Structure of the SDS/1-dodecanol surfactant mixture on a graphite surface: A computer simulation study

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ABSTRACT

Molecular dynamics simulations of mixtures of sodium dodecyl sulfate (SDS) and 1-dodecanol molecules on a graphite surface were carried out at low and high concentration to investigate the formation of aggregates on the solid plate. The simulations showed that at low concentration the surfactants were well adsorbed on the surface by forming layers structures or a hemicylinder aggregate for a slightly higher surfactant concentration whereas at the highest concentration the surfactants formed monolayer-like structures localized away from the graphite surface with a water bin between the monolayer and the graphite plate. Therefore, we obtained different arrays of those observed in recent simulations of pure SDS adsorbed on graphite at the same concentration reported in the literature. The unexpected water layer between the 1-dodecanol and the graphite surface, at the highest concentration, was explained in terms of the Hamaker constants. The present results suggest that the formation of aggregates on solid surfaces is a combined effect not only of the surfactant–surfactant and the surfactant–wall interactions but also of the surfactant concentration.

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1. Introduction

Surfactant studies at interfaces have been investigated for several years, not only for their scientific interest but also for their applicability in industrial processes such as detergency, lubrication and colloid stabilization. Therefore, several experiments have been conducted to study their behavior at liquid/air and liquid/liquid interfaces [1–8]. Most of the studies have been conducted on pure surfactant systems, however, a lot of interesting problems consist of mixtures of surfactant molecules which have richer properties than individual ones. For instance, non-ionic surfactants are generally used together with anionic surfactants as active ingredients in products like shampoo, hand dish washing liquids and washing powders. Then, people have also been interested in the study of mixtures using different experimental techniques [9–18].

All of those works have helped us to understand much better the behavior of surfactants at liquid/air and liquid/liquid interfaces, however, how surfactants behave in the presence of a solid surface has been less understood. Therefore, more works are needed to understand surfactants at solid/liquid interfaces.

Several experiments suggest that most of the aggregates observed in bulk solutions can also be observed at solid/liquid inter-

faces [19–28]. In particular, the atomic force microscope (AFM) has been very valuable to study the self-assembly of surfactants adsorbed from aqueous solution on different solid surfaces. In fact, from those experiments it was possible to see how the SDS surfactant aggregated in hemicylinders on graphite plates [29].

However, the nature, the formation and the shape of the aggregates are still matter of several studies and people keep conducting investigations to better understand how the extra solid–surfactant interaction influences the structure of the surfactant on solid substrates.

An alternative tool to investigate such complex interfacial systems has been computer simulations techniques. In fact, it is found in the literature simulations from fully atomistic [30–32] to coarse-grain models [33–36] to investigate those systems. Interestingly simulations allow us to have more information about the interfaces from a molecular level which is not easy to obtain from real experiments. For instance, some groups have investigated the formation of structures as a function of the alkyl chain length [33], other groups have studied the role of counterions of anionic surfactants on graphite surfaces [37] or the curvature effects of surfactant adsorption [38], however, only few works have investigated mixtures on solid surfaces [39,40]. Particularly, in the last references the authors showed how surfactants are oriented on a graphite surface which could explain the formation of hemicylinder aggregates on that plate.

In fact, from our previous simulations [41] we observed that SDS on graphite formed hemicylinder structures at low concentra-

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tion whereas at high concentration SDS formed complete cylinders. In the present paper we continue our simulations of SDS on solids, however, we investigate how the structure of the surfactant is modified by the presence of a second component, i.e. we conducted studies of SDS/1-dodecanol mixtures on a graphite plate at different concentrations.

2. Computational method and model

In the present work simulations of the SDS/1-dodecanol mixture on a solid surface were performed using the molecular dynamics (MD) method. In all the simulations we used the same molecular model and the force field of our previous works. Since the model has shown good tendencies with experiments of SDS/1-dodecanol mixtures at the liquid/air interface [42,43] we now used it in the liquid/solid interface. For the SDS surfactant we used a model composed of a head group (SO_4) attached to a hydrocarbon chain of 12 united carbon atoms. For the 1-dodecanol molecule we worked a molecule with the same tail length of the SDS molecule and we used the same united carbon model for the hydrocarbon tails.

The total intramolecular potential was given by,

$$E = E_{bond} + E_{ang} + E_{dih} \tag{1}$$

The bond lengths were modelled by an harmonic potential,

$$E_{bond} = K_b (r - r_0)^2 \tag{2}$$

where r_0 is the equilibrium distance between two bonded atoms and K_b is the bond constant. The angles in the chain were also constrained by an harmonic potential,

$$E_{ang} = K_\theta (\theta - \theta_0)^2 \tag{3}$$

where θ_0 is the equilibrium angle and K_θ is the force constant. The dihedral angles were modelled by the Ryckeart and Bellemans potential [44],

$$E_{dih} = \Sigma_{k=0}^{5} c_k \cos^K(\phi) \tag{4}$$

where the c_k are the energy constants and ϕ is the dihedral angle. The potential parameters were the same used in our previous simulations which were also the same used by other authors [37]. For the intermolecular interactions the Lennard Jones potential was used (using the Lorentz–Berthelot mixing rules for the unlike atoms pairs) and coulombic potentials for the long range interactions. Once again, the LJ parameters were the same used in previous works [42] and in other papers [37]. In Table 1 we summarized the parameters for the intermolecular potentials. For the solid
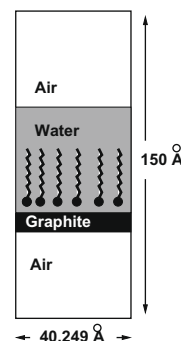
surface two layers of graphite plates were constructed using an atomistic model whereas for the water molecules the SPC model was used. Simulations with four graphene planes were also carried out, however, we did not find significant differences with the results at this molecular level.

