CRITICAL MICELLE CONCENTRATION DETERMINATION USING DYNAMIC LIGHT SCATTERING (DLS)

Surfactants may self-assemble into structures called micelles when they reach a concentration known as the critical micelle concentration (CMC). While individual surfactant molecules are too small for detection by most sizing techniques micelles are large enough for particle size analysis using the dynamic light scattering (DLS) technique. It is important to understand where the CMC is for many systems because of the interplay between micelles and lipophilic proteins. Additionally, locating the CMC is necessary when using surfactants to disperse powders as the formation of micelles is followed by particle agglomeration/aggregation. This study describes an experiment to determine the CMC of Triton X-100 using a DLS-based particle size analyzer.

Introduction

The term surfactant is a blend of the words **surf**ace **act**ive **a**gen**t**. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic (or lipophilic) groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. A basic diagram of a surfactant is shown in Figure 1.

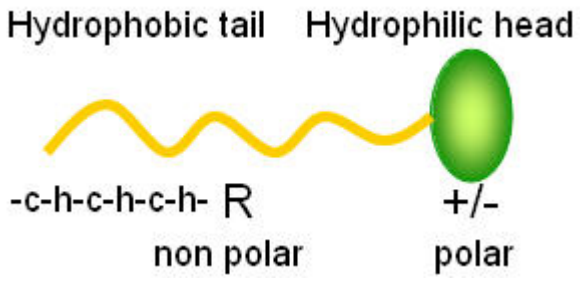

Figure 1: A surfactant molecule

Surfactants lower surface tension by adsorbing onto surfaces such as liquid/air or solid/liquid. One use of surfactants when making particle size measurements is by adsorbing the hydrophobic tail onto the particle surface, exposing the hydrophilic head to the water. Through this mechanism particles that don't naturally wet and float on the surface of water can be dispersed into an aqueous suspension.

In low concentrations, surfactants in water exist as isolated molecules. Many surfactants can also assemble in the bulk solution into aggregates called micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. Micelles can orient with either the hydrophilic head oriented to the outside in aqueous suspensions, or with the hydrophobic tail oriented outward in an organic suspension (a reverse micelle). Examples of a spherical micelle and reverse micelle are shown in Figures 2 and 3.

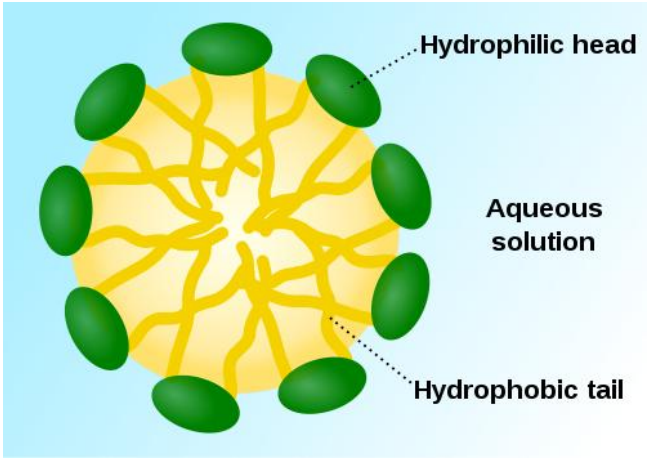

Figure 2: Cross-sectional view of a micelle

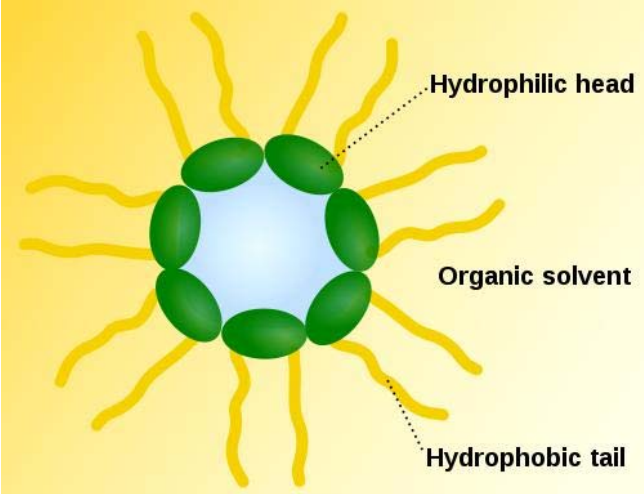

Figure 3: A reverse micelle

In the ideal case any further addition of surfactants will just increase the number of micelles once the CMC is reached.

