order parameter (Figure 3) of the carbons for SDS and the dodecanol molecules in the same monolayer is calculated separately. 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, the S_{CD} order parameter of the carbons in the dodecanol molecules presents different features in MN1 and MN2. In MN1, the dodecanol tails show a higher order than the SDS tails (top of Figure 3). In MN2, the order parameter of the two surfactants is slightly different, but in this case, S_{CD} is higher for the SDS than for the dodecanol tails (bottom of Figure 3). Probably a better representation of the order of the tails is given by the quantity $\langle |S_{CD}| \rangle$, which is the average order parameter over all the carbons in the chain. For MN1, $\langle |S_{CD}| \rangle = 0.12$ and $\langle |S_{CD}| \rangle = 0.10$ for the dodecanol and SDS tails, respectively, whereas for MN2, $\langle |S_{CD}| \rangle = 0.09$ and $\langle |S_{CD}| \rangle = 0.11$ for the dodecanol and SDS tails, respectively. On the other hand, experiments

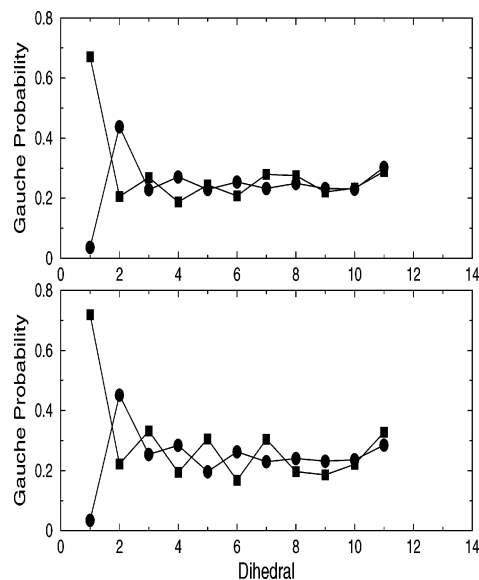


Figure 4. Probability of gauche defects as a function of the carbon position of the surfactant molecules in the SDS/dodecanol monolayer mixture. Same notation as in Figure 3.

of sum-frequency spectroscopy have observed that the hydrocarbon chains of SDS are more conformationally disordered than those of dodecanol.²⁴ Therefore, these experimental data are in agreement with the results of monolayer MN1.

The ordering of the hydrocarbon tails can also be characterized by the average number of gauche defects (i.e., the probabilities of gauche defects in the carbons of SDS and dodecanol can give us more insight about the conformation of the tails). In Figure 4, the probability of gauche defects for each carbon in the tail is shown. Once more, we have separated the cases of SDS and the dodecanol molecules in the mixture. In both monolayers, MN1 and MN2, the first dihedral, (S–O–C₁–C₂) of SDS is almost trans, whereas the first dihedral (H–O–C₁–C₂) of the dodecanol present high probability of a gauche conformation. The gauche probability for the rest of the carbons oscillates with a tendency of decreasing the trans conformation of the last carbons.

Surfactant Structure at the Interface. The arrangement of the different surfactants (headgroups) with water was investigated by the pair distribution function $g(r)$. The $g(r)$ function can give us information about where water molecules are located at the interface and their distribution around the headgroups of the different surfactants in the mixture. In Figure 5, the $g(r)$ for MN1 and MN2 are shown. Solid lines are the $g(r_{S-Ow})$ of the sulfur atom (of the SDS polar head) with the water oxygens. Dashed lines are the $g(r_{H-Ow})$ of the hydrogen atom (of the OH headgroup in the dodecanol) also with the water oxygens. In the picture, the $g(r)$ of MN1 and MN2 are represented in the top and bottom of the figure, respectively. The pictures indicate that there is a large number of water molecules around the SDS headgroups. Nevertheless, it seems that the system presents hydrogen bonds interactions between the hydrogen of the OH group of dodecanol and the oxygen of water, making the last molecules move closer to the OH groups. Both pictures of MN1 and MN2 look alike, and in both cases, the $g(r_{H-Ow})$ presents more structure with two well-defined peaks around 1.9 and 3.1 Å, where the first and second solvation shells are defined. The first peak of $g(r_{S-Ow})$ is around 4.0 Å where the first solvation shell is defined. This distance of the first water neighbor molecules from central atoms

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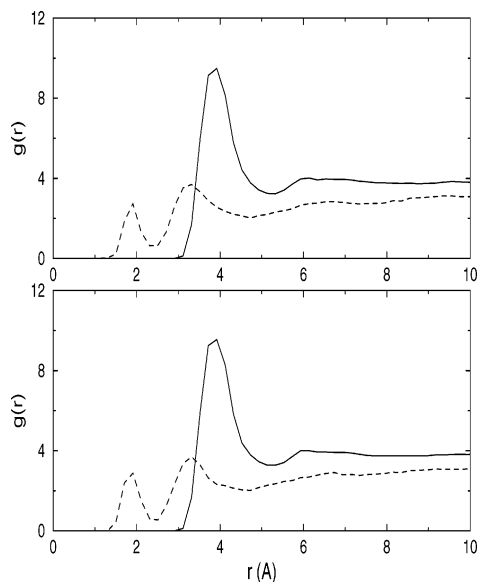


Figure 5. Radial distribution function of S–OW ($g(r_{S-OW})$, solid line) and H–OW ($g(r_{H-OW})$, dashed line) in the SDS/dodecanol mixture. Top figure corresponds to the MN1 monolayer and the bottom to the MN2 monolayer.

of a SDS molecule was also found in previous studies of SDS at the water/ CCl_4 interface.³² However, in this case, it is difficult to define a second peak for the next nearest neighbors. It is worth mentioning that the monolayer is an inhomogeneous and nonsymmetric system in the z -direction since the water is placed only in the negative z -axis. Therefore, the $g(r)$ of the surfactant–water does not go to unity, and it seems to take large values as compared to the usual $g(r)$ values of bulk systems.

