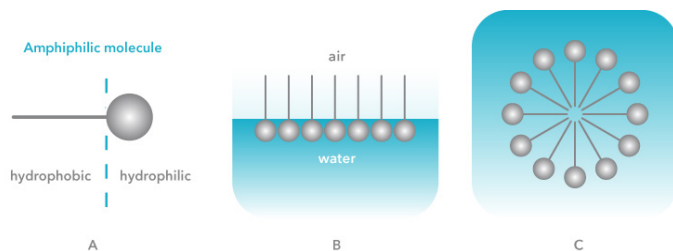


Critical micelle concentration

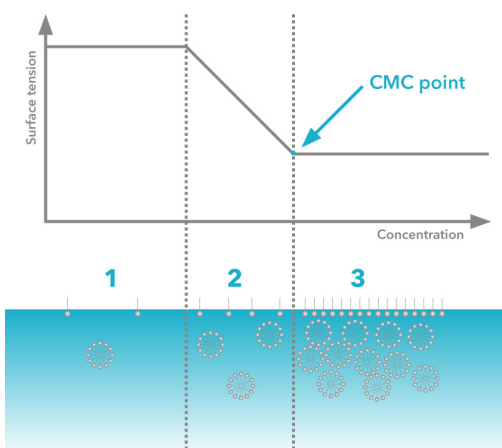
This technology note explains the concept of critical micelle concentration and how it is measured by using Attension Sigma Force Tensiometer.

Introduction

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 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 on air-water or oil-water interfaces they align so that the hydrophilic part is in water phase and hydrophobic part in air (or oil) phase (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).



[Figure 1]: A) Structure of amphiphilic molecule B) Amphiphilic molecule on air-water interface C) Micelle



<--- [Figure 2]: Surface tension against the surfactant concentration (logarithmic scale).

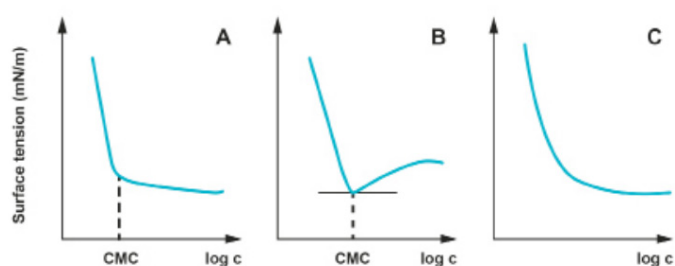


In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration above which micelles form. At low surfactant concentration the surfactant molecules arrange on the surface. When more surfactant is added the surface tension of the solution starts to rapidly 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 graph of surface tension vs. logarithm of surfactant concentration is shown in Figure 2^[1]. 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.

Shapes of the real CMC curves

In theory the determination of the CMC point should be relatively easy but in practice there are some special situations where the shape of the curve makes the CMC point determination problematic. In Figure 3, three different types of curves are shown. According to ISO 4311:1979, the graph A shows the situation where the CMC corresponds to the point on the curve at which a sharp change of slope occurs. Graph B shows a situation typical for sodium dodecyl sulfate (SDS) for example where a clear drop in surface tension value can be seen. This is thought to be because of the impurities present in the SDS solution [2]. According to ISO 4311:1979 standard the minima in the curve should be chosen as a CMC point. In graph C the curve does not have a clear sharp corner point or clear minima. In this case, the standard proposes to repeat the measurement since procedural error or a particular phenomenon may be involved making results unusable. If the curve stays the same after repetition, the CMC range cannot be determined.



[Figure 3]: Shapes of the real CMC curves

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.

References:

- [1] P. Mukerjee and K. J. Mysels, "Critical micelle concentrations of aqueous surfactant systems", NSRDS-NBS 36.
- [2] G. D. Miles and L. Shedlovsky, "Minima in surface tension-concentration curves of solutions of sodium alcohol sulfates", The journal of physical chemistry 48 (1944) 57. [ISO 4311:1979] "Anionic and non-ionic surface active agent- Determination of the critical micellization concentration- Method by measuring surface tension with a plate, stirrup or ring".