Molecular Dynamics Simulations of Oil Solubilization in Surfactant Solutions

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Received January 25, 1993

Molecular dynamics simulations have been performed on a simple water/oil/surfactant model to mimic the solubilization of nonpolar molecules into aqueous surfactant solutions. Three mechanisms have been identified through which oil molecules are transferred from the oil phase to the micelles: (1) dissolution of oil molecules in the solvent phase before being captured by micelles; (2) exchange of oil molecules between the oil droplet and the micelles during a soft collision; (3) collective desorption of surfactants and oil molecules from the oil droplet surface.

Introduction

Surfactants in solution usually form aggregates that function differently from the unassembled molecules.1 Micelles, bilayers, and vesicles are such aggregates. One of the most important properties of micelles is their capability to enhance the solubility of oily compounds that otherwise display very low solubility in water.2,3 Solubilization in micellar solutions plays an important role in biological, pharmaceutical, and industrial processes. In the human body, bile salt solubilization of fatty materials is a naturally occurring process, and in pharmacy, solubilizers are used to increase the solubility of sparingly soluble drugs.4,5 In industry, oil solubilization in micelles is an important factor in detergency, cosmetics, and improved oil recovery as well as in catalysis and separation.6,7

The mechanism of oil solubilization in surfactant solutions has been studied for almost 20 years, yet there is still a lack of understanding on the molecular level of the process of transfer of oil molecules from the oil phase to the surfactant solution.8,9 The mechanism for this solubilization depends upon the chemical features of the surfactant and the solubilized molecules, the sizes and shapes of micelles as well as the interactions between the phases, aggregates, and unassembled molecules.

The use of molecular dynamics has enabled us previously to study the aggregation of surfactants in solution into micelles and monolayers.9 In this short communication we report the results from molecular dynamics simulations of the transfer of oil molecules from an oil droplet to an aqueous solution of surfactants and micelles.

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Figure 2. Instantaneous configuration at time step 836 000. Oil molecules are drawn in green, and surfactant molecules are drawn in red (tails) and white (head groups). The water molecules are not shown. Surfactants are present in three different forms: (i) as adsorbed species at the oil droplet surface, (ii) as part of a micelle, and (iii) as free surfactants in solution. Similarly, oil molecules are present in the oil droplet, in micelles, and in the water phase.

Model and Simulation Details

The model adopted in our simulations is similar to that used by Telo da Gama and Gubbins\(^\text{10}\) and by Smit et al.\(^\text{9}\) to mimic water, oil, and surfactants. In summary, the model treats water molecules as particles that interact via a Lennard-Jones potential with a cutoff chosen to be large enough to include excluded volume effects and attractive forces. Oil–oil interactions are treated similarly to water–water interactions, while oil–water interactions are modeled using only the repulsive part (excluded volume) of the Lennard-Jones potential. Neighboring particles on the same molecule are connected by harmonic springs of length \(\sigma\), the size parameter in the Lennard-Jones potential.

The different molecules used in the simulations are (1) water molecules made of one water-like particle, (2) oil molecules made of linear chains of two oil-like particles (T2), (3) oil molecules made of linear chains of three oil-like particles (T3), and (4) surfactant molecules made of a linear chain of five oil-like particles and a head group that consists of three water-like particles centered around a fourth water-like particle. Surfactant head groups interact with each other through the repulsive part (excluded volume) of the Lennard-Jones potential and with the water using the Lennard-Jones potential with the large cutoff.

The algorithm used for solving the equations of motion has been described elsewhere.\(^\text{9}\) The simulations were performed at a reduced temperature \(kT/\epsilon = 2.4\), \(\epsilon\) being the energy parameter in the Lennard-Jones potential.

Results and Discussion

Several cases have been investigated dealing with pure oils and mixtures of oil molecules of different lengths. Here, we only report the case where the oil droplet contains initially an equimolar mixture of T2 and T3 molecules.

The water/oil/surfactant system is started in the following way: First, a micellar solution is created by adding water molecules to free monomeric surfactants, resulting in a molecular concentration of 0.02. The simulation results indicate the formation of spherical micelles in coexistence with surfactants in solution. Simultaneously,
an oil droplet is created in water without surfactants. Next, the oil droplet was transferred to the micellar solution.

The initial configuration is shown in Figure 1. At this stage the system contains one oil droplet of 426 T3 and 426 T2 molecules, 471 surfactants incorporated in 23 micelles and 30 additional surfactants that are not parts of micelles, and 25 096 water molecules. In all, the motion of 31 755 particles was followed for 1 600 000 time steps on a parallel computer with 400 processors.

