

Molecular Dynamics Simulation of Adsorption from Microemulsions and Surfactant Micellar Solutions at Solid-Liquid and Liquid-Liquid Interfaces

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ABSTRACT

In enhanced oil recovery, the production is influenced by the ability of injected surfactants to adsorb and to modify interfacial tension at different interfaces. It has previously been demonstrated that surfactant and microemulsion additives enhance the production to a different extent but the mechanisms behind the differences in their action are not fully understood. Recent molecular dynamics simulation shows that the adsorption at a solid surface differs for these two systems. Furthermore, it shows that the solvent solubilized in a microemulsion is transported to the solid surface together with the surfactant, and hence the surface modification can be controlled by designing the chemistry and composition of the self-assembled structure.

Here, we report salient new results on the adsorption from microemulsion at graphite-liquid, and liquid-liquid interfaces. The simulation involves an aqueous solution in the presence of an oil (heptane) phase. The solution consists of nonionic surfactant dodecylhepta(oxy-ethylene)ether or $C_{12}E_7$, and a solubilized terpene solvent. We found that the presence of solvent inside the micelles causes the mechanism of adsorption behavior to deviate from those expected for adsorption from micellar surfactant solutions. In the case of solubilized terpene, the swollen micelles adsorb on the surface as one entity. The delivery of a surfactant to the interface and the associated reduction of the interfacial tension is influenced by the change in interaction potential between the surface and surfactant aggregate, and it is controlled by the solvent concentration.

Molecular dynamics simulation also reveals the complex distribution of fluids at the capillary wall. The terpene swollen micelle merges with the thin film of oil on the wall. The surfactant deposits on the interface between the aqueous phase and the oil, thereby reducing its interfacial tension. The solvent originally solubilized in a microemulsion droplet, penetrates the thin film of oil. The resulting mixture of oil and solvent has different properties from the oil alone, indicating a primary difference between the mechanism of action between surfactant and a combination of surfactant and solvent. For comparison, the same simulation conditions were applied to the case of $C_{12}E_7$ micelles without solvent. As expected, the whole micelle did not adsorb at the interface.

The results are important for our understanding of microemulsion behavior under confinement and its application to organic rich shale oil recovery.

Keywords: enhanced oil recovery, microemulsion, adsorption, interfacial tension, molecular simulation

1 METHODOLOGY

Computer simulation of surfactants and micelles for various applications has been an active area of research[1-5]. A general rule of thumb is that the accuracy and flexibility of atomistic simulations are increased at the expense of computational power and time. In molecular dynamics simulations, the size of the system is typically on a nanometer scale and the time to be simulated is on the order of nanoseconds. In this work, Gromacs package (with gpu acceleration) was employed to perform the simulations and VMD package was used for visualization purposes [6-8]. The OPLS (Optimized Potentials for Liquid Simulations) force field [9,10] was chosen to represent fluid molecules due to its accuracy for liquid simulations. CLAYFF force field [11] was chosen to represent the rigid capillary wall. The simulation conditions are typically at normal room temperature and pressure ($T=300K$, $P=1bar$). Starting from an initial configuration, where the molecules making up the fluids are aligned randomly and uniformly, NPT (constant pressure, temperature and number of atoms) ensemble was first applied to bring the system to equilibrium. The equilibrium structure of $C_{12}E_7$ was a spherical micelle of aggregation number 42 and diameter of 4 nm. The production runs were performed next in the NVT ensemble to extract the properties of interest.

To quantify the influence of solvent amount in the emulsion droplet on the adsorption kinetics, we performed a series of microemulsion simulations in the presence of an organic wall. $C_{12}E_7/d$ -limonene concentration ratio inside the micelles is fixed to a particular value in each simulation and the self-diffusion coefficient corresponding to that ratio is numerically estimated. A single oil droplet from previous microemulsion simulations is extracted and placed inside an empty computational box. The number of $C_{12}E_7$ units (molecules) in the droplet is 42 and the number of d-limonene units is 54. The diameter of the droplet is around 6nm. The box is then filled up with water. In each simu-

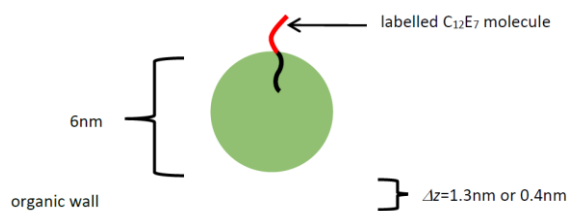


Figure 1. Simulation setup to study adsorption kinetics of a microemulsion droplet on the graphite wall.

