



# Adsorption of phenol molecules by sodium dodecyl sulfate (SDS) surfactants deposited on solid surfaces: A computer simulation study



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## ABSTRACT

Adsorption studies of phenol molecules on a sodium dodecyl sulfate (SDS) micelle were investigated by molecular dynamics simulations. Simulations were carried out in bulk and on three distinct solid surfaces, silicon dioxide, titanium dioxide and graphite. It was observed that different surfactant micellar shapes were formed on the surfaces. For the silicon dioxide and titanium dioxide surfaces the surfactants were adsorbed by their headgroups whereas for the graphite surface they were adsorbed mainly by their tail groups. It was found that the amount of phenol adsorbed on the SDS micelle was altered by the surfactant shape deposited on the solid surface. However, the best phenol adsorption was obtained by the surfactant modified silicon dioxide surface. Moreover, in all cases, from structural investigations, it was determined that the phenol molecules were located inside the surfactant micelle with their hydroxyl groups close to the SDS headgroups.

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## 1. Introduction

It is well known that the presence of phenol in nature has become a major concern in recent years due to its toxicity and negative effects on the environment. Moreover, phenol and its analogues have shown toxic effects not only on aquatic flora and fauna [1] but also on human beings. In fact, due to phenol, several biochemical functions seem to be affected in humans [2,3]. Therefore, phenol has been classified as a priority pollutant by the US Environmental Protection Agency [4].

The technological treatments for phenol removal from waste waters may be either by biological or physicochemical methods. Biological methods are suitable for low phenol concentrations while physicochemical methods allow to handle from moderate to high levels of phenol. Furthermore, biological processes have long-term biodegradation which make them inefficient for wastewater treatment.

Various chemical and physicochemical methods have been proposed for wastewater containing phenol [5–9]. The adsorption technique is recognized as a feasible method for phenol removal due to its simplicity and its availability to be used with a wide range of adsorbents. In fact, during the last decades, new materials

capable to adsorb nonionic organic compounds from aqueous solutions have been synthesized. Some of them are surfactant modified materials [10–12].

Since most surfactants can be adsorbed at solid/water interfaces they can be used to improve adsorption of hydrophobic compounds that would not be typically adsorbed on a particular solid. This process is known as surface solubilization [13], coadsorption [14] or adsolubilization [15].

Nowadays it is well known that surfactants can aggregate on solid surfaces by forming admicelles or hemimicelles with changes in their concentration. In particular, hydrophobic admicelles, formed by the hydrocarbon surfactant tails, might create sites capable to solubilize water-insoluble molecules such as phenol. However, where the hydrophobic solubilized molecules are deposited in the micelle depends on several factors such as the surfactant head (ionic or nonionic), the alkyl chain length and even of the aggregate shape [16].

The aim of this work is to use molecular dynamics simulations to compare the adsolubilization process of phenol on different solid surfaces with an anionic surfactant. In particular, we study the adsolubilization of phenol molecules by the sodium dodecyl sulfate surfactant (SDS) on silicon dioxide, titanium dioxide and graphite surfaces.

## 2. Computational method and model

The present work was divided in two different stages: the study of phenol with sodium dodecyl sulfate in aqueous solution and the

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**Table 1**  
Spatial dimensions and number of molecules used to build the solid surfaces.

Solid surfaces				
Surface	$I_x(\text{Å})$	$I_y(\text{Å})$	$I_z(\text{Å})$	No. of molecules
Silicon dioxide	43.702	43.702	150.0	578
Titanium dioxide	39.942	40.246	150.0	468
Graphite	40.523	38.995	150.0	1232

coadsolubilization of phenol by the sodium dodecyl sulfate modified surfaces.

For the first stage a cubic box ( $58 \text{ Å}^3$ ) with 40 phenol molecules, 36 SDS and 5500 water molecules, was constructed. Then, simulations were carried out in an NPT ensemble using periodic boundary conditions in all directions. For the second stage, three different solid surfaces (with adsorbed SDS surfactant molecules) were employed, silicon dioxide in its cristobalite form (with cell orientation 001), titanium oxide as rutile (with orientation 110) and graphite. The modified surfaces were prepared with 36 SDS molecules (initially placed perpendicularly to the surfaces with their head groups pointing to the solid) and 3000 water molecules in a rectangular box. The final structure of the SDS aggregate, in each surface, was similar to those reported in previous works [17,18]. Once the SDS molecules aggregated on the surface 40 phenol molecules, to the final configuration, were added on the top of the SDS structure. All simulations with solid surfaces were carried out in the NVT ensemble using periodic boundary conditions. Dimensions of the simulations boxes are given in Table 1. In all cases the Z-dimension was long enough to prevent the formation of a second liquid/solid interface due to the periodicity of the system. Instead, a liquid/vapor interface was present at one end of the box ( $z > 0$ ).

