

Surface Electrostatic Potential and Water Orientation in the presence of Sodium Octanoate Dilute Monolayers Studied by Means of Molecular Dynamics Simulations

Kalil Bernardino[§] and André F. de Moura^{§,}*

§ Departamento de Química, Centro de Ciências Exatas e de Tecnologia, Universidade Federal de São Carlos, Rodovia Washington Luiz km 235, CP 676, CEP 13565-905, São Carlos, SP, Brasil.

Supporting Information

This Supporting information material is organized as follows: First, a phenomenological description of the spontaneous film formation in the smaller systems (3300 water molecules) are given as well as a qualitative picture of the interaction between the surfactant monolayers and the micelles formed in the more concentrated systems, with also give qualitative insights over the monolayer saturation of a soluble surfactant as sodium octanoate. These information are discussed in length here instead of the main manuscript since the latter focus in equilibrium

properties and are based in some considerations about the system homogeneity that are valid in the absence of bulk aggregates, but, at least in the current accessible time and size scales for computer simulations, not in the more concentrated systems where micelle formation takes place. In the second section, are given the results for the charge density, electrostatic potential and water orientation in the larger systems (11600 water molecules) that are discussed in the Results and Discussion section of the manuscript in comparison with the smaller ones.

Spontaneous film and micelle formation in smaller systems

The model systems were initially random and, as a consequence, some octanoate and sodium ions were already located at or near the interfaces at the outset of the simulations. As regards the surfactant molecules in the bulk, they spontaneously diffused to the vacuum-solution interfaces within a timescale ranging from a few nanoseconds to tens of nanoseconds, for dilute and concentrated systems, respectively. Typical snapshots of the process are depicted in the graphical representations of the initial and final structures of the system with 40 octanoate ions (Figure 1 in the Methodology section of the article). As expected for ionic surfactants, the charged heads tend to remain in contact with the aqueous solution whereas the hydrophobic tails preferably lie outside the solution. The reorganization of the sodium counter-ions during the formation of the surfactant films also follow the expected behavior, with most of the cations close to the octanoate anions at the interfaces. The quantitative description of the electrostatic potential generated by the films is discussed in the Results and Discussion section of the article. In the remaining of this Supporting Information section, we shall present the phenomenological aspects of octanoate adsorption and self-assembling.

The surfactant concentration profile in the z -direction evolved in time during the simulations as showed for the $N=40$ system in Figure S1, with a progressive increase in the octanoate concentration at the two interfaces (around $z=-2$ and $z=2$ nm) and the simultaneous decrease in the bulk concentration until the system reached equilibrium after 15 ns. Despite the asymmetry of the starting configuration, which presented more octanoate ions near the interface at $z=2.0$ nm than in the interface at $z=-2.0$ nm, the equilibrium distribution spontaneously became symmetric along the z -direction, as expected for two equal interfaces at equilibrium.

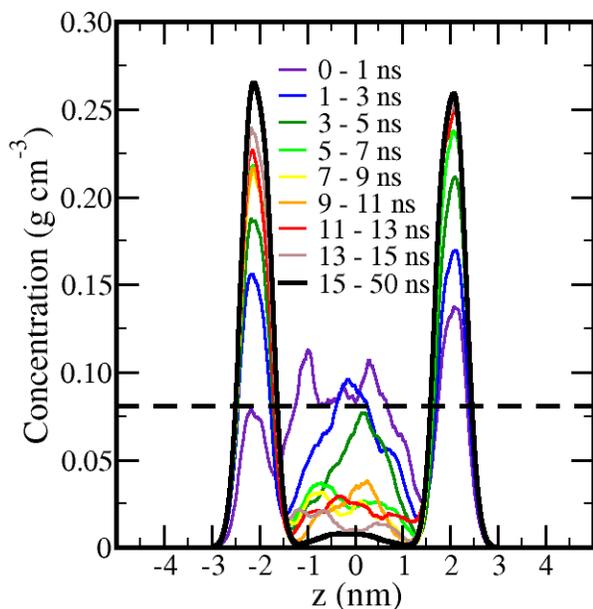


Figure S1. Evolution of the octanoate concentration along the direction perpendicular to the water-vacuum interface for the system with 40 octanoate anions. The different colors stand for the time windows used in each calculation, whereas the dashed black line stands for the bulk concentration at the outset of the simulation.

