Overview

Critical micelle concentration

- What is it and how to measure it

To understand critical micelle concentration, we need to first talk about surfactants. Surfactants are compounds that lower the surface tension of the liquid, the interfacial tension between two liquids or interfacial tension between a liquid and solid. Surfactants can act as detergents, wetting agents, emulsifiers, foaming agents and dispersants.

Surfactants are amphiphilic

Surfactants are amphiphilic molecules that contain the hydrophobic hydrocarbon tail and hydrophilic head. Therefore, surfactant molecule contains both a water soluble and water insoluble (or oil soluble) component (figure 1A). When these molecules are at the air-water or oil-water interfaces they align so that the hydrophilic part is in water phase and hydrophobic part in air (or oil) (figure 1B). Another energetically favorable form for the surfactant molecules in water solution are micelles where the hydrophobic tails are protected by the hydrophilic head groups (figure 1C).

Critical micelle concentration can be determined with surface tension measurements

In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration above which micelles form. At low surfactant concentration the surfactant molecules arrange on the surface. When more surfactant is added the surface tension of the solution starts to rapidly decrease since more and more surfactant molecules will be on the surface. When the surface becomes saturated, the addition of the surfactant molecules will lead to formation of micelles. This concentration point is called critical micelle concentration. A simplified graph of surface tension vs. logarithm of surfactant concentration is shown in figure 2.

Three different phases can be identified;

1) At very low surfactant concentration only slight change in surface tension is detected.

2) Addition of surfactant decreases the surface tension drastically

3) At CMC point, surface becomes saturated and the addition of surfactant molecules do not effect on the surface tension.

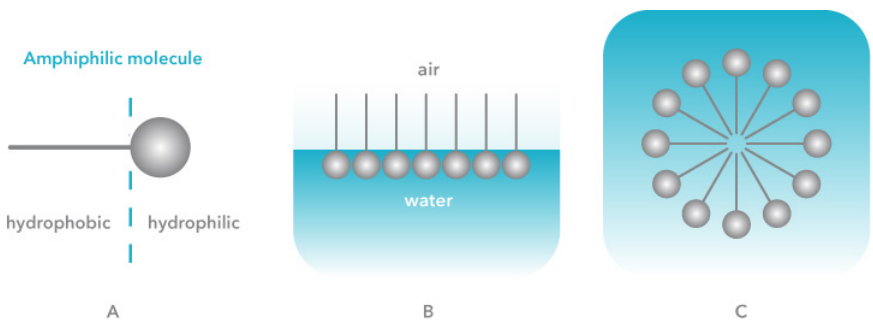

Figure 1: (A) Amphiphilic molecule, (B) Amphiphilic molecule at the interface (C) Micelle

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Why measure CMC?

Critical micelle concentration determines the concentration at which the micelles start to form. Below that concentration, surfactant molecules are still soluable in water. Above that, the micelles are found throughout the solution. The effectiveness of surfactant is partly determined by its ability to lower the surface tension. How much surfactant is needed can be determined by critical micelle concentration measurements. Adding more surfactants than needed to reach the lowest possible surface tension is neither economical nor environmentally friendly. In practice though, the optimimum surfactant concentration is typically slighly higher as surfactants are depleted during the industrial process. Micelle formation is often at least somewhat reversible, allowing more surfactant molecules to be liberated in case the ones in a solution are depleted due to adsorption, for example.

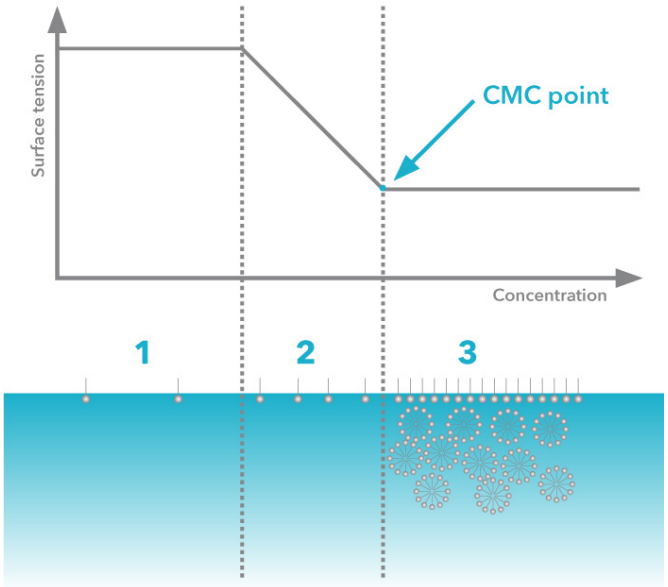

Figure 2: Surface tension as a function of concentration (logarithmic scale)

Critical micelle concentration measurements by using Sigma force tensiometer

Sigma force tensiometer can be utilized to measure critical micelles concentration by combining it with one or two dispensers. Both of these methods are explained below.

One dispenser

In the one dispenser approach the known volume of pure water is put on the beaker and the surfactant solution is added to the beaker little by little by using the dispenser. The concentration of the surfactant solution should be low enough, so that the first addition (minimum volume 0.01 ml) of the surfactant solution does not drastically decrease the surface tension of the water. This is because too large additions can lead to noisy CMC curve due to insufficient mixing of the surfactants. On the other hand, the surfactant concentration should be large enough that the CMC point is reached before the beaker is full. To avoid overflow of liquid, it is important to mark the volume of the beaker correctly in the CMC measurement recipe. The biggest disadvantage of this method is that the dispenser will be contaminated by the surfactant solution so extensive cleaning of the dispenser is required when the surfactant solution is changed.

Two dispensers

In the two dispenser approach, the known volume of the concentrated surfactant (well above the CMC point of the surfactant) solution is placed in the beaker. Water is added with the one dispenser and the other dispenser is used to take the equal amount of liquid off the beaker. With this approach the beaker cannot fill up since equal amount of liquid is always taken out as is added. Also there is no contamination issues since the adding dispensers is only filled with water and the dispenser taking out the liquid goes directly to waste.

Surface tension measurement provides easy and economical solution for critical micelle concentration measurement