lation for diffusion near a wall, the number of d-limonene molecules in the droplet is decreased systematically while the number of surfactant molecules remains the same. There are two important considerations for the study of the influence of d-limonene on the wall interaction: the initial separation distance Δz between the droplet and the wall, see **Figure 1**; and the time needed for the droplet to reach the wall and the adsorption to begin. The initial distance should be close enough for the droplet, or part of the droplet, to “feel” the wall and the time duration should be reasonable for the completion of the simulations in a timely manner. We performed preliminary simulations to identify the optimum distance and time for the investigation. In these test runs the $C_{12}E_7$ /d-limonene molecular ratio is kept constant and equal to 42/54 for simplicity in the analysis. During the first simulation, the droplet-wall separation distance Δz is kept at 1.3 nm. After 10 nanoseconds, we stopped the simulation to observe the state of the droplet. It was still wandering in the aqueous phase, and the adsorption had not taken place yet. We concluded that the distance was too large for the wall to attract the droplet in a reasonable timeframe. Reducing the distance to 0.4 nm, allowed the adsorption to occur. Therefore, this Δz value is chosen for the study explained below.

Several experimental methods were used to verify the simulations. The diameter of $C_{12}E_7$ /d-limonene microemulsion droplets measured by Photon Correlation Spectroscopy using a ZetaSizer Nano instrument (Malvern) is 6.7 ± 1.8 nm, compared to 6 nm from simulation. The surface tension calculated from simulation of the liquid/vapor interface is 22 mN/m, compared to an experimental value of 31 mN/m as measured by the Wilhemy plate method using a K100 tensiometer (Kruss). The final interfacial tension calculated from simulation of the aqueous/heptane interface is 0.22 mN/m, and measured as 0.2 mN/m by a spinning drop method using a SVT-20 spinning drop tensiometer (Data Physics).

2 RESULTS AND DISCUSSION

2.1 Solubilization of oil within micelles and micro-emulsion formation

To investigate the solubilization of d-limonene inside the $C_{12}E_7$ micelles, we performed a series of simulations of aqueous phase surfactant-oil solutions, where the number

ratio between surfactant and oil molecules in water is varied systematically within one order of magnitude from 11.4 to 1.0. The molar concentration of the surfactant is changing in the range from 0.15 to 0.54 moles/l. At the beginning of each simulation, both the surfactant and the d-limonene molecules are randomly dispersed inside the simulation box. As the simulation progresses and the aqueous solution approaches thermodynamic equilibrium, we observe the formation of microemulsion droplets where d-limonene molecules, due to their hydrophobic nature, are facing the hydrocarbon tails of the surfactants and, hence, have a tendency to stay at the central portion of the micelles. The micellization involving d-limonene is shown in **Figure 2**. Clearly, most of the d-limonene molecules have been solubilized in the micelles, forming a discontinuous oil phase within the continuous aqueous phase. There are also a few free surfactant molecules that are staying as monomers outside of the micelles.

2.2 Adsorption in the presence of an organic wall

Diffusion of a micelle under the influence of a nearby organic wall is quantified by measuring the self-diffusion coefficient of a labeled surfactant belonging to the droplet. The labeled surfactant is selected from the portion of the droplet farthest from the wall as shown in **Figure 1**. During the simulation of diffusion and adsorption, the trajectories of the labeled surfactant are recorded. Later, this information is used to calculate the time of flight for the surfactant to travel through the droplet and reach to the wall at the bottom. **Table 1** shows that the measured time decreases significantly with increasing amounts of d-limonene inside the droplet. Our results in Table 1 indicate that the wall imposes a local attractive force and, hence, an affinity towards the droplet which is stronger in magnitude as the amount of d-limonene increases in the microemulsion. This attraction leads to the droplet depositing onto the surface as a whole, with surfactant and solvent together. This is consistent with previous experimental observations on adsorption from microemulsions [13,14]. For comparison, values of the self-diffusion coefficient in the bulk (without the wall) were also computed. The value of the self-diffusion coefficient of

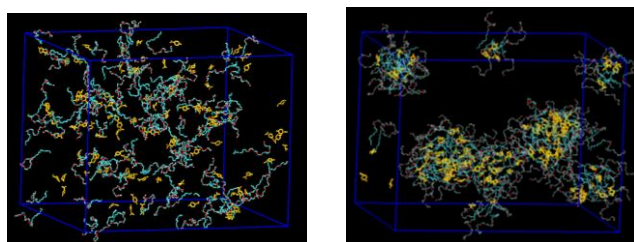


Figure 2. Two snapshots of the simulation of aqueous phase solution with surfactant/oil ratio equal to 1.00. Left: Initial configuration of the surfactant and oil in the solution; Right: Later configuration of the surfactant and oil in the solution showing development of a microemulsion after 10ns. Water molecules are not shown for clarity.

