

Computer simulation studies of surfactant monolayer mixtures at the water/oil interface: charge distribution effects

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Abstract

Charge distribution effects on polar head groups for a mixture of amphiphilic molecules at the water/oil interface were studied. For this purpose a model which allowed us to investigate the charge effects exclusively was created. As a molecular model we used the structure of sodium dodecyl sulfate. Then we prepared molecules with the same molecular structure but with different charge distributions in order to have one cationic and one nonionic molecule. So, in this way, we were able to focus only in the charge effects. The monolayer mixtures were composed of anionic/nonionic and cationic/nonionic surfactants. Simulations of these systems show that the location of the different surfactants at the interface is determined by the interaction and the charge distribution of the molecules. Due to the difference in the charge distribution of the surfactant monolayers, the water molecules present distinct orientations in the mixture. Finally, it was found that the electrostatic potential difference across the interface depended on the interactions (charge distribution) of the anionic, cationic, and nonionic molecules in the mixture.

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1. Introduction

Studies of surfactant molecules at liquid/vapor and liquid/liquid interfaces have been the subject of investigations for a long time, not only for their scientific interest but also for their applicability in industry. Consequently, a variety of experiments have been conducted on one-component monolayers [1–9]. However, most commercial products consist of mixtures of surfactants, which have richer properties than individual surfactants. Therefore, surfactant mixtures have also been investigated using several experimental techniques such as calorimetry, X-ray, neutron scattering, and surface tension measurements, among others [10–22]. Moreover, mixtures of anionic–anionic, cationic–cationic, and nonionic–nonionic surfactants and combinations of those molecules have been also treated from the theoretical point of view [23,24].

Over the past years, authors have been investigating the structure and composition of surfactant mixtures, e.g., the arrangement of the surfactants at the interface, the extension

of the chains, and the thickness of the monolayer mixture [15,18,20–22,25]. For instance, in neutron reflection experiments Lu et al. [22] investigated mixtures of dodecanol and sodium dodecyl sulfate (SDS) at the air/water interface and they found variations in the position of the different molecules along the interface. The SDS seemed to penetrate more into the solvent than the dodecanol. They also found that the dodecanol molecule is slightly thicker than the SDS and it is less tilted than the SDS in the monolayer. On the other hand, Penfold et al. [18] conducted experiments with cationic–nonionic (C₁₆TAB/C₁₂E₆) surfactants and they found an increasing change in position of the nonionic molecules at the interface relative to the solvent with increasing solubility of the nonionic molecules.

The position of the different surfactants in the interface is attributed to the different polar groups of the molecules. For instance, surface tension experiments have shown that mixtures with similar hydrophobic tail lengths but with different head groups may show different properties which can affect the structure of the monolayer at the interface. Furthermore, Goloub et al. observed that nonionic mixtures present more ideal behavior compared to anionic/nonionic mixtures [10].

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On the other hand, over the past years computer simulations have been shown to be a powerful tool to study such complex interfacial systems [26–33]. Using this tool is possible, at a molecular level, to extract more information about dynamical and structural properties of such systems which are not easy to get from real experiments. A practical convenience of using computer simulations is the possibility of studying, with an appropriate model, either general or particular properties of a system. Moreover, variations of the model could help us to better understand situations which are not possible in real experiments. For instance, with an appropriate model it is even possible, sometimes, to focus on one particular property of the problem while we keep the other parameters fixed. In this way it is possible to analyze the effect of one particular parameter and its influence on the system. In the present work, the main interest is in studying the effect of the charge distribution on surfactant mixtures at interfaces. Therefore, we prepare a molecular model which allows us to investigate the effect of this unique contribution only. For this purpose, we investigate anionic/nonionic and cationic/nonionic surfactant mixtures at the water/carbon tetrachloride interface. Moreover, in the present work we concentrate on the structure of the surfactants in the vicinity of the interface rather than in the tails as in other works [34]. We analyze how the charge distribution of the molecule heads might affect the monolayer configuration at the interface.

The structure of the prototypical surfactant model which we used was sodium dodecyl sulfate (anionic molecule, SDS). The nonionic and cationic surfactants were created by a model which has an identical SDS molecular structure except in the distribution of the atomic charges; i.e., we were able to have different molecules by changing the charge distribution of the head group. A better description of the molecules and the results will be presented in the next sections.

