

Why does the nano-scale association between surfactants and polymers influence the rheology of waterborne systems?

Understanding the interaction between surfactants and polymers in solution is very relevant in many applications including water borne coatings as described by Holmberg¹ and Odeh²

Surfactants, as is well known, form nano-aggregates in water in the form of micelles with hydrophobic core and hydrophilic corona. A certain critical concentration called as CMC has to be crossed for micelles to form. Below the CMC, the molecules of a surfactant are present in the solution (after saturating the surface) as individual molecules, called as unimers. These unimers are active species possessing high kinetic energy imparted by the hydrophobic part. These can associate with any hydrophobic moiety in the solution and can get immobilized. If polymeric molecules that possess hydrophobic segments are present in water, then the surfactant unimers will show associative interaction forming a combined moiety. This hydrophobic interaction between a surfactant and a water soluble polymer varies depending upon the chemical nature of the polymer and the surfactant; and their respective concentrations. This nanophasic association is of immense significance for the bulk properties of such systems like surface tension, rheology and phase separation. The essential requirement for such interactions is the presence of a hydrophobic segment in the polymer molecule.

Hydrophobic interactions do occur in case of all types of surfactants and the hydrophobe containing polymers.

The behavior of surfactant–polymer–water system in comparison to conventional surfactant-water system is profiled in *Figure: Surfactant-Polymer Association: CAC and CMC*. When a surfactant is gradually added to a solution containing a polymer with a hydrophobic segment, its surface tension drops much more rapidly at low concentrations. This is due to the fact that the surface already contains hydrophobic chain ends of the polymer which lower the surface tension. This situation requires less amount of surfactant to saturate the surface. With further addition of surfactant, an inflexion point is reached at a concentration much lower than the CMC, where the surface tension plateau is formed.

This point marks the beginning of the hydrophobic association between the polymer and the surfactant inside the solution. This point is called as Critical Association Concentration (CAC). At a yet higher concentration of the surfactant, the polymer molecules are fully saturated with the associated surfactant and the plateau region ends and surface tension begins to drop further. Since all the polymer molecules are fully hydrophilized due to association of the surfactant on the hydrophobic segment, the concentration of polymer in the surface drops down which creates more room for accommodating more surfactant molecules in the surface thereby decreasing the surface tension. A stage is soon reached where the surface is saturated with the surfactant and further surfactant molecules start forming micelles in the solution. This is the conventional CMC point. Another plateau region now starts at a lower surface tension. Thus a surfactant–polymer–water system shows three points of inflexion compared to only one in the normal surfactant water system.