Since the structure of pure SDS on graphite was already known [41] the first simulations were conducted for a system composed only of 1-dodecanol molecules. The initial configuration for this system was prepared from 36 1-dodecanol molecules in all-trans configuration, with the polar groups initially pointed to the graphite surface of dimensions $X = Y = 40.249$ Å. Then 2416 water molecules, in bulk phase, were added in the system, i.e. we had an overall concentration of ≈ 0.8 M. The usual periodic boundary conditions were imposed, however, to prevent the formation of a second water/solid interface (due to the periodicity of the system) the box in the z-direction was extended to 150 Å (see Fig. 1), i.e. a liquid/vapor interface was present at one end of the box ($z > 0$).

Then, simulations for the SDS/1-dodecanol mixture were carried out by using the same number of SDS and 1-dodecanol molecules in the mixture, i.e. we had a ratio of 50–50% in number density (concentration of ≈ 0.4 M for the 1-dodecanol and the SDS-the CMC for the SDS is 0.0082 M). The initial configuration was prepared in the same way as the 1-dodecanol system, however, half of the 1-dodecanol molecules were randomly replaced by SDS molecules and by adding a sodium cation (Na^+) for each SDS molecule.

In order to study the concentration effects on the structure of the surfactants at the solid/liquid interface, other series of simulations were conducted. Firstly, another system with 49 molecules of pure 1-dodecanol (≈ 1.1 M) was constructed in the same way as the previous simulations. Then, another simulation with 25 SDS molecules and 24 1-dodecanol molecules (concentration of each component ≈ 0.57) was prepared in the same way as the first mixture described above. Finally, two more systems were prepared at even higher concentration, one of pure 1-dodecanol with 81 molecules (≈ 1.8 M) and the last one with 41 SDS molecules and 40 1-dodecanol molecules (concentration of each component ≈ 0.9), prepared as the other mixtures. The total number of molecules (SDS and 1-dodecanol) were chosen in order to have the same total surfactant concentration of our previous simulations of pure SDS. So, the structures from the present calculations could be compared with those of the previous simulations.

All simulations were carried out in the NVT ensemble using the DL-POLY package [45] with a time step of 0.002 ps at temperature of $T = 300$ K using the Hoover–Nose thermostat with relaxation time of 0.2 ps [46]. The long range electrostatic interactions were handle with the Particle Mesh Ewald method with precision of 10^{-4} and the van der Waals interactions were cut off at 10 Å. Finally, simulations up to 20 ns were conducted using the last 4 ns for data acquisition.

Table 1
LJ 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
1-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
Water and graphite			
OW	−0.82	3.166	0.155
HW	0.41	1.782	0.000
C(graphite)	0.00	3.400	0.056

Fig. 1. Schematic representation of the surfactant system at the liquid/solid interface.

3. Results

3.1. Surfactants at low surface coverage

As it was stated before, it is known that SDS on a graphite surface forms hemicylinder aggregates at low concentration [41]. In the present paper we are interested how the SDS structures are modified by the presence of a second surfactant, i.e. we want to investigate the structure of the SDS/1-dodecanol mixture on a graphite plane.

Therefore, the first analysis were conducted on the structure of pure 1-dodecanol. In Fig. 2 a snapshot of the last configuration of the 1-dodecanol molecules is shown where it can be observed that all molecules lay on the surface. In fact, due to the affinity between the carbon tails and the carbons in the surface the 1-dodecanol chains were fully adsorbed on the plate.

The structure was also confirmed by analyzing the density profiles. In Fig. 3a the density profiles, for the headgroups and the tails, were calculated in the z-direction (normal to the liquid/solid interface) where formation of two well defined layers were depicted. From those profiles we observed that the second layer was well solvated by water molecules whereas the first layer (close to the wall) was just solvated by few water molecules, although it was not appreciated in the figure due to the scale (the water density profile had small values close to the wall). On the other hand, water showed some structure close to the 1-dodecanol indicated by the peaks close to the 1-dodecanol profiles.

The structure of alcohols on graphite has been studied experimentally by some authors [47] and they have observed formation of adsorbed 1-dodecanol layers on the solid surface [48]. In fact, the array of the molecules on the surface has been investigated and people have observed herringbone structures at low temperatures (above the bulk melting point) and parallel structures at high temperatures [49] which it was the main structure we found in our simulations (see Fig. 4a).

When the SDS/1-dodecanol mixture was studied it was also observed the formation of two 1-dodecanol layers attached to the wall (Fig. 5) in the same positions of those layers of the pure 1-dodecanol system (Fig. 3b). In Fig. 3b was also depicted two peaks in the SDS tail profiles. Moreover, the SDS profiles indicated that the tails and the heads extended more into the water phase with the polar groups located even deeper into the water.