2. Computational method and model

For the present study we performed computer simulations for two different systems, the anionic/nonionic and the cationic/nonionic monolayer mixtures. For the anionic molecule we used a molecular model of a hydrocarbon chain with 12 united carbon atoms (sites 6S–C12 in Fig. 1) attached to a head group (sites 1S–5S in Fig. 1). The present configuration has been used to model the sodium dodecyl sulfate surfactant. Moreover, the intermolecular and intramolecular potential parameters for that model were calculated and reported in the literature as well as the charges used for the different sites [29]. Therefore, in this paper we used those parameters (Table 1) to represent the common sodium dodecyl sulfate surfactant [29]. Therefore, we call this molecule SDS. We chose this molecule since its molecular structure is simple and it has been used in other simulations [29,34]. In order to concentrate only on the effects of the charge distribution, we constructed two other surfactants using the same

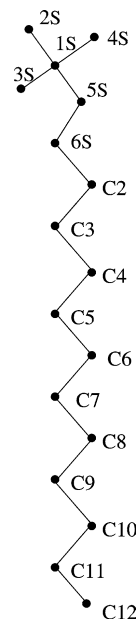


Fig. 1. Molecular model for the anionic surfactant. The cationic and nonionic surfactants have the same structure but different charge distributions (see Table 1). The sites are given by 1S, 2S, 3S, . . . , etc., and the sites of the cationic and nonionic molecules are represented with a C (for the cationic) or E (for the nonionic) at the end of the label, i.e., 1SC, 2SC, etc., and 1SE, 2SE, etc., respectively.

Table 1
Atomic charge for each site of the SDS, SDSC and SDSE molecules

q (charge, site)	SDS	SDSC	SDSE
1	1.284	−1.284	−1.284
2	−0.654	0.654	0.654
3	−0.654	0.654	0.654
4	−0.654	0.654	0.654
5	−0.459	0.459	0.459
6 attached to 5	0.137	−0.137	−1.137
C2–C12	0.000	0.000	0.000
Counterion	1.000	−1.000	

See also Fig. 1 (the SDS charges correspond to the sodium dodecyl sulfate molecule with the SO_4 head group).

structure of the previous anionic molecule. However, we changed the charges of the new surfactants to have a cationic or a nonionic molecule. For the nonionic molecule the signs of all charges were reversed from the anionic model; i.e., we replaced positive charges by negative ones and vice versa and we removed the counterion. The charge of the counterion was included in the head group (Table 1). The tails for all the molecules were kept the same as in the SDS molecule. We call the new nonionic molecule SDSE. The selection of this model has shown good experimental tendencies for simulations of anionic/nonionic monolayers [34]. Finally, for the cationic molecule we employed the same model used by Berkowitz and coworkers [30] (Table 1), where the molecule is identical to the SDS except that the signs of all charges, including the counterion, are reversed. We call the new molecule SDSC. It is worth to mention that the new molecules (SDSE, SDSC) do not represent real surfactants,

since the charge sites might not correspond to the charges of real molecules. However, by using the same anionic molecular structure for the nonionic and cationic molecules we will be able to maintain the same surface coverage, chain length, and head group geometry, while focusing only on the effects of the polar interactions.

Therefore, due to the model of nonionic and cationic molecules we have to be careful with any direct comparison with experiments. Nevertheless, even though the new molecules might not have the structures of real nonionic (cationic) surfactants, the model of these surfactants will allow us to investigate the role of the polar groups in the structure of monolayer mixtures at the water/oil interface. Moreover, the model will help us to obtain more information about the behavior of the different surfactants at the interface that sometimes is not easy to get from experiments. Therefore, we believe that the present model will give us new insight (from a microscopic point of view) and it will establish how the polar head group of the surfactants affects the structure of the monolayers. Furthermore, when and where possible, a comparison with experimental situations could be performed.

For water molecules we used the SPC model and for carbon tetrachloride, CCl_4 , we used the same rigid molecule as in a previous work [33]. All simulations were carried out in the NVT ensemble with a time step of 0.002 ps using the DL-POLY package [35]. Bond lengths were constrained using the SHAKE algorithm with a tolerance of 10^{-4} . The temperature was controlled using the Hoover–Nose thermostat with a relaxation time of 0.2 ps. All simulations were performed at $T = 300$ K. For the long-range electrostatic potential we used 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 prepared as in Ref. [33]. Initially, we constructed a monolayer of 56 SDS molecules in the all-*trans* configuration placed in a box of dimensions x and y of 46.09 Å. This configuration corresponds to an area per head group of $37.9 \text{ \AA}^2/\text{molecule}$, which is lower than the saturation area of $59 \text{ \AA}^2/\text{molecule}$ for a SDS monolayer at the water/ CCl_4 interface [4]. The z -dimension of the box was set to 150 Å. This length was enough to accommodate two liquid slabs and to prevent the formation of a second water/ CCl_4 interface. Instead, two vapor/liquid interfaces at the opposite ends of the box (on the $z < 0$ side the vapor/water interface and on the $z > 0$ side the liquid CCl_4 /vapor interface) were present in the box.