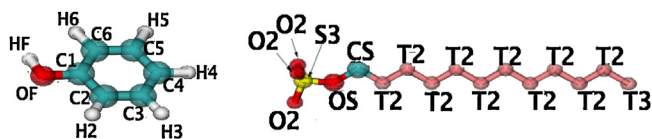
All simulation parameters for the phenol, the sodium dodecyl sulfate and the solid surfaces were taken from previous works [19–22]. For water molecules the Simple Point Charge (SPC) model was used [23]. The surfaces were constructed using an atomistic model with parameters already reported in the literature [17,18]. The structure of the phenol and SDS molecules used in the present work are shown in Fig. 1.

Simulations were run in the DL-POLY package [24] with a time step of 0.002 ps using the Nosé-Hoover thermostat at temperature  $T = 298 \text{ K}$  with a relaxation time of 0.2 ps [25]. Bond lengths were constrained using SHAKE algorithm with a tolerance of  $10^{-4}$ . The short range interactions were calculated with a Lennard Jones potential with a cut-off radius of 10 Å and using the Lorentz-Berthelot rules for the unlike interactions [26]. The electrostatic interactions were handled with the particle mesh Ewald method [27,28]. All simulations were run up to 14 ns and configurational energy was monitored as a function of time to see when systems reached equilibrium (plots of those energies for the last picoseconds of the simulations are given in the supplementary data). Then, analysis were conducted for the last 2 ns.

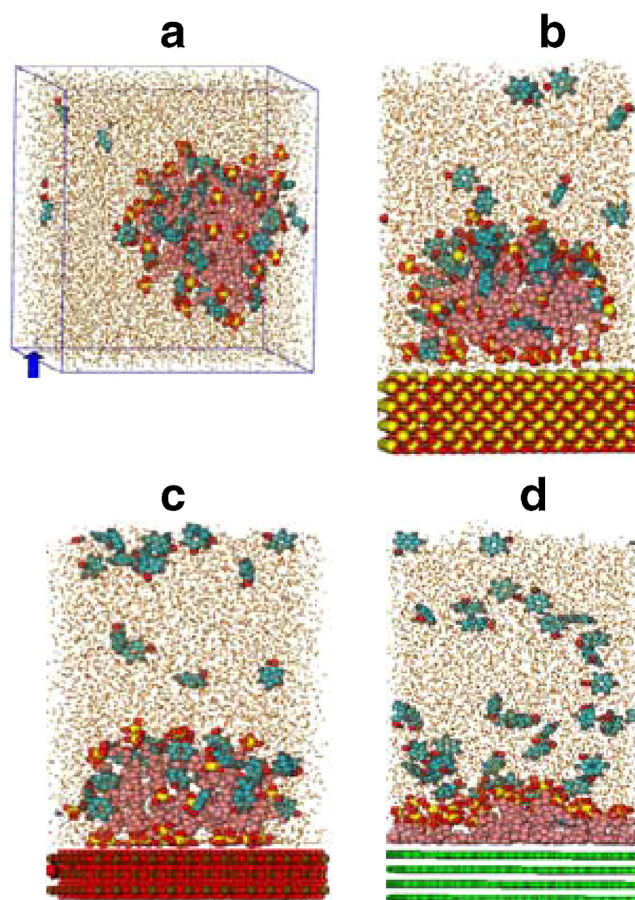
### 3. Results

#### 3.1. Phenol–SDS system

The initial simulations were conducted for the phenol–SDS system in water solvent. The final size of the simulation box for this



