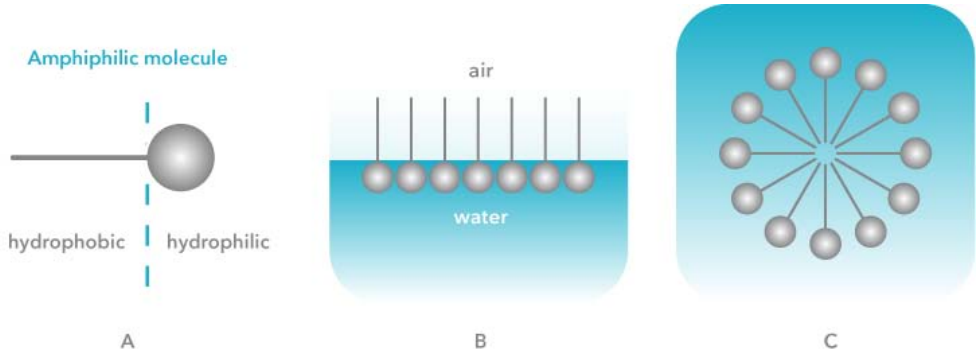
Application note #3:

CMC theory and measurement techniques

This application note offers an explanation of the concept of critical micelle concentration and the use of Attension Sigma Force Tensiometer to measure CMC.

What is critical micelle concentration?

Certain molecules may be said to contain two distinct components, differing in their affinity for solutes. The part of the molecule which has an affinity for polar solutes, such as water, is said to be hydrophilic. The part of the molecule which has an affinity for non-polar solutes, such as hydrocarbons, is said to be hydrophobic. Molecules containing both types of components are said to be amphiphilic (illustration A).

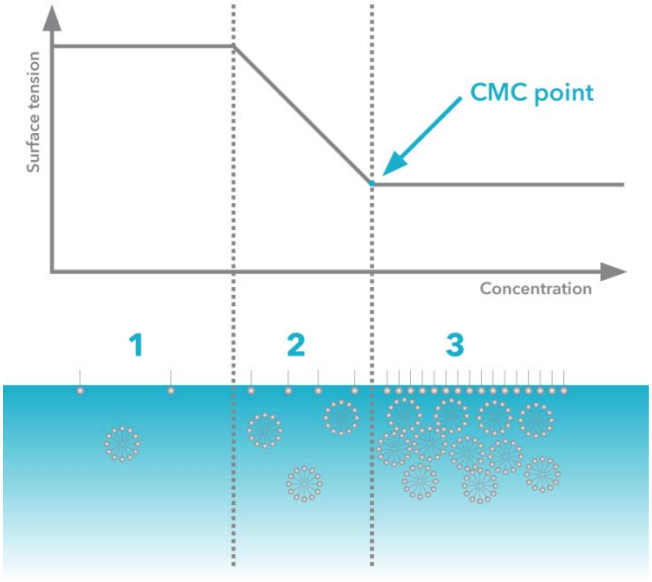


Such molecules display distinct behavior when interacting with water (illustration B and C). The polar part of the molecule seeks to interact with water while the non-polar part shuns interaction with water. There are two ways in which such a molecule achieve both these states.

An amphiphilic molecule can arrange itself at the surface of the water such that the polar part interacts with the water and the non-polar part is held above the surface (either in the air or in a non-polar liquid) as shown in Illustration B. The presence of these molecules on the surface disrupts the cohesive energy at the surface and thus lowers the surface tension. Such molecules are called ‘surface active’ molecules or surfactants.

Another arrangement of these molecules allows each component to interact with its favored environment. Molecules can form aggregates in which the hydrophobic portions are oriented within the cluster and the hydrophilic portions are exposed to the solvent. Such aggregates are called micelles. An example of a spherical micelle is diagrammed above (Illustration C).

The proportion of molecules present at the surface or as micelles in the bulk of the liquid depends on the concentration of the amphiphile. At low concentrations surfactants will favor arrangement on the surface. As the surface becomes crowded with surfactant more molecules will arrange into micelles. At some concentration the surface becomes completely loaded with surfactant and any further additions must arrange as micelles. This concentration is called the critical micelle concentration (CMC). It follows that measurement of surface tension may be used to find CMC. A graph of surface tension vs log of concentration of surfactant added will appear as follows:



In this graph you can see three phases:

1) At very low concentrations of surfactant only slight change in surface tension is detected.
2) Additional surfactant decreases surface tension
3) Surface becomes fully loaded, no further change in surface tension.