Figure 2 shows the configuration after 836 000 steps. Surfactants are present in three different forms: (i) as adsorbed species at the oil droplet surface, (ii) as part of a micelle, and (iii) as free surfactants in solution. Similarly, oil molecules are present in the oil droplet, in micelles, and in the water phase. Oil molecules are dispersed in the water phase due to the nonzero solubility of T2 and T3 molecules in water. Analysis of the locus of solubilization in micelles shows that oil molecules are dispersed between the surfactants chains at the onset of oil solubilization. At the later stages of the simulation, oil molecules can be found either between the chains or in oil pools in micellar centers (Figure 3). This analysis supports the predictions that oil molecules first penetrate into surfactant chains and then form cores as the oil concentration is increased.\(^{11}\)

As a result of their amphiphilicity, surfactant molecules adsorb at interfaces and significantly change the behavior of the surface.\(^{12,13}\) An investigation of the adsorption mechanism can help in understanding important phenomena such as the time dependence of the surface tension of aqueous surfactant solutions, the flow of thin liquid films, the drainage of foam films, and wetting kinetics. Figure 4 shows the amount of adsorbed surfactants at the droplet–water interface versus time. Two mechanisms have been identified for surfactant adsorption at the oil droplet–water interface. In the first mechanism monomeric surfactants adsorb directly at the interface, while in the second mechanism surfactant adsorption occurs via micelle–oil droplet collisions, as indicated by peaks in the adsorption curve. We predict that the collision mechanism is more likely with nonionic surfactants and less likely with ionic surfactants due to the presence of long range repulsions between surfactant head groups from the oil droplet and micelles. One of the significant details of the adsorption–time curve is the presence of a strong decrease in the number of adsorbed surfactants at time step 920 000. An explanation for this effect will be given later.

In addition to the adsorption process, we have investigated the process through which oil molecules are transferred from an oil phase to micelles. The simulation results indicate the presence of three mechanisms for this transfer: (1) In the first mechanism, oil molecules that exit the oil droplet are trapped by micelles in the immediate vicinity of the droplet. This mechanism is a direct effect of the finite solubility of oil molecules in water. In the presence of micelles, oil molecules in water are being constantly trapped by micelles, effectively creating a chemical potential difference between the oil and water phases, and thus a net oil diffusion from the droplet toward water until the correct partition is reached. (2) In the second mechanism, oil molecules are transferred through droplet–micelle collisions during which an exchange of surfactants and oil molecules occurs. Collision mechanisms have been speculated for solubilize exchange between water in oil microemulsions and quencher exchange between micelles.\(^{14}\) In this mechanism, micelles play a carrier role similar to the role played by biological cells. (3) In the third mechanism, oil molecules exit the
there is a net transfer of molecules, while the other two are more prominent for the adsorbed surfactants at the oil droplet surface. Zana, R., Ed.; Dekker: New York, 97.

Surfactants, accompanied by an increase in the number of adsorbed surfactants together with an increase of T2 and T3 molecules that are not in the oil droplet (time step 920 000). Point A is the step at which collective desorption of surfactants and oil molecules occurs. After 1 576 000 time steps the amount of T2 in micelles (81) is higher than the amount of T3 (38). For T2 molecules there is a net transfer of 50 molecules through dissolution (mechanism 1) and 31 molecules through micelle–oil droplet soft collisions (mechanism 2) and collective surfactant and oil desorption (mechanism 3). For T3 there is a net transfer of 16 molecules through mechanism 1 and 22 through mechanisms 2 and 3.

Thus mechanism 1 is likely to be dominant with small molecules, while the other two are more prominent for the large oil molecules, i.e., the importance of mechanism 1 decreases with increasing free energy of transfer from oil to water phases. As a direct result of difference in solubility, T2 is solubilized more than T3. This is in agreement with experimental data which indicate that molecules with smaller molecular volumes are preferentially solubilized by micellar aggregates, given identical flexibility and polarity of the molecules.5

Conclusions

In summary, this letter presents a simple model of a surfactant/water/oil system which retains the essential physical characteristics. By applying the technique of molecular dynamics simulation, we have witnessed the capacity of surfactant molecules to self-organize into micellar aggregates and, for the first time, the solubilization of oil molecules by such structures. Although the water structure (hydrogen bonding) was not present in this simple model, the self-assembly of surfactants into micelles and the transfer of oil molecules from an oil-rich phase to a micelle-rich phase were prominent outcomes of our simulation studies. This strongly suggests that the self-assembly in surfactant systems does not require the presence of hydrogen bonds and that perhaps a rethinking of the concepts of the hydrophobic effect is needed.15 This work was not intended to perform quantitative comparisons with experimental data but is mostly an indication that computer simulations are capable of providing an insight into the dynamics of real systems. This can be expected to become more important in the future as faster computers become available. The knowledge gained from these simulations will improve our understanding of the mechanism of oil solubilization and its pertinence to practical applications in fields as diverse as detergency, improved oil recovery, catalysis, pharmacy, and the treatment of oil contaminated water.16 In addition, close analogies to the micellar solution can be made with other systems in biology such as cells or enzymes that could effectively act similar to micelles. In chemistry, the simulation of the oil solubilization process opens a new field for development of new surface active agents that are tailored exactly for the solubilization of a particular type of oil or to enhance the rate of solubilization.

Acknowledgment. We thank B. Smit, B. W. van Beest, and I. Siepmann on helpful comments on the paper.