**Fig. 1.** Phenol (left) and SDS (right) structures.

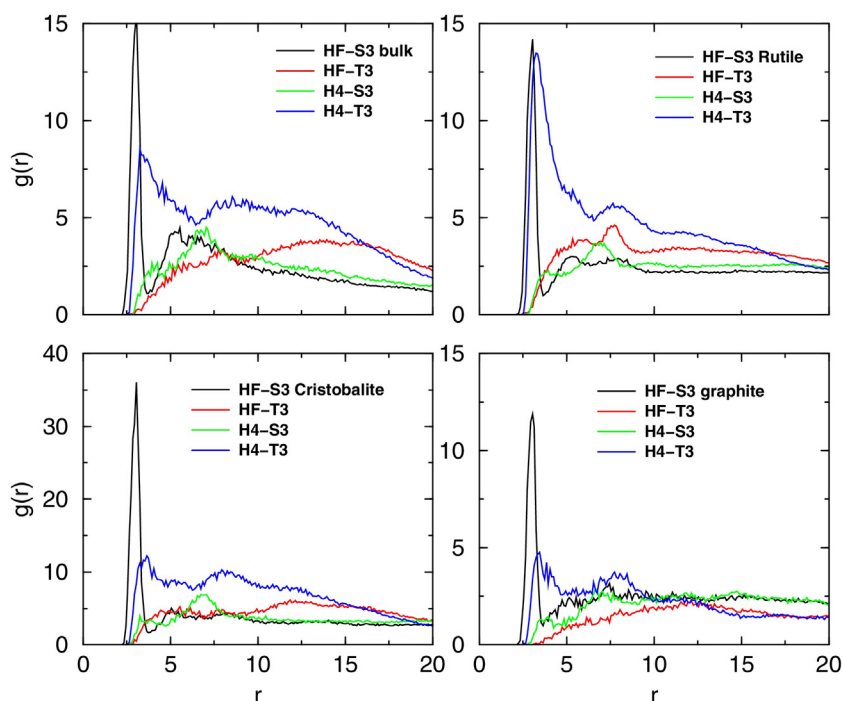


**Fig. 2.** Snapshots of last configurations (a) phenol/SDS bulk, (b) phenol/SDS in the  $\text{SiO}_2$  surface, (c) phenol/SDS in the  $\text{TiO}_2$  surface and (d) phenol/SDS in the graphite surface.

system was  $57.208 \text{ Å}$ . In Fig. 2 a snapshot of the final configuration of the phenol–SDS system is shown where it is possible to observe that most of the phenol molecules are close to the SDS micelle. The structure of the micelle was characterized by their moments of inertia and its average radius. Since the SDS tails moved randomly inside the micelle the analysis was conducted for the sulfur atom (S3) in the headgroups. From those results is observed that  $I_{xx}$ ,  $I_{yy}$  and  $I_{zz}$  are slightly different (see Fig. 2 in the supplementary data). Then, the eccentricity was measured,  $\epsilon = 1 - (I_{min}/I_{avg})$  where  $I_{min}$  is the moment of inertia with minimum magnitude and  $I_{avg}$  is the average of all three moments of inertia, and it was found the value of 0.09. For a sphere this value should be zero. In our case the eccentricity is small but not zero, nevertheless, the radius of the micelle was calculated as the average distance of the sulfur atoms to the micelle center of mass and a value of  $17.9 \text{ Å}$  was obtained. That value was slightly smaller than that calculated in previous simulations ( $19.6 \text{ Å}$ ) [29]. An experimental value of  $18.1 \text{ Å}$  has been reported [30].

On the other hand, the average distance from the center of mass of the SDS tails to the center of mass of the micelle was also calculated and it was found a value  $11.9 \text{ Å}$ . This result indicates that the chains are located inside of the micelle structure. The minimum distance between the headgroups (sulfur–sulfur) in the micelle was also measured, to see the structure of the micelle, and it was not observed significant variations in the simulation time. All plots can be seen in the supplementary data.

In order to determine the affinity of phenol with the surfactants the radial distribution function ( $g(r)$ ) was calculated. In Fig. 3 a the  $g(r)$  for different atoms of phenol with the surfactant are shown. In



**Fig. 3.** Pair distribution functions of phenol/SDS in bulk (top left), phenol/SDS in the SiO<sub>2</sub> surface (bottom left), phenol/SDS in the TiO<sub>2</sub> surface (top right) and phenol/SDS in the graphite surface (top bottom). The sites, HF, S3, H4 and T3 are represented in Fig. 1.

that figure is observed the phenol OH group (HF) close to the SDS sulfur atom (S3) (first peak of black line) and the outmost phenol CH group (H4) close to the last carbon (T3) of the SDS tail (first peak of blue line). These results suggest that phenol is located inside the micelle with its OH group next to the SDS headgroups. The amount of phenol molecules retained by the micelle was calculated by counting the number of those molecules inside a sphere of radius 22 Å (the micelle radius plus the distance of the first minimum of the S3-HF  $g(r)$ ). The fraction of adsorbed phenol was 0.85 ( $n_f/n_t$ ,  $n_f$  is the number of phenol in the micelle and  $n_t$  is the total number of phenol molecules in the system).