Table 1. Solvent-droplet (water-oil) pair simulations in the presence of organic wall performed at varying C₁₂E₇/d-limonene molecular ratio showing the time of flight for the labeled surfactant molecule to travel through the droplet and reach to the wall at the bottom.

| case | Ratio C ₁₂ E ₇ /LIM | Self-diffusion (x10 ⁻⁵ cm ² /s) | | time of flight (ps) |
|------|----------------------------------------------|-------------------------------------------------------|-------|---------------------|
| | | bulk | wall | |
| 1 | 42/54 | 0.137 | 1.100 | 2,230 |
| 2 | 42/42 | 0.066 | 0.951 | 4,040 |
| 3 | 42/21 | 0.071 | 0.711 | 4,250 |
| 4 | 42/11 | 0.076 | 0.429 | 6,490 |
| 5 | 42/0 | 0.143 | 0.381 | 7,890 |

water in the bulk (2.32 +/- 0.15) is similar to the experimental value (2.3 x 10⁻⁵ cm²/s). The value of the self-diffusion coefficient of the surfactant micelle without the wall is (0.143 x 10⁻⁵ cm²/s), roughly four times larger than the Stokes diffusion coefficient of a 6 nm particle in water. While the absolute value of the micellar diffusion coefficient is larger than expected, there is no strong d-limonene influence in the simulated bulk diffusion coefficient. The increase in near-wall diffusion coefficient indicates an increase in attraction that is d-limonene concentration dependent.

2.3 Behavior of complex micelle at the water-oil interface by the organic wall

The simulation setup in **Figure 3** shows a relatively complex distribution of fluids at the organic wall. A thick film of n-heptane (oil) molecules are separating the aqueous phase with a terpene swollen micelle from the organic wall at the bottom. During the simulation, the micelle first comes in contact with the oil-water interface. Influenced by the interface and by the organic wall below, the micelle disintegrates and the monomers that were making it up (C₁₂E₇ and d-limonene) are released and adsorbed. The adsorbed molecules that are spreading across the oil-water interface are shown in Figure 3 after 3 ns of interactions. The surfactants stay at the interface and reduce the interfacial tension therein while d-limonene molecules penetrate through the interface and migrate deep into the bulk of the oil film towards the organic wall. The distribution of the surfactants at the interface and the d-limonene molecules in the oil film are also shown in Figure 3 at a time of 10ns. In essence, the components of the droplet are distributed between the surfaces: C₁₂E₇ is taken by the oil/water interface and d-limonene by the oil and organic wall. If the amount of d-limonene is high enough, its molecules create another oil film right by the organic wall. The conditions in the n-heptane oil film have been changed. Now oil molecules are at a distance from the wall and, hence, the wall interactions should be reduced. In parallel, the interfacial tension between the oil and water has dropped. These modified local conditions may give mobility to the n-heptane phase. For comparison, the same simulation conditions were applied for the case of C₁₂E₇ micelles without solvent. In agreement with conventional