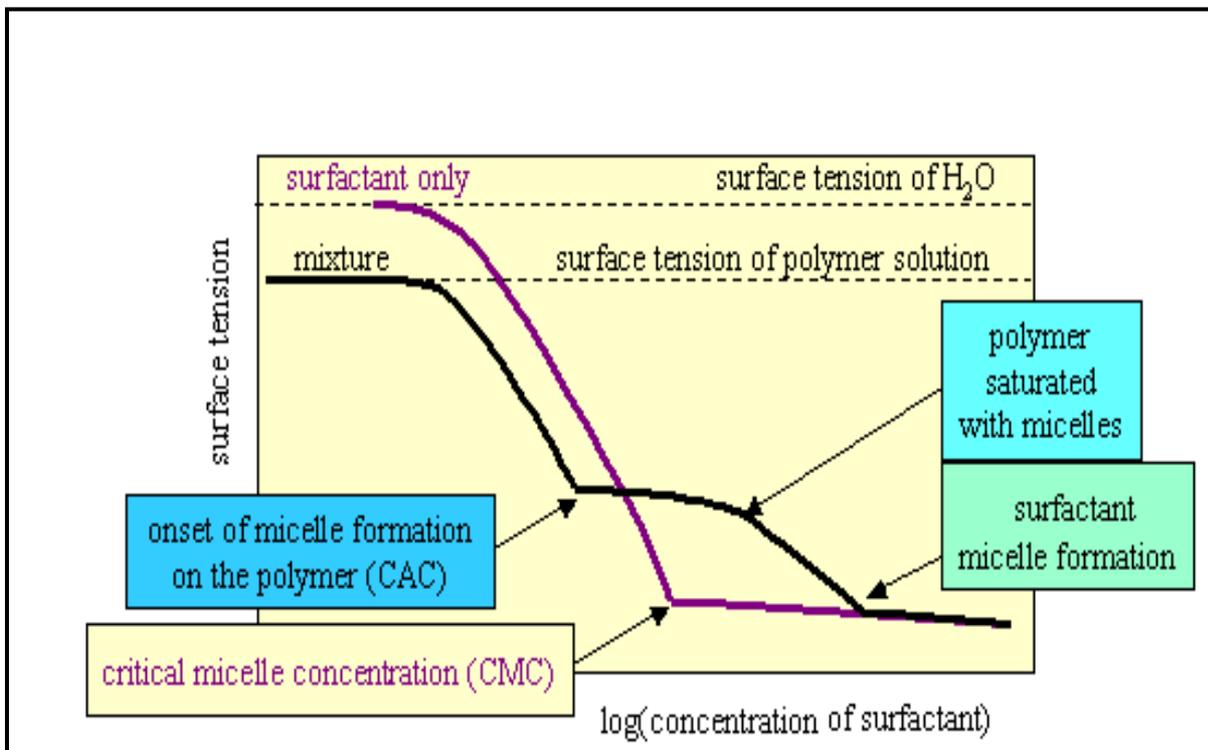


Figure: Surfactant-Polymer Association: CAC and CMC (Source: Ref.2)

Hydrophobically modified polymers like the derivatives of cellulose and polyurethanes are often used in paints as protective colloids and rheology modifiers. Such systems almost always contain surfactants. The interaction between the surfactants and the

polymers alters the rheology of the system significantly as shown in the *Figure: Surfactant micelles as cross-linkers*. These interactions are further influenced by ionic strength, pH and temperature of the system.

For a given concentration of a polymer, there are three different types of interactions with the surfactant as follows:

- Low surfactant concentrations: The surfactant molecules associate individually with the hydrophobic segments and the aggregation with the polymer is intramolecular with respect to the hydrophobic segments. This really does not significantly influence the rheology of the system.
- Intermediate surfactant concentrations: When the number of micelles is within a certain band, the hydrophobic core of the micelles acts as a nanoparticle cross-linker for the hydrophobic segments on the different polymer molecules. This brings about intermolecular network formation, leading to sudden increase in the viscosity. In other words, the surfactant acts as viscosity booster for the polymer solution. The configuration of polymer and micelles in this state is some times referred to as “Pearl- Necklace Model”, with the micelles as the pearls linked by the polymer chains.
- High surfactant concentrations: As the number of micelles starts to increase in comparison to the number of hydrophobic segments of the polymer, every single micelle encapsulates a single hydrophobic segment. This behavior of micelles is more like chain termination rather than cross linking, in polymer parlance. As a result of this, the polymer network earlier formed via the micelles collapses and the viscosity of the solution drops.

This role of surfactant micelles as nanoscale cross-linkers for hydrophobically modified water soluble polymers is significant in many systems. This leads to synergistic increase in viscosity depending upon the relative concentration of the surfactant and the polymer.