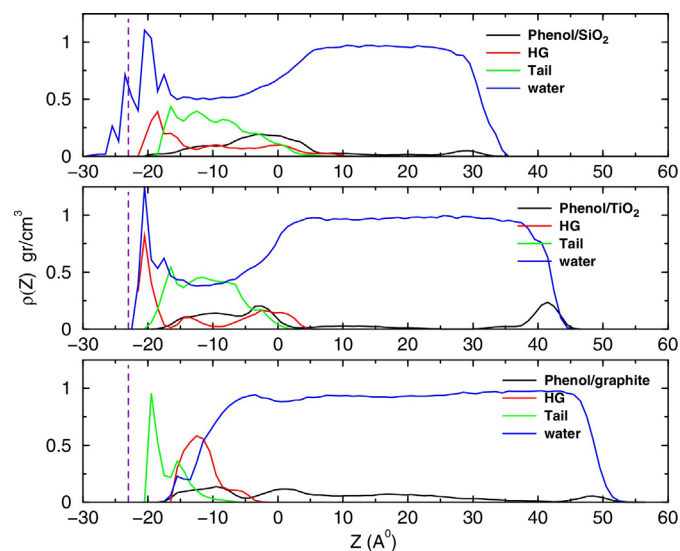
### 3.2. Phenol with SDS-modified surfaces

The second part of the work was carried out to investigate adsorption of phenol molecules on a surfactant aggregate deposited on different solid surfaces. Three surfaces were studied, silicon dioxide (SiO<sub>2</sub> in cristobalite form), titanium dioxide (TiO<sub>2</sub> in rutile form) and graphite. In Fig. 2 snapshots of the final configurations are shown for all the surfaces.

Even though several works have reported dissociation of water on titanium and silicon dioxide surfaces [31–33] we did not include that effect in our simulations. The classical force fields used in the present simulations describe atomistic interactions, however, they cannot give any chemisorption or reaction which are involved in a dissociation mechanism. Different approaches (force fields) should be used to consider those effects [31,33] such as the use of a dissociative water model [33]. Here, our main interest is in the study of surfactant (phenol) adsorption on surfaces which are mainly conducted by the surfactant-solid, van der Waals, interactions. Therefore, the water dissociation effects have less influence in our case. On the other hand, among all the titanium surfaces, the one we used (rutile (110)) has been reported with lower dissociation reactivity than the others [31].

For the system phenol on SDS-modified SiO<sub>2</sub> surface is observed that not all phenol molecules are adsorbed on the SDS aggregate,

i.e. few phenol molecules remain in the solvent (Fig. 2b). The distribution of the molecules along the axis perpendicular to the surface (Z-axis) are represented by the density profiles shown in the top of Fig. 4. In that figure is noted that water layers are well formed on the solid surface. Moreover, some water molecules went inside the solid as also observed in some experiments [34,35]. It is also noted that the surfactants are adsorbed on the surface by their headgroups. On the other hand, most of the phenol molecules are located on the top of the SDS aggregate (black line). From the  $g(r)$  plots (left bottom of Fig. 3) it is observed a strong interaction



**Fig. 4.** Density profiles of phenol/SDS in the SiO<sub>2</sub> surface (top), phenol/SDS in the TiO<sub>2</sub> surface (middle) and phenol/SDS in the graphite surface (bottom). Black lines are for the phenols, red for the SDS headgroups (HG), green for the SDS tails and blue for water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

between phenol hydroxyl groups with the SDS headgroups, even stronger than in the bulk system. Moreover, the high first HF-S3 peak suggests that a large number of phenol molecules are close to the SDS headgroups. In fact,  $g(r)$  plots and density profiles indicate that phenol is located inside the SDS micelle as seen also in the bulk system.

Different issues are depicted when the phenol–SDS system interacts with a rutile surface, for instance it seems that more phenol molecules remain in the bulk solvent (Fig. 2c). Here, it is observed a strong adsorption of the SDS on the surface indicated by the high surfactant headgroup peak in the density profiles (red line in the central graph of Fig. 4). In this case the phenol molecules were also located inside the micelle with a tendency to be in the top of the structure. The amount of phenol molecules located at the water/vapour interface is the highest of all the studied systems. This could be explained due to the concentration of surfactant headgroups and phenol molecules on top of the aggregate that present an electrostatic repulsive effect with phenol molecules. When the radial distribution functions are analyzed it is noted that the first peak of the hydroxyl phenol–SDS headgroup was as high as the first peak of the CH phenol group–methyl SDS tail group. For this system it is also noted that the hydroxyl group with the SDS tails presents less structure on this surface than that on the SiO<sub>2</sub> surface. These results suggest that phenol molecules penetrate deeper into the micelle.