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. We calculated the probability distribution $P(\cos \theta)$, where θ is the angle of the vector going from one water oxygen to the sulfur (or hydrogen, OH) atom of the SDS (or dodecanol) surfactant molecule and the water dipole vector of the same water molecule. The distribution was calculated in the two surrounding shells defined by the distance of the first and second nearest neighbors in the $g(r_{S-OW})$ and $g(r_{H-OW})$ values calculated previously (Figure 5) for each monolayer mixture.

Figure 6 shows the S–OW and H–OW angular distributions for the MN1 and the MN2 mixtures. The top and bottom panels are the probabilities of SDS (left) and dodecanol (right) for MN1 and MN2, respectively. Basically, the graphs have the same shape for MN1 and MN2. However, from the SDS pictures, we observe that in the first solvation shell, the water dipole has the highest probability pointing approximately $\approx 51^\circ$ away from the water oxygen-to-sulfur vector. This value is in agreement with previous simulations of SDS at the water/oil interface.^{32,35} As mentioned previously, in this system, there is not a second solvation shell, and then we calculated the angular distribution of water molecules in the interval from 5.2 to 7.8 Å of the $g(r_{S-OW})$, where it was found that water was uniformly oriented around the SDS headgroup. On the other hand, the angular distribution of water around dodecanol presents a different shape with respect to those next to the SDS molecules. In this case, the water dipoles in the first solvation shell completely point in the opposite direction of the oxygen(H_2O)-to-hydrogen(OH) vector. In the second solvation shell, the water dipoles were more uniformly oriented.

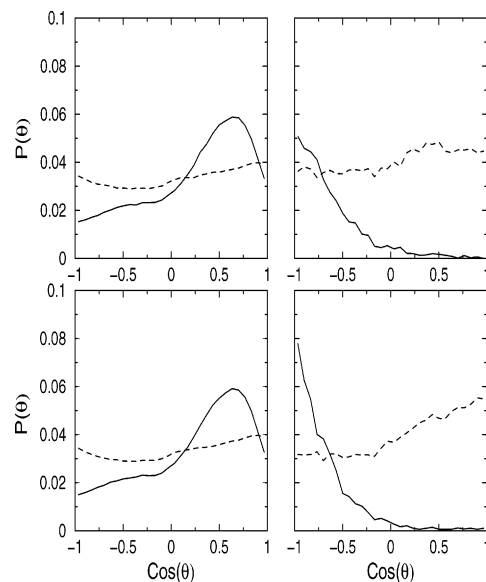


Figure 6. Orientational distribution function of water in the first (solid lines) and second (dashed lines) solvation shell. Top figures correspond to the MN1 monolayer of water distribution around the sulfur atoms of the SDS (left) and around the hydrogens in the OH group of the dodecanol molecules (right). Bottom figure corresponds to the MN2 monolayer of the water distribution around the sulfur atoms of the SDS (left) and around the hydrogens in the OH group of the dodecanol molecules (right).

We also measured the average orientation of the water dipoles at the interface, and an angle of $\approx 80^\circ$ pointing to the positive z -axis with respect to the normal to the interface was found.

Discussion

We performed a series of molecular dynamics computer simulations on a SDS/dodecanol mixture at the air/water interface.

Two mixtures were used at the same dodecanol concentration but prepared in two different ways. For the first mixture, the nonionic molecules were placed all together (monolayer MN1), whereas for the second mixture, those molecules were distributed on the surface area separated from each other (monolayer MN2). In both cases, it is observed that the anionic molecules penetrate more deeply into the water phase. However, the main difference between the two monolayers was in the arrangement of the tails. While the SDS chains do not change their configuration too much, the dodecanol chains present different features. When the dodecanol molecules are close to each other, they arrange in such a way that they become straighter than when they are separated. In that case, the dodecanol tails are thicker and more ordered when they are together than those of SDS.

Finally, for the configuration of the water molecules around the surfactant headgroups, no difference was observed when the dodecanol molecules were closer or separated. Water moves closer to the dodecanol (forming two well-defined solvation shells) than to the SDS molecules.

Actual experiments of the same system have been conducted, and researchers have observed, for instance, that the mixture presents a phase transition (forming condensed domains)^{12–14} and that the dodecanol is thicker and straighter than SDS.²² However, how each surfactant arrays at the interface is difficult to see from those

experiments. Although the experiments were conducted at different SDS and dodecanol concentrations, our results (for monolayer MN1) indicate similar tendencies shown in real systems; therefore, we believe that the present results give us new insights in understanding the conformation of SDS and dodecanol molecules at the interface. They suggest that to explain experimental data, the dodecanol molecules need to be close to each other to form

a stable monolayer; therefore, the system with the dodecanol molecules far from each other probably represents an unstable situation.

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