With the head groups of the molecules initially pinned, we performed a short MD simulation at $T = 300$ K. Then the temperature was increased to 400 K in order to randomize the tails. Subsequently, the temperature was decreased in short runs until we reached $T = 300$ K. At this point, we added 1185 water molecules surrounding the head groups and a layer of 415 CCl_4 molecules was placed in the region of the tails. Water was placed at $z < 0$ and CCl_4 at $z > 0$. The system was then equilibrated for 100 ps. Finally, 56 counterions

were randomly inserted in to the interfacial region. This final configuration was equilibrated for 300 ps.

The anionic/nonionic (SDS/SDSE) monolayer was constructed from the single SDS monolayer. We replace 18 SDS with 18 SDSE molecules, also removing 18 counterions. The cationic/nonionic (SDSC/SDSE) mixture was prepared from the SDS monolayer by replacing 38 SDS molecules by 38 SDSC molecules (with their counterion atoms) and the other 18 SDS molecules by SDSE molecules (removing the same number of counterions).

In this way we prepared two different monolayer mixtures which were simulated for 25 ps with the head groups pinned. Finally, with the head groups free, each system was equilibrated for an extra 300 ps. All the simulations were performed up to a 1.25-ns run and we collected data from the last 500 ps for analysis. Configurational energy was monitored as a function of time to determine when the system reached equilibrium.

It should be mentioned that the behavior of the nonionic (SDSE) surfactant is affected not only by contact with the two distinct cosurfactants but also by contact with the other molecules in the system. Since water molecules should have different arrangements around the SDS or SDSC surfactants, the counterions can be located at different positions along the interface (depending on the water molecules' orientations) in each mixture. Therefore, the electrostatic interactions between the SDSE and the SDS or SDSC molecules should also be influenced by the interactions with the counterions and the different water molecules in the two mixtures. This point will be discussed furthermore in the results.

3. Results

In this section we present the calculations of the monolayer mixtures. Analysis of the structure and the orientation of the surfactant molecules in the mixture is also discussed.

3.1. Density profile, head group, and hydrocarbon chain length

The first analysis was performed for the density profiles. In Fig. 2 we show the profiles for the neat water/ CCl_4 interface (top), SDSC/SDSE (middle), and SDS/SDSE (bottom) mixtures at the water/ CCl_4 interface. The z -dependent density profiles for the liquids, headgroups, and hydrocarbon tails of each surfactant molecule are plotted separately. The head group density profile includes the polar group and, when it is the case, the counterion. In the SDS/SDSE mixture (bottom of Fig. 2) we have more SDS than SDSE molecules. Thus the profiles of the SDS molecule are higher than those of the SDSE molecule. It is also observed for this system that the head group of the SDS (anionic molecules) penetrates more into the water phase than the SDSE head group (nonionic molecules). What is interesting to analyze is the

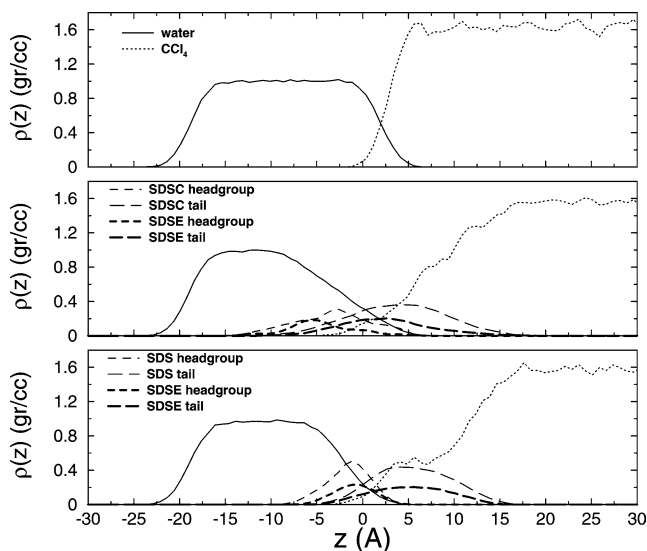


Fig. 2. Density profiles for the neat water/ CCl_4 interface (top) and the cationic/nonionic (SDSC/SDSE) (middle) and the anionic/nonionic (SDS/SDSE) (bottom) monolayers at the water/ CCl_4 interface. The middle picture corresponds to the monolayer of 38 SDSC molecules with 18 SDSE molecules. The bottom picture represents the monolayer of 38 SDS molecules with 18 SDSE molecules. Water is depicted by the solid line, CCl_4 by the dotted line, the SDS (SDSC) head groups by the short light dashed line, and the SDS (SDSC) tails by the long light dashed line. The SDSE head groups are given by the short dark dashed line and SDSE tails by the long dark dashed line.