Even though the SDS and the 1-dodecanol also formed layers on the surface the structure of the first layer was different from that of the pure 1-dodecanol since it was not possible to see any particular
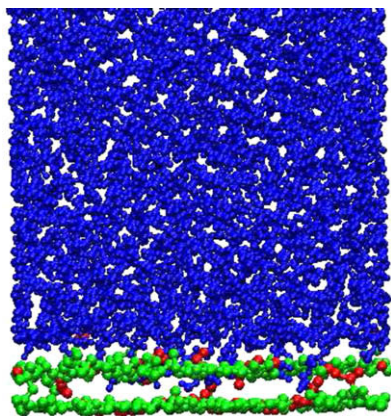
Fig. 2. Snapshot of the pure 1-dodecanol molecules on a graphite surface at the lowest concentration (36 molecules). Water is shown in blue, 1-dodecanol headgroups and tails in red and green, respectively. The graphite plate is located at the bottom side of the molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
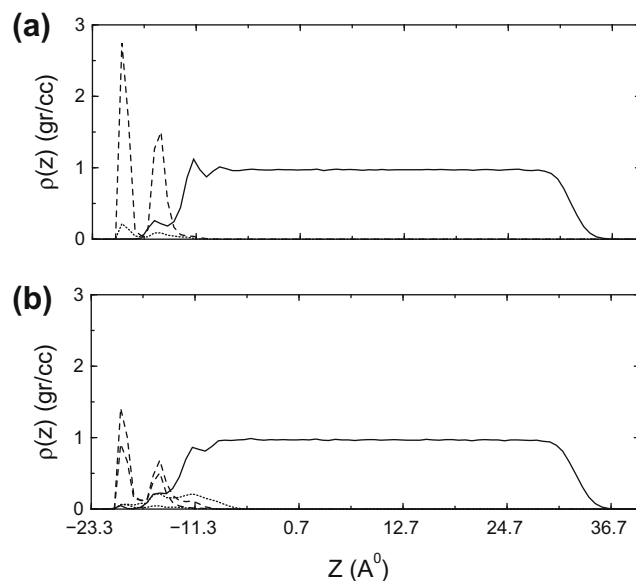

Fig. 3. Density profiles: (a) the pure 1-dodecanol and (b) the SDS/1-dodecanol mixture systems at the lowest concentration. The 1-dodecanol head groups and tails are depicted by the dotted and the dashed light lines, respectively, whereas the SDS headgroups and tails are depicted by the dotted and the dashed dark lines, respectively. Water is shown by the dark solid line. The graphite surface is located at the left of the plot.

array of the molecules (see Fig. 4b), i.e. the molecules accommodated without any particular order.

The position of the sodium cation (Na^+) with the SDS (sulfur atom) was evaluated in terms of the density profiles and of the pair distribution function $g(r)$ as shown in Fig. 6. In Fig. 6a we observed that the Na^+ atoms were located in the same z-interval of the SDS-head groups. Moreover, from Fig. 6b it was depicted that the first Na^+ ions were located at a distance of 3.7 Å of the sulfur atoms which it was in good agreement with the value found by Berkowitz et al. in their simulations of SDS micelles in water [50]. It is worth mentioning that the systems is an inhomogeneous system in the z-direction, therefore, the $g(r)$ does not go to unity, and it seems to take large values as compared to the usual $g(r)$ values of bulk systems.

It was also interesting to note that water with the mixture was less structured (close to the surfactants) than water with pure 1-dodecanol (see the water density profile in Fig. 3b). Since the SDS headgroup–water interaction is more attractive than the 1-dodecanol headgroup–water interaction (the SDS ϵ-LJ parameters are stronger than the 1-dodecanol parameters) then the SDS headgroups should be much better solvated by water than the 1-dodecanol headgroups. Therefore, that water somehow, forms a more continuous structure with the bulk. We think this could explain the observed feature.

The structure of the tails was also characterized by the length of the chains. Therefore, the total length of the tails was measured by the distance from the first to the last carbons in the chains. It was found an average length of 13.1 Å for the pure 1-dodecanol system whereas for the mixture it was found lengths of 11.9 Å and 12.2 Å for the 1-dodecanol and the SDS tails, respectively. It seemed that the 1-dodecanol was more bent when it was mixed with the SDS, however none of both tails were completely straight since the total length of the tails in their all-trans configuration is ≈15 Å. The chain conformations can also be characterized by the probability of gauche defects (Fig. 7a). From Fig. 7a we observed that the first dihedral, $H-O-C_1-C_2$, had 50% and 30% trans character for the pure 1-dodecanol and 1-dodecanol in the mixture, respectively. The
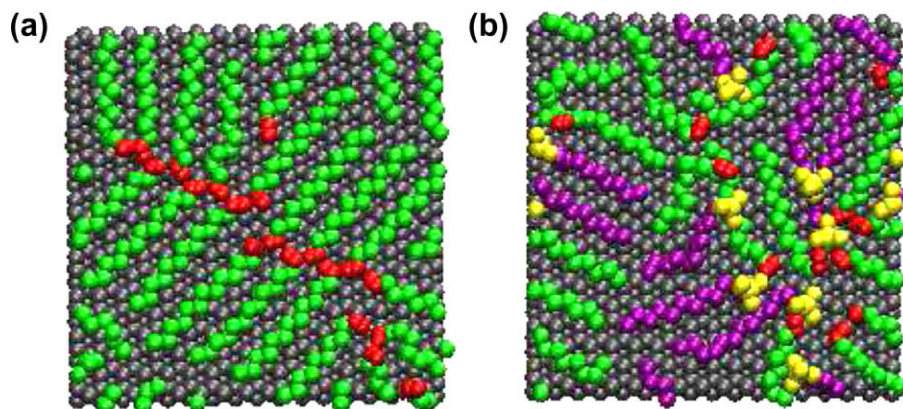
Fig. 4. Snapshots of the first layer adsorbed on the graphite surface at the lowest concentration. (a) The pure 1-dodecanol system and (b) the SDS/dodecanol mixture. In (b) in order to accommodate the tails on the graphite surface some headgroups did not lay on the layer. For better visualization the periodic boundary conditions were not removed, therefore some molecules seem to be broken. The graphite atoms are shown in grey whereas the rest of the molecules have the same colors as in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
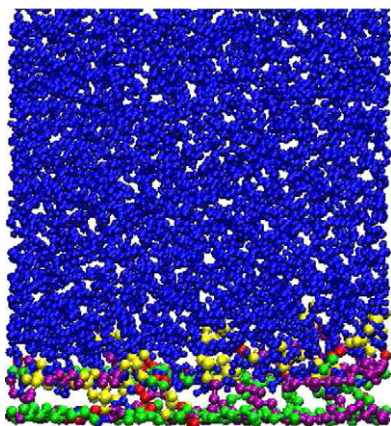
Fig. 5. Snapshot of the SDS/1-dodecanol mixture on a graphite surface at the lowest concentration (36 total molecules). Water is shown in blue, 1-dodecanol headgroups and tails in red and green, respectively. SDS headgroups and tails are in yellow and purple, respectively. The graphite plate is located at the bottom side of the molecules. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

