



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



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ARTICLE INFO

Article history:

Received 23 December 2015
Received in revised form 15 February 2016
Accepted 25 February 2016
Available online 2 March 2016

Keywords:

Phenol adsorption
Surfactant micelles
Surfactant-modified surfaces
Computer simulations
Atomistic molecular dynamics

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 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

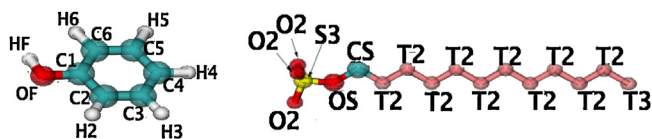


Fig. 1. Phenol (left) and SDS (right) structures.

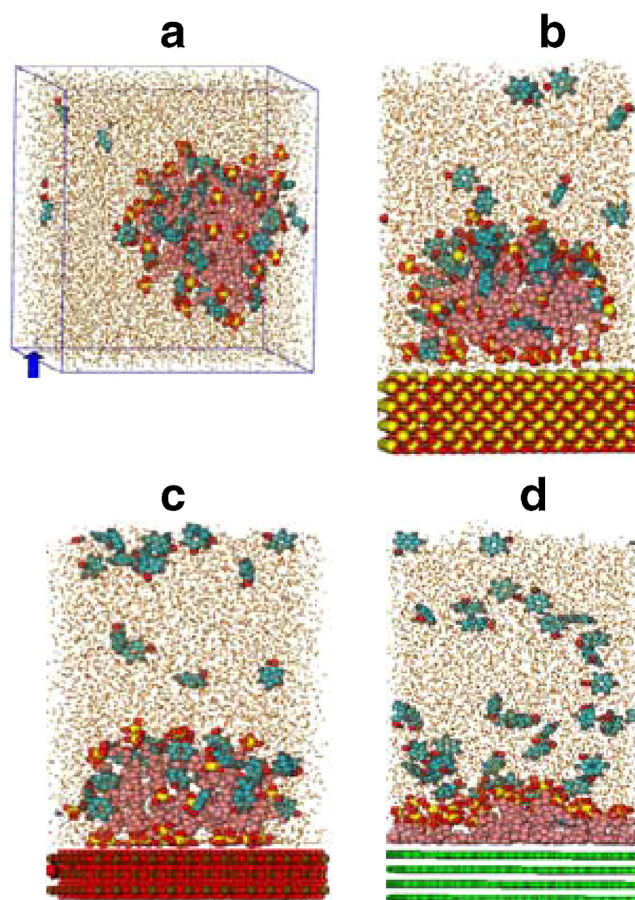


Fig. 2. Snapshots of last configurations (a) phenol/SDS bulk, (b) phenol/SDS in the SiO_2 surface, (c) phenol/SDS in the TiO_2 surface and (d) phenol/SDS in the graphite surface.

system was 57.208 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, $\epsilon = 1 - (I_{\min}/I_{\text{avg}})$ 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 Å was obtained. That value was slightly smaller than that calculated in previous simulations (19.6 Å) [29]. An experimental value of 18.1 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 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

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