average position, calculated by fitting a Gaussian, in the profiles of the head groups and the tails,

$$\rho = \rho_0 \exp\left(\frac{-4(Z - Z_0)^2}{\sigma^2}\right). \quad (1)$$

The mean average position of the SDS head group (Z_0 in the Gaussian) is located around $Z_0 = -1.4 \text{ \AA}$, whereas for the SDSE, the head is around $Z_0 = -0.850 \text{ \AA}$. The last results agree with previous simulations of the same system at different concentrations [34]. In neutron reflection experiments at 300 K on monolayer mixtures of SDS/dodecanol at the water/air interface it is observed that the SDS volume fraction profile is displaced toward the water from the dodecanol profile [18,22]; i.e., the SDS seems to be closer to the solvent [36].

For the SDSC/SDSE mixture (middle) it is observed that the profiles are more spread at the interface, even though the head group profile of the SDSE (nonionic) molecules seems to be deeper into the water than the SDSC (cationic) molecules. In previous experiments on $\text{C}_{16}\text{TAB}/\text{C}_{12}\text{E}_6$ at the water/air interface [18] it was observed that the volume fraction profiles of both molecules coincide for lower C_{12}E_6 concentrations. In experiments on benzyl alcohol with C_{16}TAB at the air/water interface, it was observed that the relative positions of the volume fraction distributions are not too different [37]. Also, experiments on C_{16}TAB and C_{12}E_6 show similar positions of the volume fraction distribution at the air/water interface for both surfactants [38]. In other experiments on dodecane and C_{12}TAB , that the C_{12}TAB is slightly

deeper into the solvent [36]. However, for systems richer in C_{16}TAB than in C_{12}E_6 the distribution of the nonionic molecules seem to be slightly shifted to the solvent [18]. In our case we conducted simulations of those experiments at much lower surface coverage areas and the SDSC/SDSE monolayer was richer in cationic than in nonionic molecules. So that could be the reason for this behavior. We also observe from the profiles that the SDSC/SDSE monolayer extent is greater than that of the SDS/SDSE mixture at the water/oil interface. Computer simulations of pure cationic surfactants (using the same model described above) showed that the head and the tail groups of these molecules penetrate more into the water than the head and the tail groups of pure SDS molecules at the same water/ CCl_4 interface [30].

It is also possible to observe the reduction of the surface tension of the water/oil interface due to the surfactant monolayer by observing the width of the interfaces. The middle and bottom pictures of Fig. 2 show a large increase in the width of the interfacial region relative to the pure water/ CCl_4 system (top). However, it is also possible to calculate the surface tension by the quantity

$$\Gamma = L_z(\langle P_n \rangle - \langle P_t \rangle), \quad (2)$$

where $\langle P_n \rangle$ is the normal pressure, $\langle P_t \rangle$ is the average tangential pressure, and L_z is the length of the box in the z -direction. When the simulation box contains several interfaces, the value of Γ is equal to the surface tension γ of each interface,

$$\Gamma = \sum \gamma_i. \quad (3)$$

For instance, in the vapor/water/ CCl_4 /vapor system

$$\Gamma = \gamma_{v/w} + \gamma_{w/o} + \gamma_{o/v}, \quad (4)$$

where $\gamma_{v/w}$ is the surface tension for the vapor/water interface, $\gamma_{w/o}$ is the surface tension for the water/organic liquid interface, and $\gamma_{o/v}$ is the surface tension for the organic liquid/vapor interface. In the presence of surfactant molecules at the water/ CCl_4 interface the surface tension of the interface water/organic liquid will be changed, $\tilde{\gamma}_{w/o}$.