It is interesting to note that a non-zero surfactant concentration was observed inside the solution after equilibrium was attained due to the momentary solubilization of octanoate anions,

as might be expected for a short-tail, slightly soluble surfactant. The concentration inside the solution is larger at the center of the water slab, which is consistent with the minimization of the electrostatic repulsion between the negatively charged surfactant molecules and the negative electrostatic potential at the parallel interfaces. This scenario presents two opposing driving forces: while the hydrophobic effect and the high surface tension of water both tend to push the surfactant molecules to the interface, there is an increasing electrostatic repulsion which tends to force the surfactant molecules back into the bulk solution. Considering that the latter contribution increase with the number density of surfactant molecules at the interface, there should be a limiting concentration of surfactant, above which the addition of any extra amount of surfactant would increase the bulk concentration without appreciable effects on the interface composition. Obviously, the extra surfactant that would no longer be transferred to the interfaces would increase the bulk concentration, which would eventually become larger than the surfactant CMC, leading to the spontaneous micelles formation.

We may apply this reasoning to the more concentrated systems ($N=60$, 80 or 100), which presented a slow diffusion of octanoate anions from the bulk solution to the interface and eventually formed micellar structures (Figure S2 and video). Whereas in the system with 60 octanoate ions the micelle broke up after 60 ns followed by a further and slower migration of the octanoate ions to the interface, in the systems with 80 and 100 octanoate ions, the micelles formed seems to be stable in the simulation timescale. At the end of the simulations, it was observed an aggregation number of 19 for the micelle formed in the $N=80$ system and of 41 for the micelle formed in the $N=100$ system. These sizes can be compared with those reported in our previous work for the spontaneous formation of sodium octanoate micelles by means of

molecular dynamics simulation bulk solution,¹ which shows that the N=19 micelle is consistent with the sizes observed in bulk solution whereas N=41 micelle is larger than the greatest cluster observed in bulk solution (N=36), however, the differences in the concentration and the interaction with the interfacial film and the electric double layer affect the micelle structure and stability, with the micelle assuming an oblate shape due to this interaction (Figure S2). This effects and the fact that the simulation time scale may be not long enough to guaranteed the proper equilibration in these more concentrate system can justify the difference in the aggregation number.

1 de Moura, A. F.; Bernardino, K.; de Oliveira, O. V.; Freitas, L. C.G. Solvation of Sodium Octanoate Micelles in Concentrated Urea Solution Studied by Means of Molecular Dynamics Simulations. *J. Phys. Chem. B* **2011**, 115, 14582–14590.

