

Study of the solubilization of octyl-amine and octyl-ammonium chloride in Sodium Octanoate Micelles by Molecular Dynamics Simulation

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Introduction

The comprehension of solubility properties of organic solutes in micelles are of theoretical and practical interest because these systems are the simplest models of biological membranes responsible to separate, spatially and temporally, the biochemical process that happen inside a cell and that control cellular functions like osmotic equilibrium, recognition, transport and intercellular interaction.^{1,2} The present work aims to study the solubilization of octyl-amine and octyl-ammonium in sodium octanoate micelles by means of molecular dynamics simulations and analyze the effect of the protonation of the solute in the micellar structure and in the interaction energy compounds of the system.

Results and discussion

The two model system consisted of one micelle (N=30) of sodium octanoate taken from a previous simulation, 30 sodium counter-ions, 2500 water molecules, 5 molecules of the amine or ammonium ion, with 5 chloride counter-ions in the last. The simulations conditions are exactly the same used in a previous work³ and reached a total time of 100 ns. Both solutes are incorporated in the micelles with the carbon tail inside the micellar core, avoiding the contact with water like expected, and didn't happen any exchange of solutes molecules between the micelle and the solution after the system reaches the equilibrium besides exchanges of octanoate ions occur throughout the whole simulation. The lost in the interaction between the solutes tail and water when the solute is incorporated in the micelle are similar for the two system and are balanced by the van der Waals interaction with the octanoate tail. On the other hand, the interaction between the solutes head and the water demonstrated pronounceable differences: The interaction energy between octyl-amine head CH_2NH_2 and the water varies from (-64 ± 12) kJ/mol to (-41 ± 10) kJ/mol when the solute is incorporated in the micelle, what isn't fully compensated by the interaction energy between solute head and the octanoate of (-14 ± 5) kJ/mol, and the interaction energy between ammonium ion

head CH_2NH_3^+ and water showed a greater variation with the solubilization in the micelle, increasing from (-262 ± 30) kJ/mol to (-50 ± 11) kJ/mol, but this variation is compensated by the strong ionic interaction energy between octyl-ammonium and octanoate heads at the micellar surface of (-270 ± 60) kJ/mol. The hydrogen bonds also show interesting differences due the solubilization in the micelle: In both systems, the life time of hydrogen bonds between organic solutes and water grow due the incorporation of the solutes in the micelle and, in the case of octyl-ammonium, the hydrogen bonds with the octanoate ions are very stable, presenting a life time of 177 ps, while the occurrence of hydrogen bonds between octyl-amine and octanoate is a rare event and show a life time of only 5,2 ps.

Conclusions

The molecular dynamics simulations have demonstrated plausible differences in the solubilization of protonated and deprotonated long-chain amines in ionic micelles, showing that the solubilization of octyl-ammonium is energetically favorable to the ion due the strong interaction with the opposite charge surfactant while the solubilization of octyl-amine is energetically unfavorable to the molecule due the lost in the interaction with water. The computer simulations have provided detailed molecular interpretations to understand the solubilization phenomena that could not be obtained in another way.

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