The surface tensions for the systems are $128.0 \pm 4 \text{ Nm/m}$, $87.2 \pm 5 \text{ Nm/m}$, and $83.1 \pm 5 \text{ Nm/m}$ for the water/ CCl_4 , water/SDS–SDSE/ CCl_4 , and water/SDSC–SDSE/ CCl_4 interfaces, respectively; i.e., the surface tension of the water/ CCl_4 interface decreases in the presence of the surfactant mixtures. For the surface tension of the air/water and CCl_4 /air interfaces we found 68.8 Nm/m and 21.4 Nm/m , respectively [33]. However, since the same interfaces are present in all the systems, those values are constant in Eq. (4). Due to the strong interactions between the water molecules and the polar head groups (of the surfactants) compared to those between the water and the CCl_4 molecules these last molecules try to move away from the interface, leading the water molecules closer to the polar groups than to the oil molecules. Therefore, since there are a large number of surfactant molecules at the interfacial area we just observe few CCl_4 molecules close to the water.

The orientation of the head group of each surfactant in the mixture is measured from the total length from the most opposite atoms, sites 2–5 (Fig. 1), (δ_{hg}) and the projection of the head group along the normal to the interface (δ_{zhg}), δ_{zhg}/δ_{hg} . In the SDS/SDSE mixture, the angle that the SDS head group makes with the normal is slightly lower than that of the SDSE, indicating that the head group of the SDSE somehow is more bent toward the interface plane. The angles of the head groups with the normal to the interface are 54° and 58° for the SDS and SDSE molecules, respectively. For the SDSC/SDSE mixture we found angles of 51° and 53° for the SDSC and SDSE molecules, respectively. It seems that in the last case the headgroups of both surfactants have similar inclinations with respect to the normal to the interface.

The thickness of the tails was also measured for each surfactant of the SDS/SDSE and SDSC/SDSE mixtures. We found that in the SDS/SDSE monolayer the thickness (measured as the projection of the total tail length along the normal to the interface) is 9.4 and 10.3 Å for the SDS and the SDSE tails, respectively. Experiments on SDS/C₁₂E₆ shown that the thickness of the adsorbed layer at the oil/water interface varies from 8.0 to 15.0 Å [39]. With these values, the tilt angles were estimated as 36° and 31° for the SDS and the SDSE tails, respectively. These results are in agreement with experiments where people see that the tails of non-ionic molecules are thicker and more straight than the tails of the anionic molecules [22]. For the SDSC/SDSE monolayer mixture we found that the thicknesses of the tails are 9.6 and 9.9 Å for the SDSC and SDSE tails, respectively. The tilt angles are 35° and 33° for the SDSC and the SDSE, respectively. Therefore, for this mixture, under the present conditions, the tails of both surfactants have nearly the same length and inclination.

3.2. Structure of the molecules at the interface

The arrangement of the head groups of the surfactant molecules with water was also analyzed by the pair distribution function $g(r)$. $g(r)$ can give us information about how water molecules are located at the interface and their distribution around the head groups of the different surfactants in the mixture. Then, we looked at the relative positions of the central atoms (sites 1S, 1SC, and 1SE for the SDS, SDSC, and SDSE, respectively, in Fig. 1) with the water oxygens and we calculated the $g(r)$. Fig. 3 shows the $g(r_{1S-OW})$ and $g(r_{1SE-OW})$ of the SDS/SDSE monolayer. The picture indicates that there are more water molecules and they are closer to the 1S (anionic head groups) than to the 1SE (nonionic head groups) atoms. The first peak of $g(r_{1S-OW})$ is around 4.0 Å, where the first solvation shell is defined. This distance of first water neighbor molecules from central atoms of a SDS molecule was also found in previous studies of SDS at the water/CCl₄ interface at low coverage [29]. However, in this case it is difficult to define a second peak for the next nearest neighbors. It is important to mention that the monolayer is an inhomogeneous and nonsymmetric system

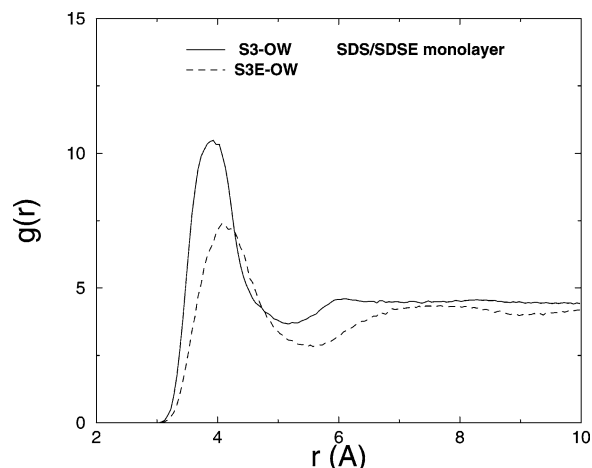


Fig. 3. The radial distribution function, $g(r)$, of S3-OW ($g_{S3-OW}(r)$, solid line) and S3E-OW ($g_{S3E-OW}(r)$, dashed line) in the SDS/SDSE monolayer mixture.