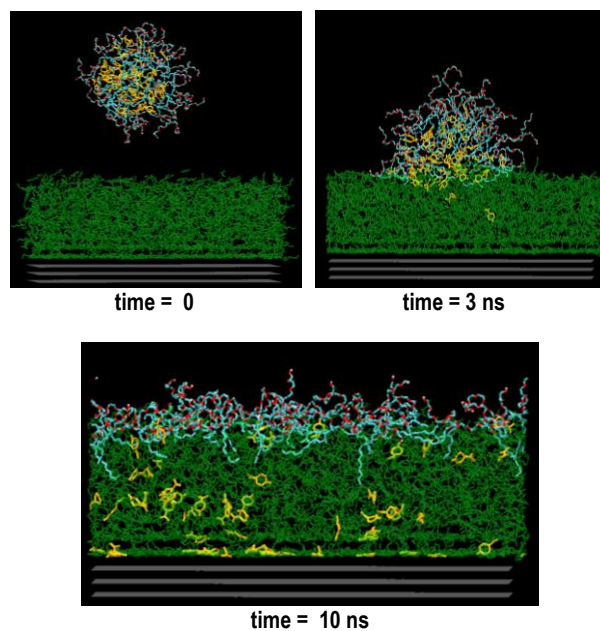


Figure 3. Adsorption of a microemulsion droplet containing C₁₂E₇ surfactant and solvent to the oil/water interface. Due to the influence of the organic wall, the solvent molecules penetrate deep into the oil phase and approach to the wall. From left to right is the snapshots during the simulation.

views [1], the micelle without the solvent did not adsorb to the oil-water interface.

2.4 Density profile across the oil-water interface and IFT estimation

Next, the interfacial tension at the water-oil interface in the presence of C₁₂E₇ is estimated from numerical simulations. The simulation box contains the two immiscible phases (n-heptane and water) in the presence of nonionic surfactant (C₁₂E₇). The computational box has periodic boundary conditions; consequently we might have more than one interface present in the box. The interface separating the water from n-heptane is rich in C₁₂E₇ as we can see from the density profiles of the oil, water and the surfactant in **Figure 4** (top).

IFT for an interface is computed using the local compressional components of the stress tensor [12]:

$$\sigma = \int_{-\infty}^{\infty} (p_N - p_T) dx = \int_{-\infty}^{\infty} \left(p_{xx} - \frac{p_{yy} + p_{zz}}{2} \right) dx$$

IFT of the n-heptane-water interface is predicted performing numerical integration. In the absence of the surfactants the IFT is 48.8mN/m, [12]. Our result agrees well with that reported in literature. However, it is expected that this value will be reduced in the presence of a

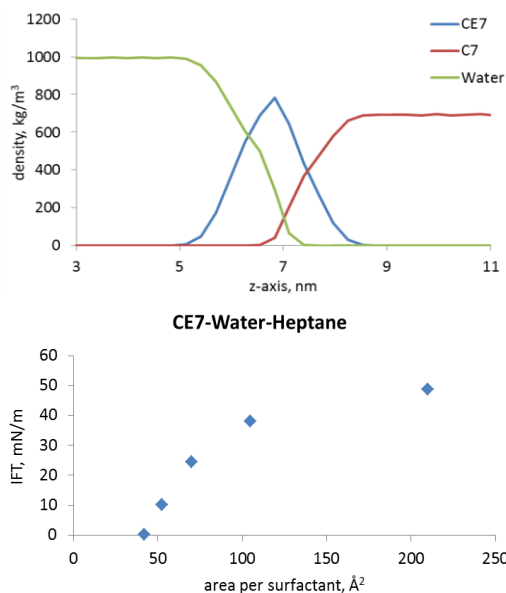


Figure 4. (Top) Density profile of water, n-heptane (C₇) and surfactant (CE7) at the oil-water interface. (Bottom) IFT as a function of surfactant concentration at the oil-water interface.

surfactant, and the extent of reduction should be dependent on the surfactant concentration. Here, the surfactant concentration at the interface is quantified in terms of area per surfactant molecule, which is, in turn, calculated by dividing the surface area of the interface by the corresponding number of occupant surfactant molecules.

The simulation study shows that the IFT decreases proportional to the amount of surfactant molecules at the interface. As we can see in Figure 4 (bottom), when the area per surfactant at the interface drops below 50 Å²/molecule, the IFT decreases to 0.22 mN/m. This corresponds to a reduction in IFT by a factor of 220. For each IFT data point shown in Figure 4, three simulations with different initial configuration are performed, and the average IFT is calculated. The standard deviation associated with this calculation is in between 0.92-1.21 which provides more confidence to our results.

3 CONCLUSION

Results from this work have provided fundamental understanding about the behavior of microemulsions at fluid-fluid interfaces and solid surfaces as well as the droplet-wall interactions that drive the adsorption process. The presence of d-limonene inside the micelles alters the adsorption process by allowing not only the single monomer but also the microemulsion droplet to adsorb at the liquid/liquid and liquid/solid interfaces. Therefore, the delivery of both surfactant and solvent molecules to the interfaces can be tailored to improve the oil recovery by controlling the microemulsion composition.

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