Journal of Colloid and Interface Science 364 (2011) 417–427

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Computational studies on the behavior of Sodium Dodecyl Sulfate (SDS) at TiO_2(rutile)/water interfaces

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ARTICLE INFO

Article history:
Received 2 July 2011
Accepted 26 August 2011
Available online 2 September 2011

Keywords:
Computer simulations
SDS surfactant
Adsorption
Rutile

ABSTRACT

Molecular dynamics simulations to study the behavior of an anionic surfactant close to TiO_2 surfaces were carried out where each surface was modeled using three different crystallographic orientations of TiO_2 (rutile), (001), (100) and (110). Even though all three surfaces were made with the same atoms the orientation was a key to determine adsorption since surfactant molecules aggregated in different ways. For instance, simulations on the surface (100) showed that the surfactant molecules formed a hemicylinder structure whereas the molecules on the surface (110) were attached to the solid by forming a hemisphere-like structure. Structure of the aggregated molecules and surfactant adsorption on the surfaces were studied in terms of tails and headgroups density profiles as well as surface coverage. From density profiles and angular distributions of the hydrocarbon chains it was possible to determine the influence of the solid surface. For instance, on surfaces (100) and (001) the surfactant molecules formed molecular layers parallel to the surface. Finally, it was found that in the solids (100) and (110) where there are oxygen atoms exposed on the surface the surfactant molecules were attached to the surfaces along the sites between the lines of these oxygen atoms.

1. Introduction

Adsorption of surfactant molecules at solid–liquid interfaces has been studied for many years due to the importance in several industrial processes such as corrosion inhibition, dispersion stabilization, detergency, crude oil refining, treatment of waste water, adsorption on activated charcoal and even in pharmaceutical preparations where surfactant molecules are used to stabilize solid ingredients dispersed in water [1–3]. In general, dispersion of solid particles in aqueous media is a process which takes advantage of amphiphilic properties of surfactant molecules. Moreover, understanding self-aggregation will help us not only to improve these important industrial processes but also will help us to provide fundamental physical insight of general self-assembly processes [4,5].

On the other hand, adsorption of surfactant molecules on solid surfaces has shown different issues from those observed at liquid/vapor and at liquid/liquid interfaces. For instance, changes in the slopes of the isotherms have been observed before the systems reach critic micellar concentration (CMC). These changes in slopes depend on the interactions between hydrophobic tails, repulsions between headgroups and interactions between surfactant molecules with the solid surface [6,7].

Nowadays, adsorption and structures on surfaces have been studied by different experimental techniques such as streaming potential methods [8], calorimetry [9], neutron reflection [10], ellipsometry [11], fluorescence spectroscopy [12] and atomic force microscopy (AFM) [13]. In fact, by AFM people have obtained detailed information about the topology of aggregation of surfactants, e.g. Manne et al. observed the self-assembling of CTAB molecules on a surface of graphite in parallel stripes [14] and similar morphologies have been seen for other surfactants on hydrophobic surfaces [15–17]. Recently, Schniepp et al. were able to obtain high resolution images of SDS aggregates on a rough gold surface where they reported a hemimicelle morphology which depended on the local curvature of the surface [18].

For these studies, different solid surfaces have been used as substrates such as graphite, gold, mica, etc. however, studies on titanium dioxide (TiO_2) surfaces have also been conducted. For instance, proteins adsorbed on TiO_2 to be used as biosensors have been investigated [19], besides, studies in assembly of materials in electronic devices due to the electronic conduction properties of titania have been carried out [20]. On the other hand, the interaction of different surfactant molecules with TiO_2 has been studied in order to determine adsorption and some factors involved on this phenomenon [21–24]. In fact, among various semiconductor materials, TiO_2 has attracted much interest due to its potential use in industry [25,26]. Moreover, surfaces of rutile have been subject of few studies from both experimental and theoretical points of

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doi:10.1016/j.jcis.2011.08.069

view [27,28]. Experimentally people have investigated three different orientations, (001), (100) and (110) [29] and by conducting studies of contact angles of drops of water on these surfaces they found different hydrophobicities; the surfaces (110) and (001) were the most hydrophobic ones, however, the surface (100) showed a smaller hydrophobicity than that in graphite.

From a computational perspective several studies have been conducted to study molecular aggregation, for instance, Coarse-grained Monte Carlo investigations have provided useful information about morphological transitions of surfactant surface aggregation [30] while molecular dynamics simulations have been carried out to investigate aggregate properties at atomistic scales [31,32]. Monolayers and their dynamics on a graphite surface have been also studied and it was found that graphite surfaces impose an orientational bias the carbon atoms in the solid and for the surfactant–solid interactions [32].

In previous papers the interaction of SDS molecules on graphite surfaces has been investigated where hemicylinder structures were reported. In the present paper we are now interested to extent the studies of the structural analysis of the same surfactant molecule in a different surface (rutile). Moreover, we focus in how different crystallographic orientations of the solid modify the surfactant structure on the surface.

2. Computational method and model

For the present study molecular dynamics simulations of surfactant molecules at three different rutile surfaces were carried out. The surfaces were constructed using an atomistic model for the three surface orientations (Fig. 1).