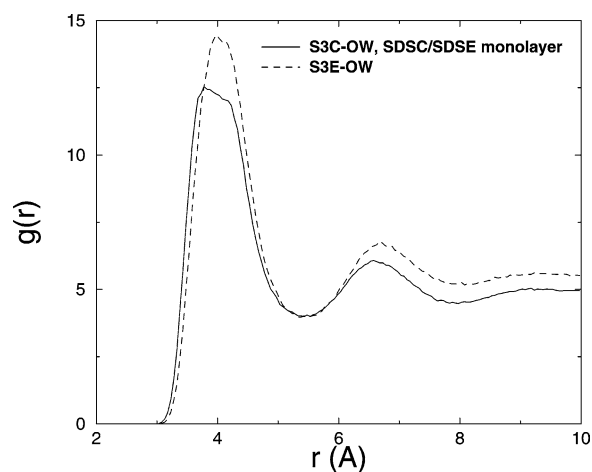


Fig. 4. The radial distribution function, $g(r)$, of S3C-OW ($g_{S3C-OW}(r)$, solid line) and S3E-OW ($g_{S3E-OW}(r)$, dashed line) in the SDSC/SDSE monolayer mixture.

in the z -direction; i.e., in our case, the water is placed only on the negative z -axis. Therefore, the $g(r)$ of the surfactant–water does not go to unity and it seems to take large values compared to the usual $g(r)$'s of bulk systems. For the SDSC/SDSE monolayer we observe that water molecules are also slightly closer to the cationic than to the nonionic surfactant (Fig. 4). It is also interesting to observe that these $g(r)$'s have more structure than those of the SDS/SDSE monolayer. We found the first solvation shell around 4.0 Å and in this case we clearly observe a second peak around 6.5 Å. It seems that there are more water molecules next to the surfactants of the SDSC/SDSE monolayer than next to the surfactants of the SDS/SDSE monolayer.

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 one central atom (1S, 1SE, or 1SC) of the surfactant molecule and the water dipole

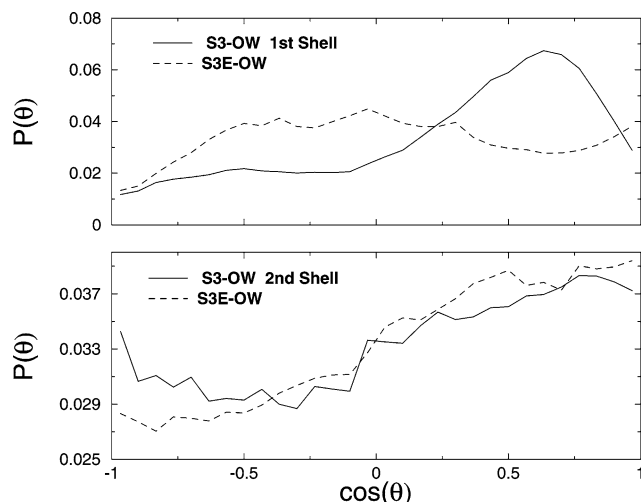


Fig. 5. Orientational distribution functions of water in the (a) first and (b) second solvation shells around the central atoms of the anionic (S3) and nonionic (S3E) mixture. θ refers to the angle between the S3(S3E)–OW (water oxygen) vector and the water dipole vector in the SDS/SDSE mixture. The solid line is the distribution of the S3–OW and the dashed line is the distribution of the S3E–OW vector.

vector of the same water molecule (1S–OW and 1SC–OW). The distribution was calculated in two surrounding shells defined by the distances of the first and second nearest neighbors in the $g(r_{1S-OW})$, $g(r_{1SE-OW})$, and $g(r_{1SC-OW})$ calculated above (Figs. 3 and 4) for each monolayer mixture.