probability of gauche defects for the next carbons indicated that they had more than 80% of trans configuration. In fact, the average numbers of gauche defects of the chains were 1.4 and 2.3 for the pure 1-dodecanol and the 1-dodecanol in the mixture. For the case of the SDS in the mixture the first dihedral, $S–O–C_1–C_2$, was almost trans while the following dihedral had only 50% trans character. For this chain the average number of gauche defects was 2.2.

The study of the tails can also be analyzed in terms of the order parameter,

$$S_{ij} = (1/2)\langle 3 \cos \theta_i \cos \theta_j - \delta_{ij}\rangle \qquad (5)$$

$i,j = x,y,z$ and θ_i is the angle between the ith molecular axis and the normal to the interface [51]. Although the order parameter S_{CD} ($= (2/3)S_{xx} + (1/3)S_{yy}$) is more useful to make comparisons with real experiments, in this work we considered more convenient to calculate the S_{zz} order parameter. This order parameter gives us information about complete order parallel to the interface ($S_{zz} = -0.5$) or complete order in the direction normal to the interface ($S_{zz} = 1.0$). Therefore, by calculating S_{zz} we obtained most of the values between -0.2 and -0.5 (see Fig. 8a) for the 1-dodecanol and the SDS/1-dodecanol systems, which indicated that the tails

were mostly parallel to the interface in agreement with the pictures and the density profiles showed above.

When the surfactant concentration was increased different features were observed. In Fig. 9 we showed a snapshot of the last configuration where it was observed that pure 1-dodecanol seemed to aggregate in a hemicylindrical like-shape composed by layers. In fact, in order to take this configuration most of the molecules on the surface (first layer) formed a parallel structure to one of the box sides (as shown in Fig. 10a). The density profile for the system is shown in Fig. 11 where formation of three layers were clearly depicted. Actually, from the same figure it was possible to estimate the high of the aggregate (which is related with the radius of the hemicylinder) by measuring the last position of the headgroup (or the tail) profile and we found a value of ≈17 Å.

The results for the mixture for the same total number of molecules, 49, were analyzed and we also observed a hemicylinder like-shape (Fig. 12). The density profiles also shown the formation of three layers (Fig. 11b). However, the structure of the first adsorbed layer (Fig. 10b) showed that the molecules had a different pattern of that for the pure 1-dodecanol. Here, not all the molecules were always parallel each other.

When the length of the chains was calculated for both system, the pure and the mixture, we found values of 12.8 Å, for the pure 1-dodecanol (slightly shorter than the chain length of pure 1-dodecanol a low concentration) and 12.4 Å and 12.1 Å for the 1-dodecanol and the SDS chains in the mixture, respectively.

The configuration of the tails was also characterized by the probability of gauche defects and it present the same trend of that at the low surface coverage, however, in this case the first dihedral had 40% probability of trans configuration (Fig. 13a) with an average number of gauche defects of 1.8 for the pure 1-dodecanol system. For the mixture we obtained an average number of gauche defects of 2.2 and 2.0 for the 1-dodecanol and the SDS, respectively. On the other hand, the order parameter was also calculated and we found that the molecules of pure 1-dodecanol were mostly parallel to the surface since the S_{zz} took values between -0.2 and -0.5 (see Fig. 13b). For the mixture we had values around -0.2 for the 1-dodecanol while for the SDS the values were between 0.2 and -0.2 (Fig. 13b) which suggested that the molecules were not all completely parallel to the surface.