The CMC is a very useful value to know for a surfactant. CMC is a measure of surfactant efficiency; a lower CMC value indicates less surfactant is needed to saturate interfaces and form micelles.

Many analytical techniques can be used to determine the CMC of a surfactant including surface tension analyzers, conductivity, various spectroscopy techniques, and various particle size analysis techniques. In this study the DLS sizing technique was used to determine the CMC of Triton-X 100. Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$) is a nonionic surfactant which has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group, see Figure 4.

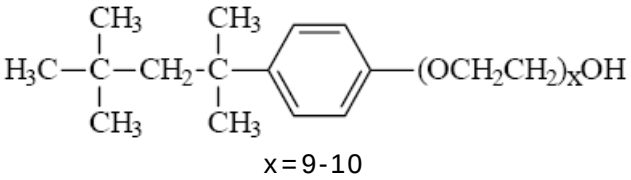

Figure 4: Triton X-100

Experimental

Most CMC data is published as a function of weight percent (wt%) of the surfactant. The first step of this study was determining the weight a drop from the pipette used for the experiments. Five drops of Triton X-100 (Sigma Aldrich, CAS#9002-93-1) were weighed on a tared beaker and divided by five to calculate the weight per drop. A single drop was then also weighed on a tared beaker and found to be essentially the same as the averaged weight value.

A solution of 10 mMol NaCl was prepared in a beaker and mixed using a stir bar. The temperature was kept at 25 °C. Increments of five drops of Triton X-100 were added to the beaker and mixed for ten minutes. A small aliquot of the material was removed via clean pipette and transferred to a cuvette for analysis using DLS. The DLS measurements were made using the HORIBA LB-550 system, see Figure 5.

Figure 5: LB-550 DLS Nanoparticle Size Analyzer

The light scattering intensity was recorded for each concentration analyzed. The sample was then returned to the original beaker since DLS is a non-destructive test. Once the light scattering intensity increased above 4 (arbitrary light intensity units) it was possible to perform a particle size analysis measurement and calculate the hydrodynamic diameter of the micelles.

Results

The data collected during this study is shown in Table 1.

Triton X-100	Conc. wt%	Intensity	Size (nm)
10mMol NaCl	0	0.94	-
1 drop	0.0017	1.78	-
5 drops	0.0086	2.35	-
10 drops	0.0172	3.18	-
15 drops	**0.0255**	**4.78**	**9**

Table 1: DLS results from the LB-550

Discussion and Conclusions

The CMC of Triton X-100 at 25 °C in this study was determined to be 0.0255 wt% and agrees very well with published values (1). This has practical application for laboratories using surfactants when dispersing samples for particle size analysis. The concentration of Triton X-100 should never exceed the CMC during a particle size measurement for three reasons.

1. Above the CMC the micelle will add to the light scattering intensity and may be reported as a separate particle population from the actual sample particles being analyzed.
2. The goal of adding surfactants to disperse particles is to coat the surface of the particles. Once the CMC is reached the surfactant will strip from the particle surface and form micelles, leaving the particle surface free of surfactant, and free to possibly re-agglomerate.
3. Micelles exhibit different chemistry than individual surfactant molecules. Micelles may solubilize lipophilic proteins and produce unwanted effects.

References

1. Bhairi, Srirama; Detergents: A guide to the properties and uses of detergents in biological systems; Calbiochem-Novabiochem Corporation; available at: http://www.google.de/url?sa=t&source=web&ct=res&cd=3&url=http%3A%2F%2Fwww.antibodybeyond.com%2Fbooks%2FCalbiochem_Detergents_Booklet.pdf&ei=Mlp5SvGQG6jJ_gbe8cyKBg&usg=AFQjCNEi82BPFBndPBM2DjKxW2ks6lrXig&sig2=9W2kWv6FJKM-b3pH_-dmRQ

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