Molecular Dynamics Simulation of Spontaneous Micelle formation of Sodium Octanoate and 1-Octanol in Aqueous Solution

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Introduction

The spontaneous self-assembling of surfactants molecules is a challenging subject on the field of molecular modeling, due to the inherently entropic nature of these phenomena and to the fact that the relaxations times to be considered increase exponentially with the number of hydrophobic groups comprising the tail.[1] We have recently demonstrated that the short-chained anionic surfactant sodium octanoate spontaneously forms equilibrated micelles in aqueous solution during a typical molecular dynamics simulation with tens on nanoseconds,[2] lending itself adequate to studies on the micellar solubilization of organic molecules. The present work is aimed at analyzing the effects of cosurfactant 1-octanol molecules on the structure and dynamics of the octanoate aggregates in solution.

Model System

The model system consisted of 60 octanoate anions, 60 sodium counter ions and 10 1-octanol molecules, surrounded by 3320 water molecules. All molecules were randomly rotated and randomly placed into a cubic box, avoiding strong repulsive contacts between different molecules. The OPLS-AA forcefield was employed to describe the potential energy surface of octanoate anions and 1-octanol molecules, along with the SPC model for water molecules and Åqvist's parameters for sodium ions. The simulation conditions were exactly the same used in our previous studies, allowing the direct comparison between the results of each model system. The total simulation time reached 100 ns.

Results and Discussions

The total energy and the density of the system reached equilibrium after *ca.* 10 ns, although some structural relaxation could still be observed up to 40 ns, a time scale larger than that observed for the total relaxation of the system containing just sodium octanoate. Which structural patterns are being rearranged becomes clearer if we partition the total energy into its components, and analyze them separately. The Coulomb interaction components change appreciably during the structural relaxation. For instance, the interaction among octanoate anions became more repulsive, whereas water molecules substantially decreased their electrostatic contribution to the overall energy. It is worthy mentioning that the coulombic energy due to the interaction between OH from 1-octanol molecules and the carboxylate from octanoate anions molecules did not relax during the whole simulation, indicating that this interaction should be ruled out from those actually modulating the organization of this self-assembled system. Although an individual van der Waals interaction is in general weaker than a typical Coulomb interaction, the overall change in van der Waals energy during the structural relaxation amounted to nearly the same quantity observed for the Coulomb terms.

As compared to the reference system (pure octanoate), the system containing 1-octanol presented a size distribution with a larger probability of finding monomers. At the same time, larger aggregates ($N > 30$) are favored.

We also monitored the composition of each cluster in solution along the simulation, and found out that on average the two larger micellar aggregates had a 0.13 mole fraction of 1-octanol with respect to octanoate, nearly the value for the model system. Visual inspection shows that 1-octanol molecules tend to be clustered at the middle of the aggregate.

Conclusions

The presence of the co-surfactant 1-octanol increases the relaxation time necessary for the micellization process of octanoate anions as compared to the system with surfactant molecules only. Changes in the aggregates structure were observed as well. Co-surfactant molecules are evenly distributed among the aggregates, but they tend to be clustered in the middle of each micelle.

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