Fig. 5 shows the 1S–OW and 1SE–OW angular distributions for the SDS/SDSE mixture. The top of Fig. 5 indicates that the water dipole has the highest probability pointing approximately 51° away from the oxygen-to-central atom vector with respect to the anionic molecules. This value is in agreement with that observed previously in simulations of SDS at the water/oil interface [29]. On the other hand, the angular distribution of dipole water molecules around the nonionic molecule presents a different shape with respect to that of those next to the anionic molecules. In this case, the distribution is broader and it has its maximum approximately at 92° . Therefore, the water dipoles point further away from the nonionic molecules than from the anionic ones. The angular water dipole distribution in the second solvation shell looks similar. As mentioned above, in this system there is not a second solvation shell; therefore we calculate the shell from $5.5\text{--}6.0\text{ \AA}$ to 9.5 \AA from the $g(r_{1SE-OW})$. The maximum value for both distributions is approximately at 40° . Thus, for distances larger than 5.5 \AA , the water dipoles seem to have similar orientations with respect to the central atom (1S and 1SE) for the different surfactants. We also measured the average orientation of the water dipoles at the interface (next to the head groups) and we found an angle of 78° pointing to the positive z -axis with respect to the normal to the interface.

For the SDSC/SDSE monolayer mixture different features were observed for the angular distributions with respect to the SDS/SDSE monolayers (Fig. 6). For instance, the shapes of the SDSC/SDSE distributions are different from those of the SDS/SDSE. However, if we compare the distri-

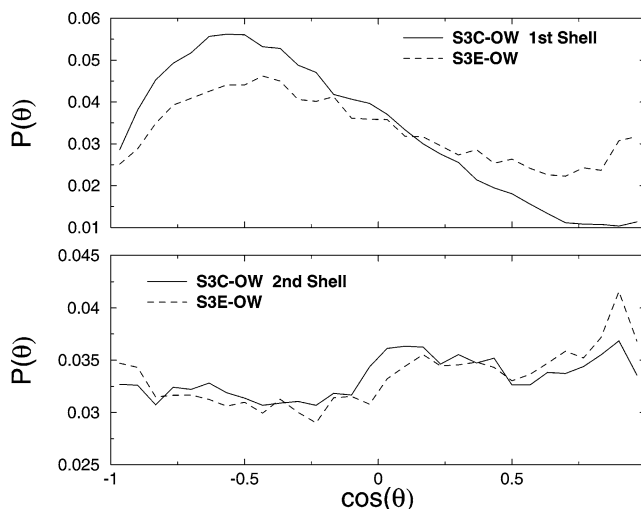


Fig. 6. Orientational distribution function of water in the (a) first and (b) second solvation shells around the central atoms of the cationic (S3C) and nonionic (S3E) mixture. θ refers to the angle between the S3C(S3E)–OW (water oxygen) vector and the water dipole vector in the SDSC/SDSE mixture. The solid line is the distribution of the S3C–OW and the dashed line is the distribution of the S3E–OW vector.

bution of the SDSC/SDSE monolayer in the first solvation shell we note that both distributions, i.e., the angle between the water dipole and the 1SC–OW or 1SE–OW vector, are similar. However, the maximum values of the distributions are at 125° and 116° for the 1SC–OW and 1SE–OW vectors (with the water dipole), respectively. On the other hand, from the bottom of Fig. 6 it is possible to observe that both distributions are quite similar and more uniform in the second solvation shell. In this case the average angle that water dipoles (at the interface) make with the normal to the interface is approximately 72° , pointing to the negative z -axis.

The common surfactant in both mixtures is SDSE and due to the symmetry of charges between the anionic and the cationic molecules the properties of the SDSE molecule could depend only on the charge distribution of the cosurfactants. However, from the last results we observed that the structure of the interfacial water molecules is different around the SDS and the SDSC molecules, as well as the average dipole orientation at the interface in each mixture. Even more, close to the SDSE headgroup, the orientation of water is also different in the two mixtures. The respective counterion distribution in each mixture might also be different. Therefore, the properties of the SDSE surfactant are influenced not only by the charge distributions of the cosurfactants but also by the interactions with the water and the counterions. For instance, the positions of the SDSE molecules and their orientations are not the same at the interface when they are with the SDS or SDSC molecules, as is observed.

3.3. Electrical potential

An important difference between the surfactant molecules in the mixture is the charge in their head groups. So

we measured a property that is directly connected with the distribution of charges in the system; i.e., we analyzed the electric potentials of the different monolayer mixtures. In computer simulations, the electrical potential is calculated using the formula

$$\Delta\phi = \phi(z_2) - \phi(z_1) = - \int_{z_1}^{z_2} dz' E_z(z'), \quad (5)$$

where the electric field is given by

$$E_z(z) = \frac{1}{\epsilon_0} \int_z^{z_1} dz' \rho_q(z'); \quad (6)$$

here $\rho_q(z)$ is the charge density. The reference potential $\phi(z_1) = 0.0$ V was chosen in the vacuum region ($z < 0$) far from the interface. For the calculation of the potential we included the surface term in the electrostatic forces discussed in early works [33,40].