3.2. Surfactants at high concentration

Simulations were also conducted even at higher concentration (81 molecules) and different features were observed. Fig. 14 shows
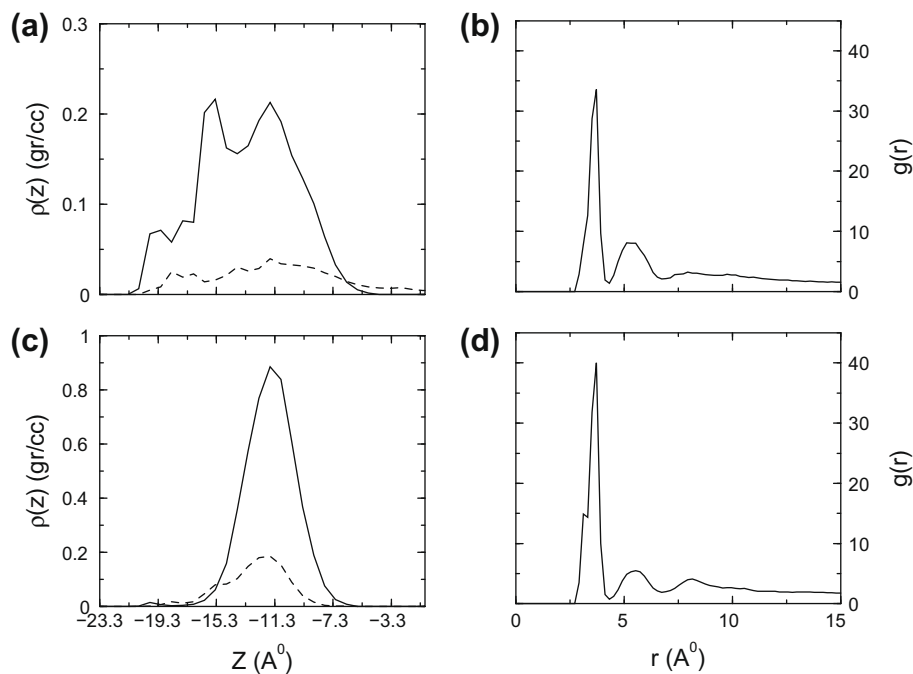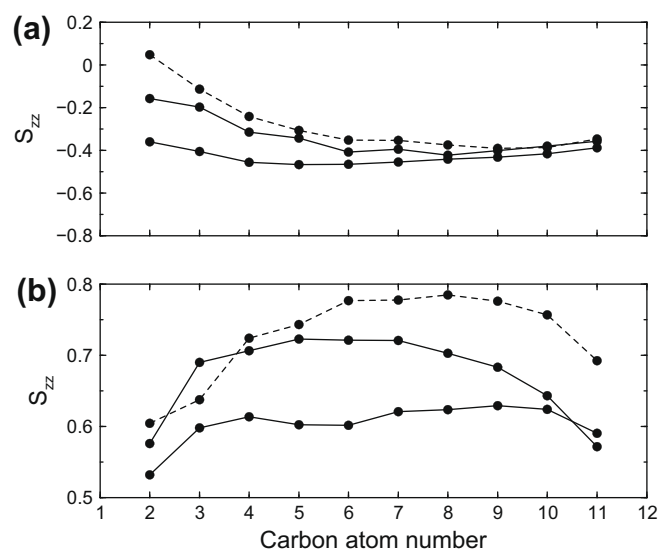
Fig. 6. (a) and (c) are the density profiles of the SDS headgroups (solid lines) and the sodium atoms (dashed lines) at the lowest (total 36 molecules) and at highest concentration (81 total molecules) for the SDS/1-dodecanol mixtures, respectively. (b) and (d) are the $g(r)$ functions of the sulfur atoms (in SDS) with the sodium atoms at the lowest and at the highest concentration for the SDS/1-dodecanol mixtures, respectively.
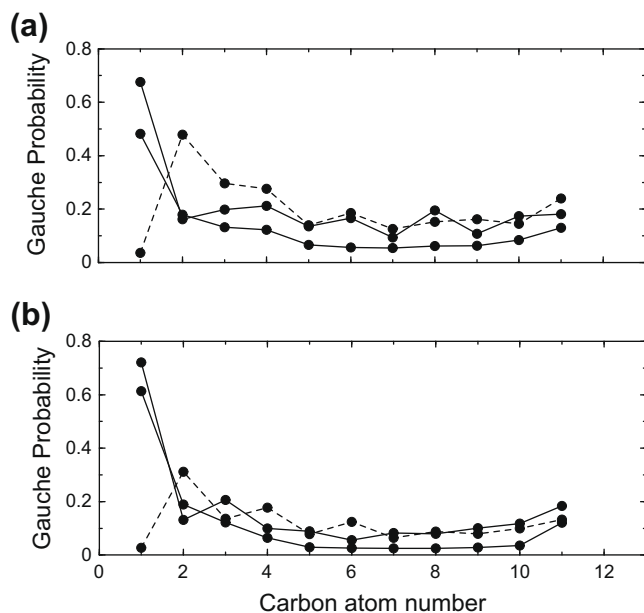
Fig. 7. Probability of gauche defects as a function of carbon position of the surfactant molecules (a) at the lowest concentration (36 molecules) and (b) at the highest concentration (81 molecules). The dark solid line is for the pure 1-dodecanol system. The light solid and the dashed lines are for the 1-dodecanol and the SDS in the mixture, respectively.

Fig. 8. The S_{zz} order parameter as a function of carbon position of the surfactant molecules (a) at the lowest concentration and (b) at the highest concentration. The dark solid line is for the pure 1-dodecanol system. The light solid and the dashed lines are for the 1-dodecanol and the SDS in the mixture, respectively.

a snapshot of the last configuration for the pure 1-dodecanol system where a monolayer-like structure was observed. Interesting from the density profiles (Fig. 15a) was the formation of two water bins, one of them between the monolayer and the graphite wall. In fact this water present strong structure close to the surface as the peaks in the density profiles showed (Fig. 15a). On the other hand, it was noted that most of the surfactant molecules were perpendicular to the interface ($\approx$95% of the molecules) while just some

molecules laid parallel to the interface (see Fig. 14). Since the initial configuration started with the molecules pointed to the solid surface, it seemed that at this high concentration the molecules did not change significantly their configuration, that is why the 1-dodecanol headgroup density profile is not symmetric at both ends of the monolayer (Fig. 15a).

