

Application note #8

Critical micelle concentration

What is critical micelle concentration (CMC)?

Generally speaking surfactants are molecules that contain two different parts: a hydrophilic head group and a hydrophobic tail. Each part of a surfactant has very different solubility properties. This causes the molecule to have limited solubility in any solvent and they tend to accumulate at the interface between two phases or form micelles. The most common examples of surfactants are soaps, which are usually sodium or potassium salts of organic fatty acids, such as oleic, palmitic or stearic acid.

Critical micelle concentration is defined as the concentration of surfactants in which micelles are spontaneously formed. Below the CMC surfactants tend to accumulate at the interface, reducing surface tension. At CMC, the surface tension of the solution does not change but remains constant, as the gas-liquid interface is already fully packed with the surfactant molecules. Above the CMC, most of the surfactant molecules are inside the bulk aggregating into micelles. When this occurs, the addition of surfactants just increases the number of micelles and the surface tension becomes independent of surfactant concentration.

There are several factors affecting the CMC of a surfactant. These include the amphiphile chain length, dissolved salts, the structure of the head group, temperature, the structure of the alkyl chain and polar additives. The effects of chain length, salts and alcohol on the critical micelle concentration have been widely studied (Shinoda, 1953).

Micelles form only above the Krafft temperature, which is a point of phase change. Below this point, the surfactant remains in crystalline form, even in aqueous solution.

The exact molar weight and impurities in the surfactant also influence the CMC, so a careful purification of the surfactant is relevant. A common and much studied surfactant found in many detergents is sodium dodecyl sulfate (SDS). SDS is easily hydrolyzed to dodecanol, which can be seen as a possible contaminant.

Miles and Schedlovsky (1944) reported surface tension data for purified SDS with various amounts of dodecanol. These curves, showed in figure 1, suggest that the impurities cause a minimum in surface tension-concentration curve. The surface tension of the impure surfactant comes back to its original value after the minimum as the micelles incorporate the impurity by solubilization and remove it from the solution. If a high purity surfactant is used, the minimum does not occur. This method can be used to detect impurities in a surfactant.

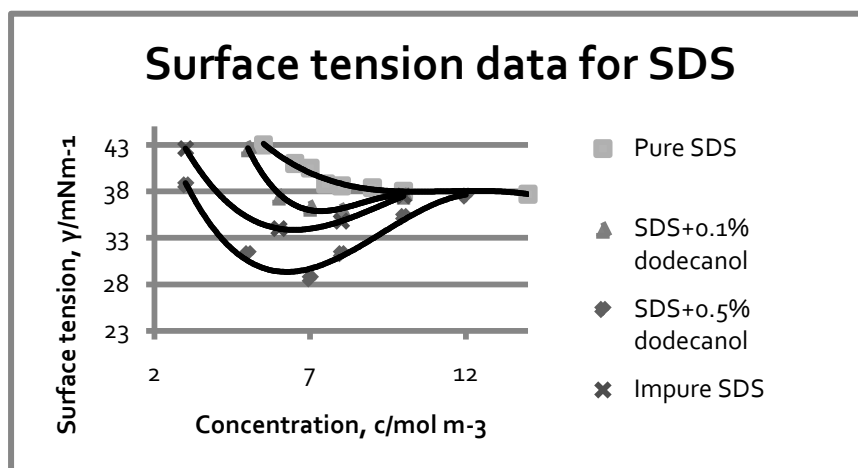


Figure 1. Surface tension data of sodium dodecyl sulfate with various amounts of contamination (dodecanol). Replotted data of Miles and Schedlovsky (1944).

Why measure CMC?

CMC is an important characteristic of a surfactant. From thermodynamics of micelle formation, useful relations between free energies and surfactant chemical potentials can be obtained. It also provides clear relations for enthalpy and entropy. The equation

$$G_{mic}^{\theta} = RT \ln CMC \quad (1)$$

combined with the Gibbs-Helmholtz equation provides an expression for the enthalpy of micelle formation

$$\Delta H_{mic}^{\theta} = -RT^2 \frac{\partial}{\partial T} \ln CMC \quad (2)$$

The equilibrium and transportation properties (optical density and electrical conduction) of the solution are affected by the aggregation process at the critical micelle concentration.

The manufacture of surfactants is a major commercial enterprise. Surfactants are mostly used in soap and detergent industries. The surfactant industry is interested in optimizing the amount of detergent and minimizing waste. These studies require a closer look of the surfactant CMC. The important aspect of detergent manufacturing is the phenomenon of solubilization in micelle formation. A water insoluble organic compound can be “dissolved” in a surfactant solution as it can move to the oily interior of the micelle. The surfactant micelles can also stabilize an oil-water emulsion by absorbing on a surface of an oil droplet. Commercial detergents contain a mixture of surfactants. These impure substances are cheaper and easier to manufacture. Mixing of surfactants also often improves the performance of a detergent. Sarmoria, Puvvada and Blankschtein have studied the CMC prediction of nonideal binary surfactant mixtures (Langmuir 1992, 8, 2690-2697).

The critical micelle concentration is a useful measure also in pharmacology and technology. Silicon surfactants are important in pharmaceutical and cosmetic industry due to their low price and technological advantages (Baquerizo, Holgado, Cabrerizo, Gallardo, 2000). Studies on interfacial properties of lysophospholipids require the full understanding of the molecule's CMC (Stafford, Fanni and Dennis, 1989). Liposomes can be used to carry non-polar drug molecules in blood.

A significant use for CMC is the process of emulsion polymerization. It is a technologically and commercially important reaction that can be used to synthesize alternatives to natural latex rubber. Emulsion polymerization is carried in the surfactant's critical micelle concentration. The CMC of the surfactant is an important factor in the particle nucleation process. The latex particles are thermodynamically unstable and can be stabilized by a mixture of surfactants. Usually these surfactant mixtures are a combination of anionic and non-ionic surfactants such as SDS and nonyphenol polyethoxylate (Chen, Lin, Chern, Wu, 1997). The CMCs of these surfactant mixtures are lower than the CMCs of the pure surfactants. This is due to the interactions between the different surfactant molecules in the formation of mixed micelles. The emulsions obtained with the emulsion polymerization method can be used in glue, coating, PVC and rubber manufacturing.

Conclusion

CMC studies have been known to be important for decades in all areas containing surfactants. Surfactants are relevant in many chemical manufacturing processes and therefore precise and accurate results of CMC studies are essential in order for these processes to be successful.

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