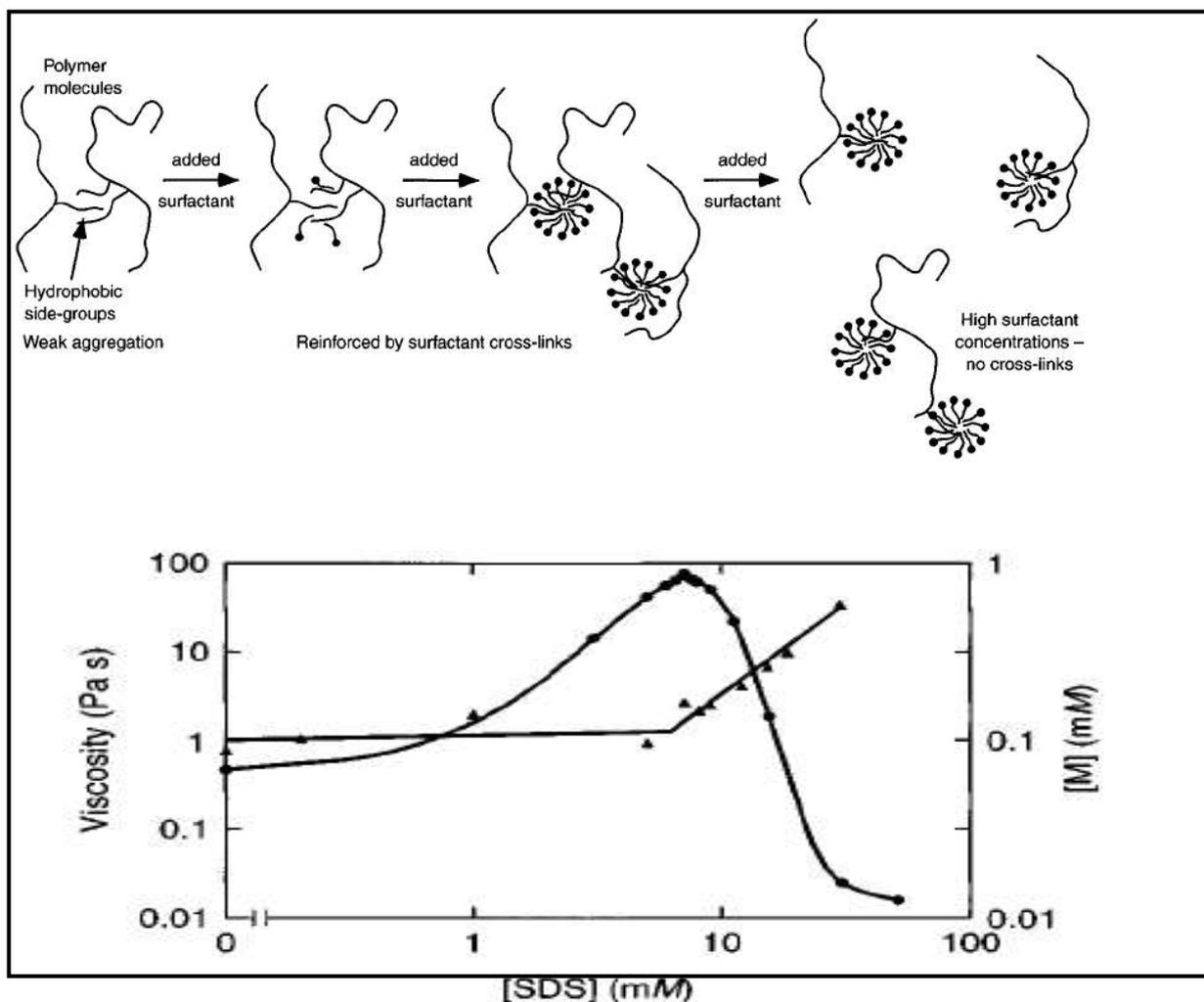


Figure: Surfactant micelles as cross-linkers (Source: Ref.2)

References:

1. Holmberg, K., "Surfactant Polymer Systems", *Proc. of Workshop on Surface Science and Nanotechnology*, SSCSCN, Nadiad, India, Feb 2010
2. Odeh, F., "Polymer-Surfactant Interaction", *Dept. of Chemistry, Clarkson University*, <http://media.clarkson.edu/ChemSem02-16-06/ChemSemSlide1.pdf>, (August 2010)