When the distance between head to head peaks was measured, from the density profile, it was found a value of $\approx$15.8 Å. This result suggested that the tails were mostly in their trans configuration which was also confirmed by the small average number of gauche defects of 1.3. From Fig. 7b it was observed that the first dihedral,
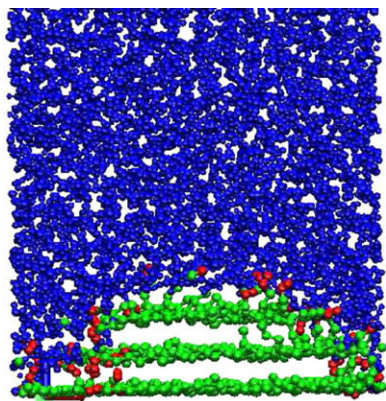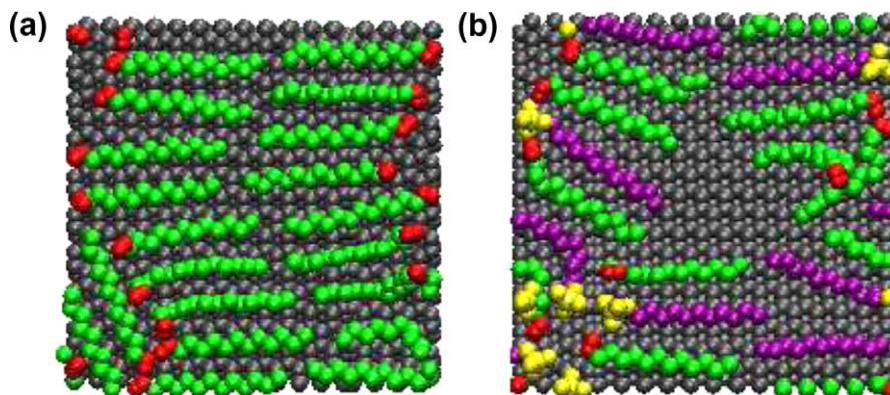
Fig. 9. Snapshot of the pure 1-dodecanol molecules on a graphite surface with 49 total molecules. Colors are the same as in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

H–O–C_1–C_2, had 40% of trans probability whereas the rest of the dihedral had more than 80% of trans probability. When the order parameter of the molecules, S_{zz}, was calculated values around 0.6 (see Fig. 8b) were obtained which suggested that the tails present high order normal to the interface.
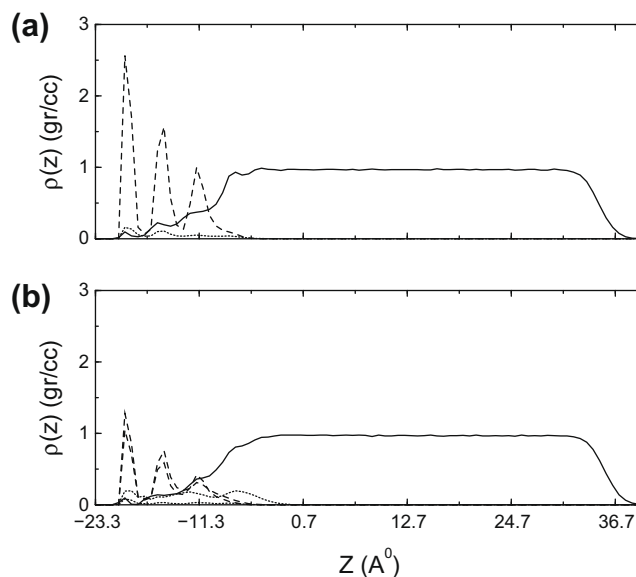
Finally a last simulation was conducted for the SDS/1-dodecanol mixture at high surfactant concentration and the formation of a layer structure was observed (see Fig. 16). In Fig. 15b the density profiles for the system were shown and it was observed structured water close to the graphite surface and a bulk water bin at the other side of the monolayer.

The thickness of the monolayer was estimated by measuring the distance between the head to head peaks from the density profiles and it was found a value of 19.5 Å. In this case the lengths the tails were measured and values of 12.9 Å and 12.8 Å were obtained for the SDS and the 1-dodecanol, respectively. Simulations of the same monolayer mixture at the water/air interface have been conducted at similar SDS–1-dodecanol surfactant ratio, and they found tail lengths of 13.5 Å and 13.2 Å, for the SDS and the 1-dodecanol molecules, respectively [43]. Therefore, those results indicated a slightly thicker monolayer than those obtained in this work.
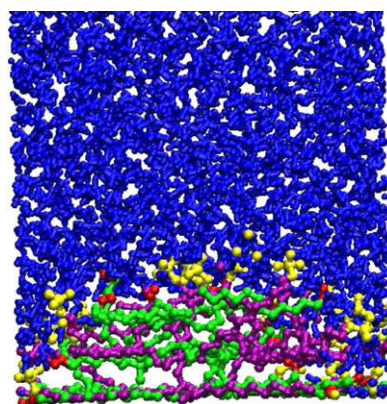
As for the pure 1-dodecanol system (at high concentration) the tails were nearly in their trans configuration (see Fig. 7b) however, from the third dihedral, the SDS and the 1-dodecanol chains pres-

Fig. 11. Density profiles: (a) the pure 1-dodecanol and (b) the SDS/1-dodecanol mixture systems with 49 total molecules. The notation is the same as in Fig. 3.

