Journal of Molecular Liquids 200 (2014) 465–473

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Desorption of decane molecules from a graphite surface produced by sodium alpha olefin sulphate/betaine surfactant mixtures: A computer simulation study

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ARTICLE INFO

Article history:
Received 25 September 2014
Received in revised form 13 November 2014
Accepted 14 November 2014
Available online 15 November 2014

Keywords:
Desorption
Decane/water interface
Surfactants
Graphite solid surface
Computer simulations

ABSTRACT

Molecular dynamics simulations of decane molecules adsorbed on a graphite substrate were carried out to study removal of alkanes from the solid surface by using two surfactants. Three different systems were prepared to understand, from the molecular point of view, the removal process. The first system was constructed with sodium alpha olefin sulphate surfactants (AOS), the second system with betaine surfactants and the third system with a mixture of both surfactants. In each case different features were observed. Studies of density profiles show how the decane molecules were adsorbed on the solid surface in a layer structure. Although both surfactants promoted the formation of an additional decane layer, indicating separation or removal from the graphite surface, it was observed that the AOS surfactant had less influence than betaine. Studies of adsorption and orientation of decane molecules were also analysed on the graphite surface, with the different surfactants and the mixture, and it was observed that those molecules present more structure on the surface with the AOS surfactant than with the betaine surfactant. However, the best removal of decane molecules was obtained with the surfactant mixture. In this case it was observed that the first layer close to the surface was modified while an extra layer of decane molecules emerged suggesting decane separation from the surface. Moreover, the maximum removal was found at AOS/betaine ratio concentration of 0.24/0.76.

1. Introduction

For several years investigations of surfactant molecules at liquid/vapour, liquid/liquid and liquid/solid interfaces have been the subject of extensive studies not only for their scientific interest but also for their industrial applications. For instance, Rosen [1], showed that attractions between the hydrophilic head groups in surfactants are mainly dominated by electrostatic interactions. Nyuta et al. [2], by conducting different experiments (small-angle neutron scattering (SANS), dynamic light scattering (DLS), cryogenic transmission, electron microscopy (cryo-TEM)) studied zwitterionic surfactant aggregation, with nonidentical headgroups, in aqueous solution and they found that aggregation strongly depended on the hydrocarbon chain length and the surfactant concentration. They observed a change in the structure from spherical to rod-like shapes to vesicle by increasing surfactant concentration.

Several studies have been carried out on single surfactants by using different experimental techniques including fluorescence, Raman scattering, vibrational sum-frequency spectroscopy, Brewster angle microscopy and atomic force microscopy [3–6], however, most of the actual problems, such as commercial products, consist of a mixture of surfactants that have more interesting properties, such as the reduction of the interfacial tension, than individual ones. For instance, anionic surfactants are generally used with zwitterionic surfactants as active ingredients for distinct industrial applications such as shampoo, washing powders and in petroleum industry to remove oil from rocks. Therefore, studies of surfactant mixtures have also been conducted using different experimental techniques such as calorimetry, X-ray, neutron scattering, and surface tension measurements among others [7–14]. One of those interesting works was conducted by Christov et al. [15] who observed, through dynamic light scattering experiments, the phase transition of micellar aggregates from spheres to rods for pure surfactants and for binary mixtures of betaine/SDS in water. They found that formation of rod micelles from spheres was more stable for a betaine/SDS fraction ratio of 0.8/0.2. They related the phenomenon to a loss of entropy (due to a decrease number in the micelle concentration) that should be compensated by a gain in the interaction energy between the molecules. On the other hand, Danov et al. [16] performed surface tension measurements of SDS and betaine in water and they found lower critical micelle concentration (cmc) for a betaine/SDS fraction of 0.75/0.25, suggesting that only a small amount of SDS in the mixture helps to reduce the contact area at the interface. In fact, several works have reported the

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http://dx.doi.org/10.1016/j.molliq.2014.11.023
0167-7322/

effectiveness of mixtures of anionic surfactants with zwitterionics [17–19] such as the work of Basheva et al. [19] who found that foaming and foam stability decrease may be impaired by the presence of surfactants.

The study of surfactants on solid surfaces has also been a subject of a lot interest, in particular to understand adsorption (desorption) processes. In fact, several of those investigations have been conducted using computer simulations which have proved to be a powerful tool to investigate such complex systems. For instance, Hu et al. [20] conducted molecular dynamics simulations to study adsorption of zwitterionic surfactants (dodecyl sulfobetaine) and divalent cations (calcium and magnesium) on a surface of silica. Liu et al. [21] investigated dodecane desorption on a silica surface in an aqueous dilution of cetyltrimethylammonium bromide (CTAB) by showing that the formation of a water–oil channel is needed for detachment. However, due to the water and oil nature, the formation of that channel is not possible without the presence of a surfactant. Wettability has also been investigated and it was found how it is modified by the presence of surfactants [22,23].

In previous works we carried out simulations of SDS and mixtures of SDS/dodecanol to obtain more insights about aggregation and adsorption of those molecules on different substrates [24–26]. In the present paper we are interested to investigate, from a molecular point of view, how surfactants help desorption of alkane phases from a substrate. In particular we focus on zwitterionic and anionic surfactants with decane molecules deposited on a graphite surface.