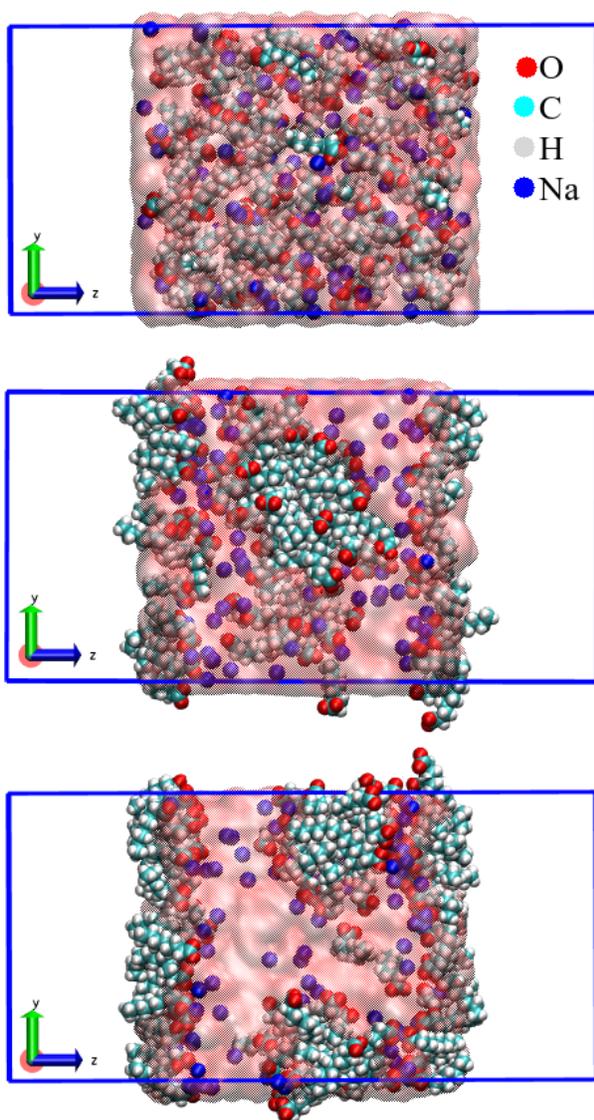


Figure S2. Representative structures for the system with 100 octanoate anions at 0 ns (top panel), 40 ns (middle panel) and 100 ns (bottom panel). The water molecules are represented by the red translucent surface.

The equilibrium distributions of octanoate anions in the direction perpendicular to the interface at different concentrations are displayed in Figure S3. The more dilute systems, which did not form micellar structures, presented highly symmetric distribution profiles, with some minor differences between the two interfaces arising from short-lived fluctuations in the octanoate

density. For these systems we assumed that small fluctuations would be averaged out in the long run, and thus these distributions should be symmetrical with respect to the center of the water slab. This consideration justifies the symmetrization of the charge density curves discussed in Results and Discussion section of this article.

On the other hand, the systems which formed stable micellar structures (N=80 and N=100) produced unsymmetrical density profiles (Figure S4), with a density bump at the region where the micelle remained most of the time. Visual inspection confirms that the micellar structures tend to stay closer to one of the interfaces (Figure S3), specially in the N=100 system, interacting with the surfactant film by means of sodium-mediated ionic bridges. This is a very interesting finding indeed, because the electric double layer models would treat the counter-ions distribution around the micelle and the interfacial counter-ion distribution as independent and different problems, whereas our model system is complex enough to spontaneously form a hybrid situation where the two structural motifs share a common counter-ion distribution. Obviously, there can be no analytical solution for a problem with this degree of complexity, and only approximate numerical models can tackle the simultaneous evaluation of both, as our molecular dynamics simulations did.

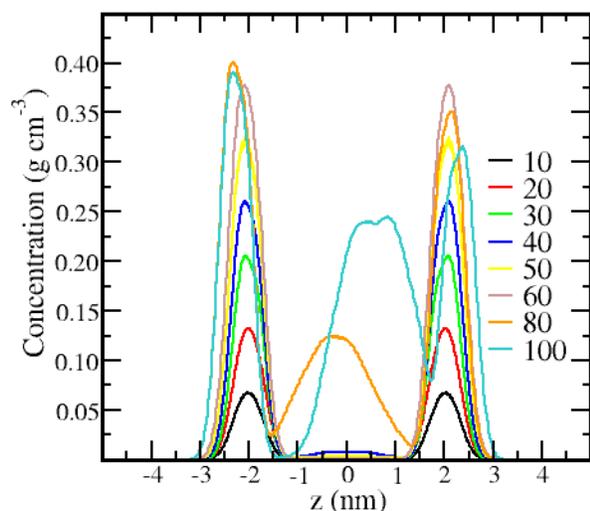


Figure S3. Equilibrium concentration of octanoate along the axis perpendicular to the water-vacuum interface. The figure for each color stands for the number of octanoate anions in the model system.

