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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.

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 interfaces [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.

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

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.

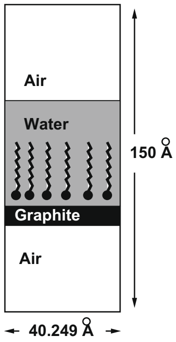

Fig. 1. Schematic representation of the surfactant system at the liquid/solid interface.