2. Computational model

Simulations of three systems were conducted using two surfactants on a graphite substrate with a layer of decane molecules; system 1 with an anionic sodium alpha olefin sulphate (AOS), system 2 with a nonionic cocoamidopropyl betaine (see Fig. 1 of Supplementary data) and system 3 with mixtures of AOS/betaine. The initial configuration started with 2416 water molecules in a bulk phase on a graphite wall where 40 decane molecules were previously deposited. Then, the system was run until decane was adsorbed on the substrate by forming a layer structure (Fig. 1a). It was used a graphite surface due to the good affinity with alkane molecules, therefore, a strong adsorption of decane molecules on the surface was expected. The dimensions of the simulation cell were $X = Y = 40.249$ Å and $Z = 150$ Å, i.e. the Z-length was large enough to have a liquid/vapour interface at one end of the simulation box to prevent the formation of a second water/solid interface due to the periodicity of the system.

Then, systems with individual surfactants at 7 different number concentrations; 0.0021, 0.0041, 0.0062, 0.0082, 0.0102, 0.0123 and 0.0143, (5, 10, 15, 20, 25, 30, 35 surfactant molecules) of AOS or betaine molecules were prepared. The concentration was calculated as the number of surfactants divided by the total number of water molecules. For the systems with anionic surfactants a sodium anion (Na^+) per each AOS molecule was included. For the mixtures (AOS/betaine) the total number of molecules was constant (19 total surfactant molecules) and the results were given in terms of the betaine concentration (number of betaines/number of water molecules) 0.0033, 0.0045, 0.0062 and 0.0078. Due to the affinity between surfactant tails and alkane groups the surfactants were initially placed with their tails close to the alkane layer to save computer time. Simulations with heads close to alkanes and tails next to water were also tested, however, the main results did not change significantly.

The AOS and the betaine force fields consisted of intra and inter molecular interactions. The intra-molecular interactions included harmonic bonds, harmonic angles and dihedral potentials whereas the intermolecular interactions consisted of Lennard Jones and coulombic potentials. The parameters for the AOS headgroup were taken from Yan et al. [27] whereas the parameters for the tail were taken from the tails of SDS reported in the literature (due to the similarity in both tails) [24–26]. The parameters for the betaine molecule were taken from references [28,29]. The charges for both AOS and betaine were obtained from quantum chemistry calculations using the GAUSSIAN software (Fig. 1 of Supplementary data). The parameters, used in the work, for both surfactants are given in Tables 1–3 of the Supplementary data. Decane molecules were simulated with the force field proposed by Nath et al. [30] whereas water was simulated using the SPC model. The water model has been used in similar systems (of SDS/water/solid interfaces, [24–26]) and good tendencies with experimental results have been observed. The graphite plate was simulated using an atomistic model constructed with four layers (2706 atoms) [24,25] where all the atoms were frozen to have a rigid wall.

All simulations were carried out in the NVT ensemble with a time step of 0.002 ps using the DL_POLY package [31]. As mentioned above there is a vapour–liquid interface at one edge of the simulation box which should allow the systems to have appropriate thermodynamic

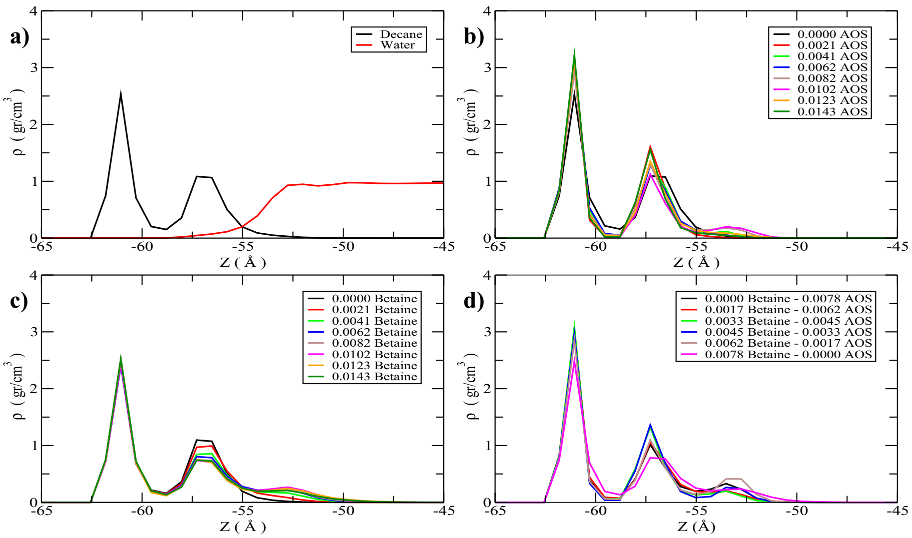

Fig. 1. Density profiles for a) the decane/water system b) decane with AOS surfactant c) decane with betaine surfactant and d) decane with the AOS/betaine mixture. The surfactant concentration in each system is given in colours as indicated in the inset tables. The graphite surface is located on the left of the plot.