The octanoate concentration at the interfaces increased without any significant variation in the bulk concentration for the systems ranging from $N=10$ to $N=60$ (Figure S4), whereas the systems with $N=80$ and $N=100$ octanoate ions presented nearly the same concentration of octanoate ions at the interfaces and at the same time presented an increase of the bulk octanoate concentration. This analysis shows that anionic surfactant molecules should preferably accumulate at the solution interface and only after a limiting concentration is reached we should observe the accumulation of surfactant molecules in the bulk solution, as is well-known by the macroscopic measures like the surface tension as a function of the surfactant concentration.²³ Although the time window of the simulations may be too short to assess the stability of this structural pattern,

2 Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press Limited: London, 1998

3 Hiemenz, P. C.; Rajagopalan, R., *Principles of Colloid and Surface Chemistry*, 3rd ed.; Taylor & Francis Group: New York, 1997

it is possible that the interfacial surfactant concentration for these systems, which amounts to *ca.* 0.80 nm² *per* octanoate, is a close estimate for the film saturation threshold.

Electrostatic Potential and Electrical Field Components in larger systems

In order to analyze the effect of the distance between the two interfaces in our model systems over the electrostatic potential and water orientation results reported in the Results and Discussion section of the manuscript, two molecular dynamics simulations with larger systems and farther water-vacuum interfaces were done, one in the presence 40 octanoate ions (and the same amount of sodium counter-ions) and other with pure water. The number of water molecules was increased from 3300 to 11600 while keeping the interfacial area equal to 24.01 nm². These effects are discussed in detail in the Results and Discussion section of the manuscript together with the results for the smaller systems, but the corresponding graphics for the larger systems are given in this supporting information section to save space in the manuscript. Figure S4 describes the charge density and the electrostatic potential along the axes normal to the interfaces (z axes) and should be compared with Figure 3, that brings the same results for the smaller systems at several surfactant concentrations, in the Results and Discussion section.

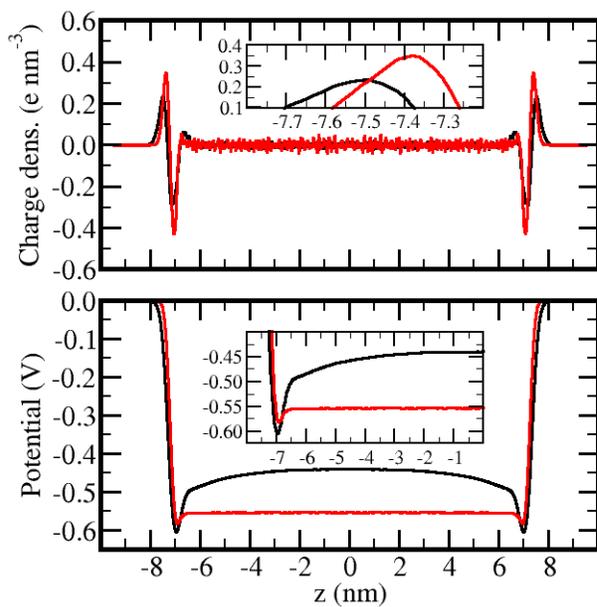


Figure S4. Local charge density (top) and the electrostatic potential (bottom) along the axis perpendicular to the interface. The red curve stands for pure water while the black curves stands for the system with the surfactant (surface concentration of $0.833 \text{ molecules nm}^{-2}$). The inset in the top expands the first peak and, for the inset in the bottom, the region between one interface and the middle of the simulation box.

Figures S5 to S8 describes contributions from the surfactant head, sodium counter-ions, surfactant tails and water to the charge density and electrostatic potential and should be compared with Figures 5 to 8 in the Results and Discussion section.