In Fig. 7, the charge density profile, the electric field, and the potential difference across the interface are plotted for the different systems. We observed that the charge density profile does not show much difference between the different monolayer mixtures in comparison with the electrostatic field, where a more significant difference can be appreciated. However, a higher difference is observed in the surface potential. Measuring the potential difference across the interface, we obtain potential differences of approximately 140 and 840 mV for the SDS/SDSE and SDSC/SDSE mixtures, respectively. This large difference (by a factor of 6) in the potential was also observed in simulations of pure cationic and anionic monolayers at the water/CCl₄ interface with the same molecular model [30]. We explain the large potential

difference in the two mixtures by two effects. The orientations of the water dipoles, at the interfaces in the two monolayer mixtures are different (as pointed out in the previous section) and the SDSC/SDSE monolayer is more spread at the interface than the SDS/SDSE monolayer.

4. Conclusions and discussion

We performed a series of molecular dynamics computer simulations of anionic/nonionic (SDS/SDSE) and cationic/nonionic (SDSC/SDSE) mixtures at the water/CCl₄ interface. The cationic surfactant was prepared with the same SDS molecular structure but reversing the atomic charges. For the nonionic surfactant we used a similar procedure; the charge distribution of the SDS molecule was changed in order to get a zero total net charge in the molecule. We studied the structure of the anionic, cationic, and nonionic surfactants in the monolayers at the interface. From the density profiles we observed the difference in the structure of the anionic, cationic, and nonionic molecules, which occurs simply because of the different charge distribution in the head groups. For the anionic/nonionic mixture it is observed that the anionic surfactant penetrates more into the water, whereas for the cationic/nonionic mixture the nonionic surfactant is slightly deeper in the water region. Orientation of the water near the surfactants in the mixture was also measured. We found for the anionic/nonionic mixture that water is closer to the anionic than to the nonionic headgroups. Moreover, the water hydrogens next to anionic molecules point toward the central group, whereas hydrogens next to nonionic molecules seem to point away from that group. For the cationic/nonionic mixture we observed that water near to the surfactants is slightly closer to the cationic than to the nonionic headgroups. In this case water oxygens are pointing to the positive head group. We also investigated the tail configuration of the monolayer mixtures. The results indicate that for the anionic/nonionic mixture the tails of the nonionic surfactant are thicker and more straight than the anionic tails. On the other hand, for the cationic/nonionic mixture, both surfactants have similar thicknesses and inclinations with respect to the interface. Finally, we also measured the difference in the electrostatic potential across the interface and we found that for the anionic/nonionic monolayer this difference is significantly lower than for the cationic/nonionic monolayer.

As mentioned before, due to the models of the cationic and nonionic molecules, the comparison with experiments is not straightforward, even though, in some cases, it was possible to observe similarities to experimental results. Therefore, these simulations would show us more insight about the role of the polar head group and the charge distribution of the surfactants in the behavior of monolayer mixtures.

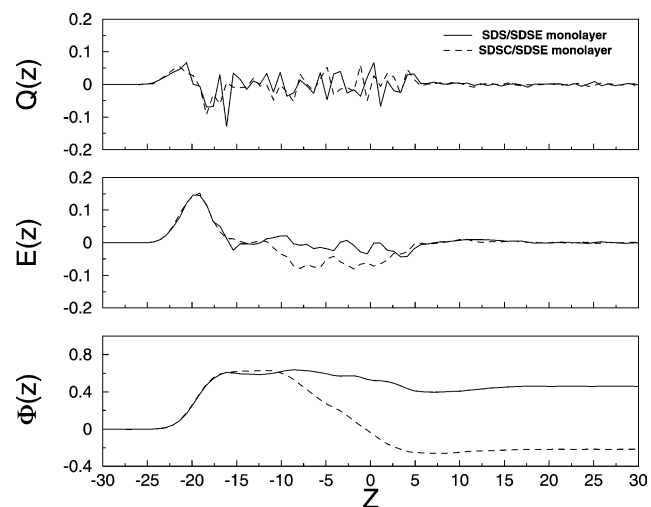


Fig. 7. Charge density profile for the SDS/SDSE and the SDSC/SDSE monolayer mixtures at the CCl₄/water interface (top panel). The electric field is depicted in the middle and the potential profile in the bottom panel. The solid line is for the SDS/SDSE and the dashed line is for the SDSC/SDSE mixture.

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