Fig. 12. Snapshot of the SDS/1-dodecanol mixture with 49 total molecules on a graphite surface. Colors are the same as in Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
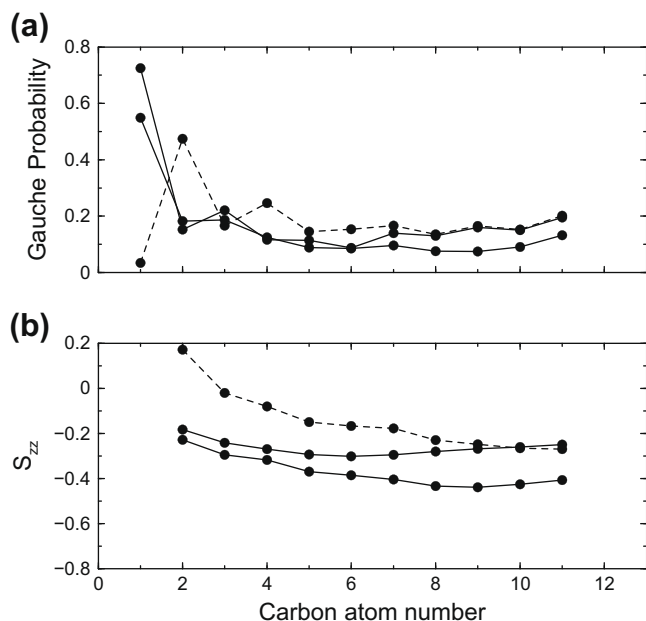

Fig. 10. Snapshots of the first layer adsorbed on the graphite surface at low concentration (49 molecules). (a) The pure 1-dodecanol system and (b) the SDS/1-dodecanol mixture. In (b) in order to accommodate the tails on the graphite surface some headgroups did not lay on the layer. For better visualization the periodic boundary conditions were not removed, therefore some molecules seem to be broken. The graphite atoms are shown in grey whereas the rest of the molecules have the same colors as in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
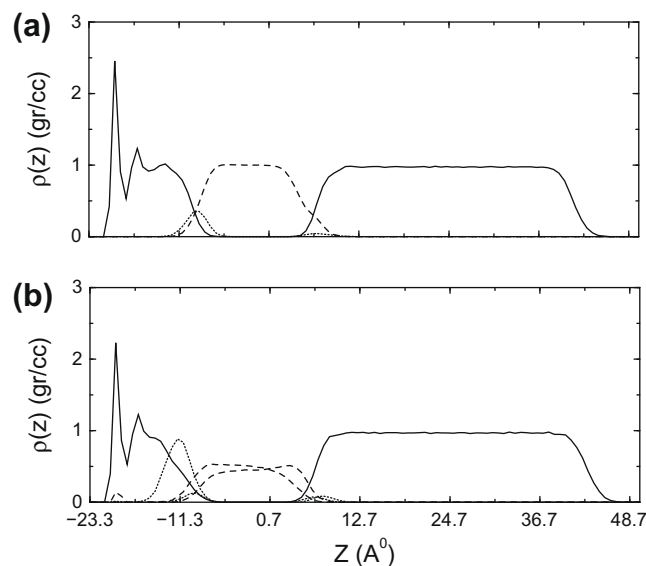
Fig. 13. (a) Probability of gauche defects for the systems with 49 total molecules and (b) the S_{zz} order parameter for the same systems. The dark solid line is for the pure 1-dodecanol system. The light solid and the dashed lines are for the 1-dodecanol and the SDS in the mixture, respectively.
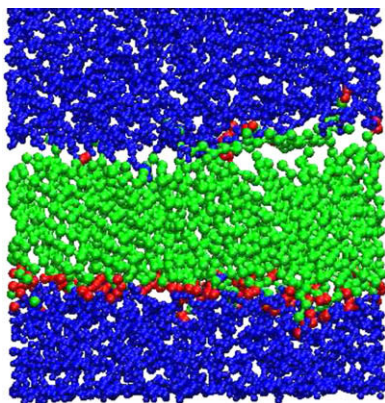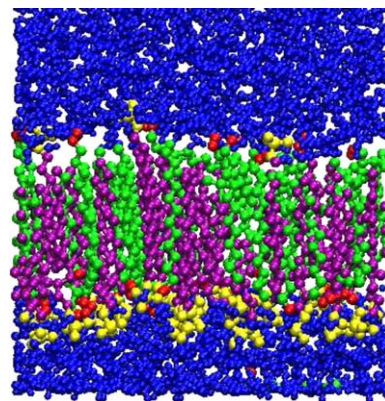

Fig. 14. Snapshot of the pure 1-dodecanol molecules on a graphite surface at the highest concentration (81 molecules). Colors are the same as in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 15. Density profiles: (a) the pure 1-dodecanol and (b) the SDS/1-dodecanol mixture systems at the highest concentration (81 total molecules). The notation is the same as in Fig. 3.

Fig. 16. Snapshot of the SDS/1-dodecanol mixture on a graphite surface at the highest concentration (81 total molecules). Colors are the same as in Fig. 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ent slightly more gauche defects than the chains of the pure 1-dodecanol system. The first dihedral of the 1-dodecanol had only 30% of trans character whereas the first SDS dihedral was almost all trans (see Fig. 7b). The average numbers of gauche defects for this system were 1.3 and 1.9 for the 1-dodecanol and SDS chains, respectively. On the other hand, the SDS and the 1-dodecanol tails present high order along the axis normal to the interface since the S_{zz} order parameter had values above 0.7 (Fig. 8b). In fact, when the average order parameter, $\langle |S_{CD}| \rangle$, was calculated it was found $\langle |S_{CD}| \rangle = 0.37$ and 0.34 for the SDS and the 1-dodecanol tails, respectively, i.e. the 1-dodecanol tails were less ordered than the SDS tails in agreement with the results of reference [43] where the same tendency was showed in the same mixture at the liquid/air interface.