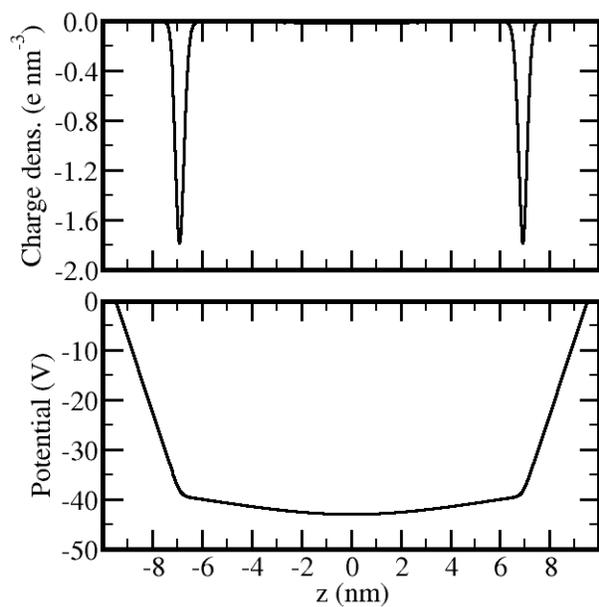


Figure S5. Contribution of octanoate charged head (CH_2CO_2^-) to the charge density (top) and electrostatic potential (bottom) in the larger system with octanoate surface concentration of 0.833 molecules nm^{-2} .

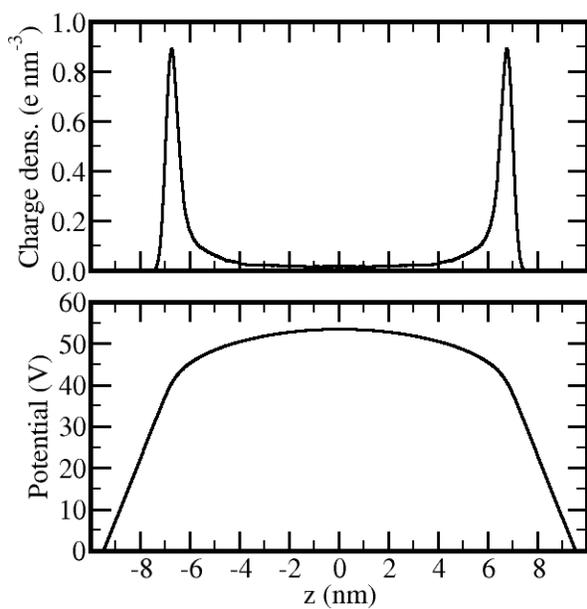


Figure S6. Contribution of sodium counter-ions to the charge density (top) and electrostatic potential (bottom) in the larger system with octanoate surface concentration of 0.833 molecules nm^{-2} .

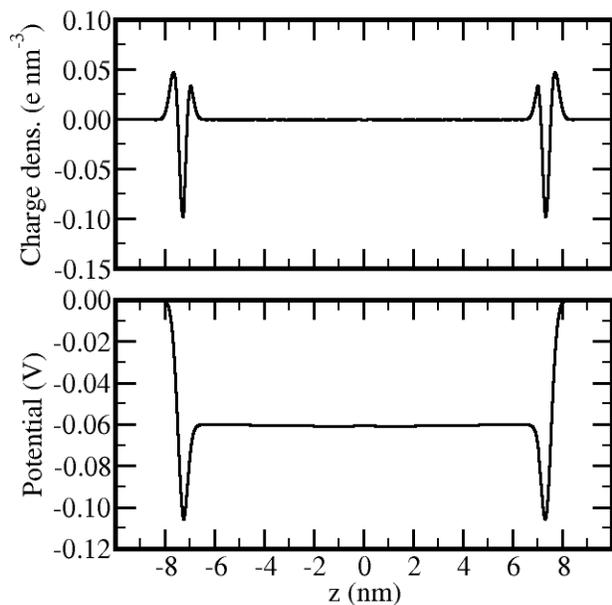


Figure S7. Contribution of octanoate aliphatic tail (C_6H_{13}) to the charge density (top) and electrostatic potential (bottom) in the larger system with octanoate surface concentration of 0.833 molecules nm^{-2} .

