

Adsorption and Desorption Behavior of Ionic and Nonionic Surfactants

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Surfactants, either designed by nature or synthesized by humans, accumulate at hydrophobic/hydrophilic interfaces. The strength of their adsorption at the interface, which implicitly affects their capacity to reduce the surface tension, can also have practical implications such as those encountered in the process of emulsion polymerization. In this work, we combine experimental and computational techniques to elucidate the adsorption properties of ionic and nonionic surfactants on poly(styrene). To represent these two types of surfactants, we choose sodium dodecyl sulfate and poly(ethylene glycol)-poly(ethylene) block copolymers, both commonly utilized in emulsion polymerization. By applying quartz crystal microbalance with dissipation monitoring we find that the non-ionic surfactants are desorbed from the poly(styrene) surface slower, and at low surfactant concentrations they adsorb with stronger energy, than the ionic surfactant. Of fact, from molecular dynamics simulations we obtain that the effective attractive force of these nonionic surfactants to the surface increases with the decrease of their concentration, whereas, the ionic surfactant exhibits mildly the opposite trend. We argue that the difference in this contrasting behavior stems from the physio-chemical properties of the head group. Ionic surfactants characterized by small and strongly hydrophilic head groups form an ordered self-assembled structure at the interface whereas, non-ionic surfactants with large and weakly hydrophilic head groups generate a disordered layer. Consequently, upon an increase in concentration, the layer formed by the nonionic surfactants prevents the aprotic poly(ethylene glycol) head groups to satisfy all their hydrogen bonds capabilities. As a response, water molecules intrude this surfactant layer and partially compensate for the missing interactions, however, at the expense of their ability to form hydrogen bonds as in bulk. This loss of hydrogen bonds, either of the head groups or of the intruding water molecules, is the reason the nonionic surfactants weakens their effective attraction to the interface with the increase in concentration.

For the ionic surfactant we have not observed this behavior, however, further analyzes were hampered by the large fluctuations in the electrostatic forces.