Fig. 1a is the surface (001), Fig. 1b is the surface (100) and Fig. 1c is the surface (110) where it is possible to see they have different structural array of atoms. In particular surfaces (100) and (110) have oxygen atoms exposed on the top of the solid surface whereas as in the surface (001) we observed that oxygen and titanium atoms are both on the surface of the solid. For the surfactant molecule we used a Sodium Dodecyl Sulfate (SDS) model of 12 united carbon atoms attached to a headgroup, SO_4, where the headgroup atoms were explicitly modeled. The initial configuration was prepared from a monolayer of 36 surfactant molecules in all-trans configuration with the SDS headgroups initially pointed to the solid surface and placed close to the rutile surface. Then 2535 water molecules were added (using the SPC model [33]) to the system and 36 sodium cations (Na^+) were also included close to the headgroups. The concentration of surfactant molecules was chosen to be similar to the critical micelle concentration area for SDS molecules at the water/vapor interface, as found in neutron reflection experiments [34]. The number of molecules corresponded to a high concentration used in real experiments, however, with this number we guaranteed that aggregation was observed in the present simulations.

The usual periodic boundary conditions were imposed in the simulations, however, the z-dimension of the box was set to 150 Å. This length was long enough to prevent the formation of a second water/solid interface due to the periodicity of the system. Instead, a liquid/vapor interface was present at one end of the box ($z > 0$) whereas at the other end of the box ($z > 0$) beyond the solid was an empty space. The simulation parameters for the solid surface and the SDS molecules were taken from previous works [35,36] and they were summarized in Tables 1 and 2. All simulations were carried out in the NVT ensemble with a time step of 0.002 ps using DL-POLY package [37]. Bond lengths were constrained using SHAKE algorithm with a tolerance of 10^{-4} and the temperature was controlled using the Hoover–Nose thermostat with a relaxation time of 0.2 ps [38] at $T = 298$ K. The long-range

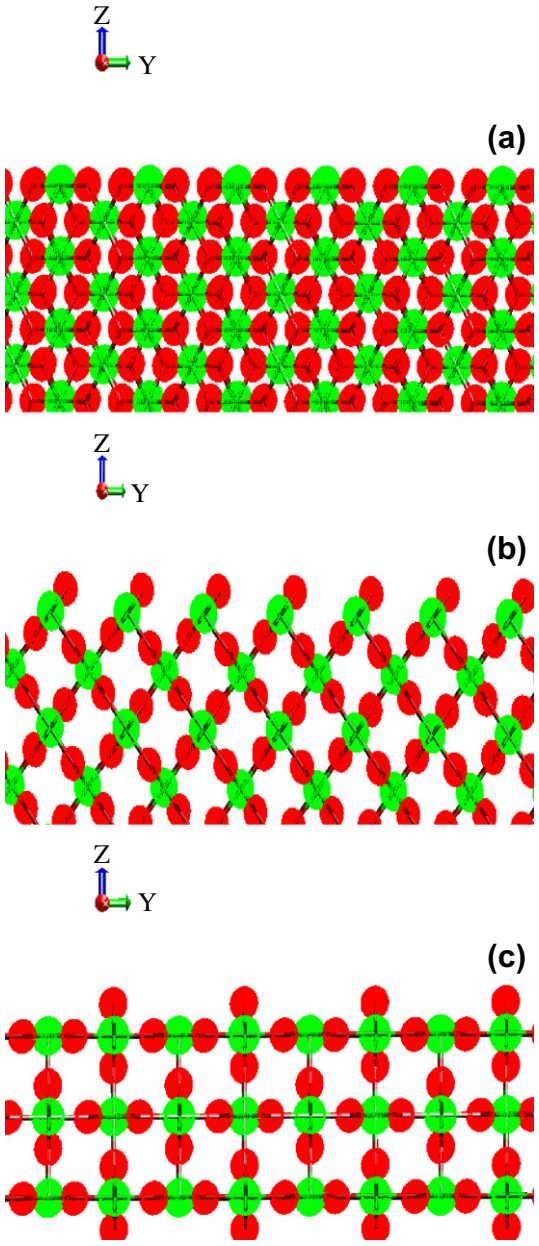

Fig. 1. Structures of solid surfaces of rutile. Oxygen atoms are red balls and titanium atoms are green balls. (a) Solid surface with (001) orientation, (b) solid surface with (100) orientation, (c) solid surface with (110) orientation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrostatic interactions were handled with the Particle Mesh Ewald method, and the Van der Waals interactions were cut off at 10 Å. Finally, all simulations were run up to 40 ns and configurational energy was monitored as a function of time to determine when systems reached equilibrium. Then, we collected data from the last 2 ns for analysis. A typical simulation took around 24 h to run 1 ns in a AMD processor in a computer with 8 nodes. In Table 3 dimensions of the solid walls and number of TiO_2 molecules used to build them are shown.

The total intramolecular potential for the surfactant included bond, angular and torsional potentials,

$$E = E_{bond} + E_{ang} + E_{tor} \quad (1)$$

The bond lengths were modeled by an harmonic potential,