As shown above the technique for assaying CMC by measurement of surface tension is simple and straightforward. A graph of surface tension vs log concentration is produced. The CMC is found as the point at which two lines intersect; the baseline of minimal surface tension and the slope where surface tension shows linear decline.

The graph of surface tension vs log concentration may be done by measuring a series of manually mixed solutions or automatically using an Attension Sigma 700 or 701 with optional dispenser. Manual mixing and testing surface tensions for a series of solutions is both time consuming and difficult. After solutions of surfactants are mixed time may be required for the surface tension to reach an equilibrium value. This time may vary from seconds to hours. When a researcher is trying to manually find CMC this may present real problems. If CMC values are found using the automated features of the Sigma range the stability of surface tension measurements can be easily handled. Simply enter the desired limits of stability and the maximum time allowed for measurement at any concentration and the tensiometer will continue measuring until these limits have been met. The Sigma 700 and 701 programs also automate the mixing of concentrations for even spacing across the log scale and assist in graphics analysis to find your CMC.

How is CMC Measured?

There are two possibilities to perform CMC measurements with Sigma 700/701; either by adding a concentrated solution of surfactants to an initially surfactant free solution or by diluting a concentrated surfactant solution with pure solvent. To perform a measurement of CMC with a Sigma you must first prepare your physical setup, software and chose the way to measure CMC.

First, a probe is chosen (Wilhelmy plate or DuNouy ring) and the measuring vessel is filled with the initial solution. The dispenser is filled either with concentrated surfactant or pure solvent depending on which type of CMC measurement that has been chosen. The software is programmed and the experiment initiated. This short procedure is all that is required of the researcher. The Sigma 700/701 will automatically complete the experiment.

The experiment will proceed in stages. First a surface tension will be measured prior to any addition. Next the first addition will be made. If you wish, you have the option of programming this as a large addition to bring the system closer to a known CMC value. The instrument will then stir the solution. Next, values of surface tension will be measured. Frequently after the addition of surfactants or pure solvent the values of surface tension will take some time to stabilize. You can set the values which will decide the required limits for stability. When the system has displayed the required stability in surface tension measurements or a maximum time limit (set by you) has passed, your Sigma will make another addition and continue as above.

Additions will be made such that data will be evenly spaced along a log scale of concentration. You will select the range of concentrations assayed and the number of data points desired and the Sigma will mix the appropriate solutions for measurement.

You may also select the AutoSearch option. This divides the experiment into two phases. The Search phase allows for larger additions to be made during the first portion of the experiment when data not critical to CMC calculations will occur. When a sufficient drop in ST values occurs the experiment will switch to the Measurement phase and obey the addition schedule of a normal experiment.

When all requested additions have been made the experiment will terminate. The data will be automatically stored to your hard drive and can be analyzed at any later time.

The software for Sigma 700/701 CMC measurements is a Windows based program which is both simple to use and yet provides the widest range of control options available. The experimental parameters which may be controlled through the software include;

Mixing Controls:

* start concentration
* end concentration
* number of concentrations assayed
* dispensing rate
* stirring rate
* stirring time
* wait after stirring
* stability of measurements
* maximum time measuring
* Autosearch: larger additions/ pressure drop trigger

Probe Controls:

Wilhelmy Plate	*DuNouy Ring*
* speed up/down	* speed up/down
* wetting depth	* wetting depth
* wait between measurements	* wait between measurements
* detect range for interface	* detect range for interface
* wet first only/wet each time	* % drop between measurements
* tare when dry/ wet	* % drop while stirring
* delay before measurement	* active taring
* integration time	* starting depth

Many researchers are interested in finding the CMC for surfactants in order to optimize detergent amount and minimize waste. Beyond the calculation of CMC the researcher will also produce a graph which shows surface tension across a range of concentrations. Data is also produced which shows the change in surface tension after mixing and time required to reach equilibrium.

References:

K.S.Birdi, Handbook of Surface and Colloid Chemistry,CRC Press,Boca Raton, FL, 1997
Paul C.Hiemenz, Principles of Colloid and Surface Chemistry,Marcel Dekker, N.Y. 1997