Here, we also analyzed the position of the Na^+ ions with the SDS. In Fig. 6c the position of the ions were observed close to the SDS headgroups. The pair distribution function ($g(r)$) was calculated between the sulfur (in the SDS) and the Na^+ and the first peak

was located in the same position of the $g(r)$ at the low concentration mixture (3.7 Å). However, at this high SDS concentration we observed a small shoulder at 3.2 Å on the left side of the first peak which correspond to the close contact between the sodium atoms and sulfur as other authors have previously observed [50,37,38]. Another difference between this system and the one at low concentration was the third peak depicted from the $g(r)$, suggesting that the Na^+ atoms were more structured around the SDS (Fig. 6c).

4. Discussion and conclusions

Molecular dynamics simulations for the SDS/1-dodecanol mixture adsorbed on a graphite surface were conducted to study the structure of the molecules. From previous simulations it was known that the SDS aggregated in hemicylindrical shapes at low SDS concentration [41] whereas at high concentration the SDS aggregated in full cylinders.

From the present simulations we observed that the structure of the SDS molecules were modified by the present of a second surfactant, in this case the 1-dodecanol.

At low concentration, due to the affinity of the tail groups with the substrate (because of the van der Waals interactions), the SDS and the 1-dodecanol molecules wanted to be on the graphite surface. Actually, when we observed the orientation of the molecules on the first adsorbed layer similar patterns were found than those observed in other simulations [39] and in experiments [49]. So, the 1-dodecanol structure combined with the low SDS concentration induced the SDS molecules to take the same layering structure.

When the total surfactant concentration was increased a different mixture aggregate was obtained. The molecules were still adsorbed on the surface, however, in this case they formed an hemicylinder aggregate. Since, this structure was observed for pure SDS on graphite at a lower concentration, it seemed that the role of the extra component (1-dodecanol) was to slow the formation of the hemicylinder structure. Therefore, the SDS–1-dodecanol interactions, somehow delay the formation of the hemicylindrical structure on the graphite surface. We are currently conducted simulations on other surfaces to determine if the same trends are observed with the surfactant concentration.

When the concentration was even higher, the SDS and the 1-dodecanol molecules formed a monolayer-like structure. Actually, the monolayer was located away from the graphite surface leaving two water bins at both ends of the monolayer. The water bin close to the surface formed well structured layers whereas the other bin was in a bulk phase. Since 1-dodecanol is insoluble in water one expected the tail groups to be close to the graphite surface as the systems at low concentration. Then, in order to check our results we carried out other simulations to see any possible error in our data. Firstly, a simulation for 64 1-dodecanol molecules were also conducted, however, we obtained similar results to those of the system with 81 1-dodecanol molecules. Since we used only two graphite layers we also conducted simulations with four graphite layers, however, once again we did not find any significant differences in the results. Then, we tried to explain the unexpected results in terms of the Hamaker constants.

It is not the purpose of this paper to show the details of calculating the Hamaker constants so, we just mention the relevant results.

The van der Waals interaction between two particles, separated by a distance r is given by $-C/r^6$, where the parameter C is related with the Hamaker constant, $A_H = \pi^2 C \rho_1 \rho_2$ (see e.g. [52]), ρ_1 and ρ_2 are the number density of the molecules of both species, respectively. For two different materials the Hamaker coefficient can be approximated by $A_{H12} = (A_{H1}A_{H2})^{1/2}$. Then, with A_H and ρ_i (calculated by the total number of carbons divided by the volume) the value for C was estimated. In Table 2 we summarized all the results. For water and graphite we took the Hamaker values reported in the literature, $A_H = 3.7 \times 10^{20}$ and $A_H = 23.8 \times 10^{20}$ J, respectively [52,53]. For the 1-dodecanol, we did not find values, so we to took the data given in the literature for hydrocarbons as an approximation, $A_H = 5.0 \times 10^{20}$ J.

We observed that the graphite-1-dodecanol C parameter decreased as the 1-dodecanol density increased ($C \approx 1/\rho_i$). In fact

for the highest 1-dodecanol density the interaction value "C" of graphite-1-dodecanol became comparable with the value of the graphite–water, i.e. the graphite–water interaction was of the same order of the graphite–1-dodecanol interaction. Therefore, due to the competition between the graphite–water and the graphite–1-dodecanol interaction (at the highest 1-dodecanol concentration) the 1-dodecanol might separate from the wall leaving water close to the surface. These results could explain why water approached to the solid wall. Moreover, the 1-dodecanol seemed to have a phase separation, however, a spherical drop was not observed because of the periodic boundary conditions and a continuous monolayer was only observed. We ran the system for a longer time (10 ns more), however, the same configuration remained.

Finally, the results showed that two different surfactants (SDS and 1-dodecanol) with the same concentration are adsorbed on the same substrate by forming different structures. Moreover, if the surfactants are mixed the new structure is determined by the concentration of both surfactants. However, the main conclusion is that the formation of structures on solid surfaces is determined not only by the surfactant–solid and the surfactant–surfactant interactions but also by the surfactant concentration.

Acknowledgments

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Table 2
Hamaker constants, ρ_i refers to water or 1-dodecanol.

	A_H (10^{-20} J)	ρ_{graph} (10^{28} m^{-3})	ρ_i (10^{28} m^{-3})	C (10^{-78} J m^6)
Graphite–H$_2$O	9.38	11.6	3.3	2.47
Graphite–1-dodecanol (36 molec.)	10.09	11.6	0.58	16.15
Graphite–1-dodecanol (49 molec.)	10.09	11.6	0.80	11.19
Graphite–1-dodecanol (81 molec.)	10.09	11.6	1.32	7.17

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