For the graphite model we have used a neutral surface composed of carbon atoms and different features were also observed. In fact this model is enough to reproduce the structure and shape shown by the experiments. Here the SDS molecules formed a hemicylinder-like shape on the surface which is in agreement with previous simulations [17] an experimental works [36].

From Fig. 2d is observed that more phenol molecules are in the aqueous phase than in the micelle. One of the main differences of this system compared with the others is that the SDS molecules are well adsorbed by the tail groups (bottom of Fig. 4, density profiles). Even though the SDS headgroups located on the top have some phenol molecules close to them there are a large amount of phenol molecules in the bulk water. The  $g(r)$  for these systems present a similar behaviour of that in bulk with smaller peaks (right bottom of Fig. 3). Since the first peak H4-T3 in  $g(r)$  (blue line) is smaller than that with the other surfaces it suggests that the phenol–SDS tail interaction is weaker than in the other systems.

By using geometric parameters (sizes of the micelles) at the projection in the X-Z plane (Fig. 2) it was possible to calculate an average contact angle of the aggregates with the surfaces. Angles of  $\approx 120^\circ$ ,  $119^\circ$  and  $73^\circ$  were found for the SiO<sub>2</sub>, TiO<sub>2</sub> and graphite surfaces, respectively. For the TiO<sub>2</sub> and graphite surfaces those angles were higher than those reported in previous works [18,37], however, those simulations were conducted without phenol molecules, therefore these values reflect the presence of those molecules in the micelles.

As it was observed in the densities profiles most of the phenol molecules are located inside the micelles. Therefore, the amount of phenol retained by those micelles were calculated from the area of those profiles. It was found that 86.7%, 60.5% and 30.5% of the total phenol was captured by the SDS surfactants in the SiO<sub>2</sub>, TiO<sub>2</sub> and graphite surfaces, respectively. From the last results is observed that the SiO<sub>2</sub> surface with the SDS micelle trapped more phenol than the other SDS-modified surfaces. The graphite surface had the lowest efficiency to retain phenol molecules on the SDS micelle. To our knowledge, experiments for the same systems have not been done, however, experiments of SDS-modified alumina show phenol removal above 80% for high surfactant solid coverage [38], meanwhile a solid waste adsorbent with SDS showed more than 76% phenol removal [39].

### 3.3. Discussion and conclusions

Molecular dynamic simulations were carried out to study adsorption of phenol molecules in SDS micelles in bulk and in different surfaces. From the present studies it is noted that the surface-micelle interaction had different effects to retain phenol on the SDS aggregate. Except for the SiO<sub>2</sub> surface, it seems that the adsorption efficiency was decreased by the presence of solid surfaces compared with the SDS micelles in bulk. Then, it is noted that a graphite surface presents the worst adsorption of all the surfaces. This could be explained by the strong interaction of the SDS tails with the surface. Since the SDS tails form well adsorbed parallel layers on the surface (also seen in previous works [17]) they do not allowed penetration of the phenol into the SDS aggregate. On the other hand, for the SiO<sub>2</sub> and TiO<sub>2</sub> surfaces the interaction with the SDS surfactant is mainly by the headgroups and consequently more penetration of phenol molecules are obtained in those cases. Since the SDS molecules form a hemispherical-like shape on the SiO<sub>2</sub> surface the SDS headgroups are more exposed to the micelle surface then, more phenol molecules are close to them. It is worthy to mention that in the present simulations we considered micelles adsorbed on the surface only, however, in more realistic systems it would be also micelles in solution which could adsorb phenol molecules. Then, the total phenol retention will be the contribution of adsorbed (on surfaces) and free micelles. Here we were just concerned about retention of phenol by surfactants deposited on solid surfaces. Finally, it is noted that the phenol–SDS tail interaction also defined the amount of phenol adsorbed by the SDS aggregate. Then, high phenol–SDS tail interaction (high first peak in the H4-T3  $g(r)$ ) means more adsorption as shown in the SiO<sub>2</sub> and TiO<sub>2</sub> surfaces. Those results suggest that not only the electrostatic forces but also the van der Waals interactions play an important role for phenol retention on micellar aggregates.

### Conflict of interest

The authors declare no conflict of interest.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmglm.2016.02.011>.

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