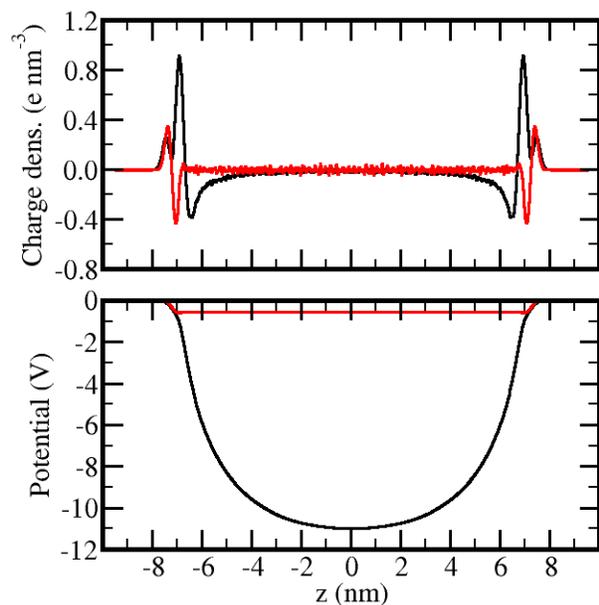


Figure S8. Water contribution to the charge density (top) and electrostatic potential (bottom) in the larger systems with octanoate surface concentration of $0.833 \text{ molecules nm}^{-2}$ (black curves) and in pure water (red curves).

Figure S9 describes the water orientation along the direction normal to the interfaces by the mean value of the angle θ between the water molecules dipole moment, μ , and the z axes. It also gives the angle distribution in selected slices of the simulation box in the presence and in absence of the surfactant. This figure should be compared with Figure 9 that brings the same information for the smaller systems at several concentrations in the Results and Discussion section.

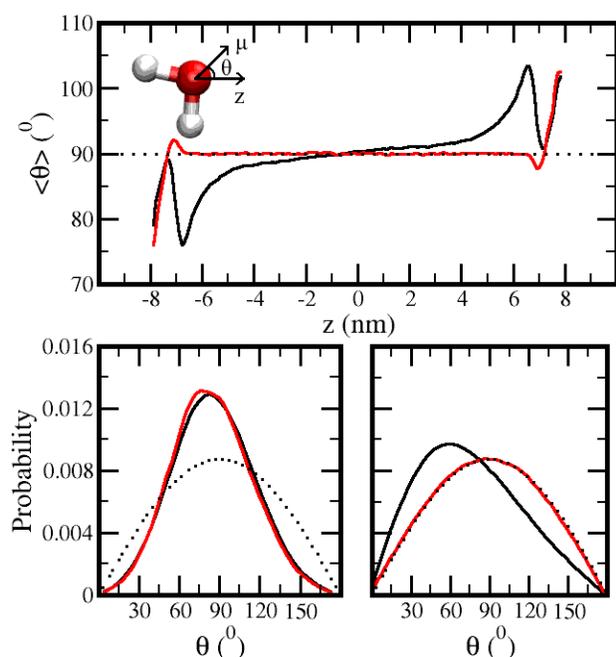


Figure S9. Top: Mean value of the angle θ between the water dipole moment and the normal to the interface as a function of the oxygen atom position along z -axes. Bottom: Orientation distribution for the slice between $z = -7.6$ and -7.3 nm (left) and between -6.7 and -6.4 nm (right). The red curves stand for pure water and the black curves for the sodium octanoate solution. The dotted curves stand for the ideal distribution (no preferential orientation).

AUTHOR INFORMATION

Corresponding Author

* André Farias de Moura

Departamento de Química

Centro de Ciências Exatas e de Tecnologia

Universidade Federal de São Carlos

Rodovia Washington Luiz km 235, CP 676, CEP 13565-905, São Carlos, SP, Brasil.

email: moura@ufscar.br

phone: +55-16-3351-8090

fax: +55-16-3351-8350

SUPPORTING INFORMATION REFERENCES