

Complexation between a Macromolecule and an Amphiphile by Monte Carlo Technique

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Using a simple modified version of Larson's model, we studied the complexation between a macromolecule and an amphiphile in a dilute range of concentrations. The main characteristic of amphiphile molecules, that is, the hydrophobicity of the tails and hydrophilicity of the heads, is used to model the self-assembling process. Contrary to the molecular thermodynamics approaches, no prior shape was considered for the aggregates and the system was allowed to choose the most stable structure. For true ensemble averaging, without any synthetic results, configurational bias Monte Carlo and reptation moves are used to produce a Markov chain of configurations. From the results, it is found that the macromolecule causes the clusters of surfactants to be formed at a concentration much lower than the critical micelle concentration. Furthermore, the shape of the clusters tends to be more spherical, which is in line with theory and experiments. From the results, it is learned how a polymer can change the behavior of an amphiphilic molecule. All of the results are in good qualitative agreement with experimental and molecular thermodynamics results. Furthermore, the model predicts network formation between bound clusters at high concentrations of the surfactant.

1. Introduction

Many industrial surfactant systems contain a mixture of polymers and surfactants.¹ These mixtures are employed to change different properties of pure solutions. They can change colloidal stability, emulsification, structuring, and suspending properties.² The presence of polymers may even cause a separation of phases in a mixed system as has been shown by Nilsson et al.³

A solution of a polymer–surfactant mixture can be classified into three concentration ranges.⁴ In the first range, there is no binding of the surfactant to the polymer, and hence, there is no measurable interaction between polymers and surfactants. In the second range, interaction between the polymers and surfactants begins. In this range, the concentration of both bound and free monomers of the surfactant is varying. In the third range, free micelles are formed and the free monomer concentration of the surfactant gradually decreases as the total concentration of the surfactant is increased. The concentration at which the onset of association of the surfactant to the polymer occurs, often termed the critical association concentration (CAC), and at which the critical micelle concentration (CMC) occurs is the concentration at which free micelles are formed. If the association of the surfactant is monitored directly (e.g., by surfactant-selective electrode, equilibrium dialysis, or other techniques), it can be possible to deduce the CMC/CAC ratio.

The amount of interaction between the surfactants and polymers depends on the type of interaction between them.

Hydrophobic interactions occur between nonionic polymers and nonionic surfactants, and on the other hand, electrostatic interactions are obvious, if both the surfactant and the polymer have opposite signs of charges. In some cases, the hydrophobic modification of a polymer can change its properties. For example, Winnik and co-workers hydrophobically modified cationic cellulose to study the interaction of a cationic surfactant with the polymer.⁵ Despite the unfavorable electrostatic repulsions, cationic surfactants associate with the polymer. In these cases, hydrophobic interactions are the driving force of the association.

Many experimental efforts have been made to study the different roles of polymers in regard to amphiphilic properties.^{6–8} To understand these effects, the experimental trends have to be compared with the predictions of either a theory or a simulation.

On the theoretical side, two important models have been proposed to describe the polymer–surfactant complexation.^{9,10} In the first model, introduced by Nagarajan, it is assumed that the polymer segments present at the micelle surface penetrate into the region occupied by surfactant heads and partially shield the contact area between the micellar hydrocarbon core and water. This effect is considered to constitute the main driving force for polymer–surfactant complexation. However, the tendency for polymer shielding is opposed by the increased steric repulsions between the surfactant heads and the polymer segments at the micelle surface. Whether the cooperative complexation process actually occurs is determined by the two competing tendencies. The second model, introduced by Ruckenstein et al., assumes that polymer adsorption at the micelle surface induces a change in the microenvironment surrounding the micelle (from pure water to an aqueous polymer solution, with the latter being more hydrophobic than the former) and that this change in the microenvironment brings about a decrease in the interfacial free energy between the micellar hydrocarbon and the solvent. This effect is considered to be the primary

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