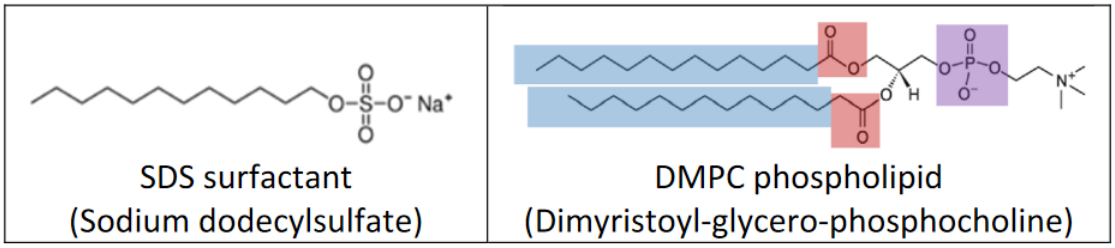
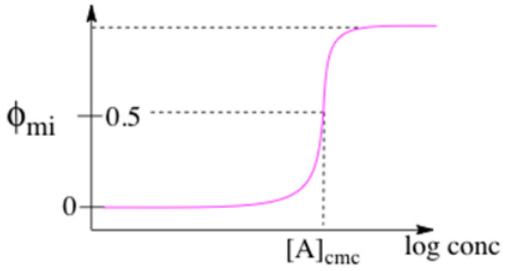
19.1: Micelle Formation

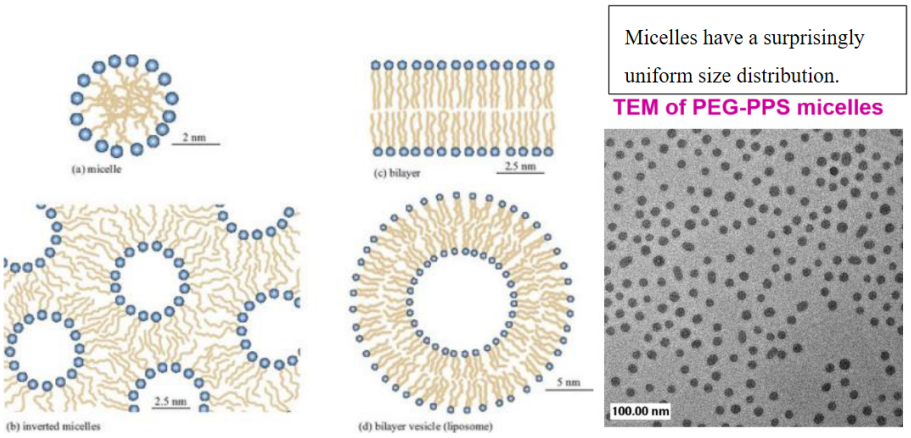
In particular, we will focus on micellar structures formed from a single species of amphiphilic molecule in aqueous solution. These are typically lipids or surfactants that have a charged or polar head group linked to one or more long hydrocarbon chains.



Such amphiphiles assemble into a variety of structures, the result of which depends critically on the concentration, composition, and temperature of the system. For SDS surfactant, micelles are favored. These condense hydrophobic chains into a fluid like core and present the charged head groups to the water. The formation of micelles is observed above a **critical micelle concentration** (CMC).



As the surfactant is dissolved, the solution is primarily monomeric at low concentration, but micelles involving 30–100 molecules suddenly appear for concentrations greater than the CMC.



Reprinted from http://swartz-lab.epfl.ch/page-20594-en.html.

To begin investigating this phenomenon, we can start by simplifying the equilibrium to a two-state form:

$$nA \rightleftharpoons A_n \tag{19.1.1}$$

K_n is the equilibrium constant for assembling a micelle with n amphiphiles from solution. n is the called the **aggregation number**.

$$K_n = \frac{[A_n]}{[A]^n} = e^{-\Delta G^0_m icelle/k_B T} \tag{19.1.2}$$

The total number of A molecules present is the sum of the free monomers and those monomers present in micelles:

$$CTOT = [A] + n[A_n]. \tag{19.1.3}$$

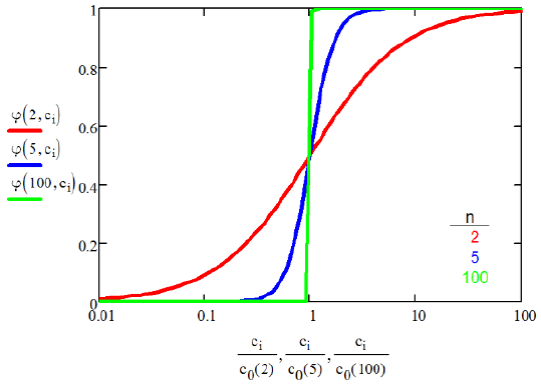
The fraction of monomers present in micelles:

$$\phi_m i = \frac{n[A_n]}{C_{TOT}} = \frac{n[A_n]}{[A] + n[A_n]} = \frac{nK_n[A]^{n-1}}{1 + nK_n[A]^{n-1}} \tag{19.1.4}$$

This function has an inflection point at the CMC, for which the steepness of the transition increases with n. Setting $\varphi_{mi} = 0.5$, we obtain the CMC (c_0) as

$$c_0 = [A]_{cmc} = (nK_n)^{\frac{-1}{n-1}} \tag{19.1.5}$$

Function steepens with aggregation number n:



Thus for large n, and cooperative micelle formation:

$$\Delta G^0_{micelle} = -RT \ln c_0 \tag{19.1.6}$$

Note the similarity of Equation 19.1.2to the results for fractional helicity in the helix-coil transition:

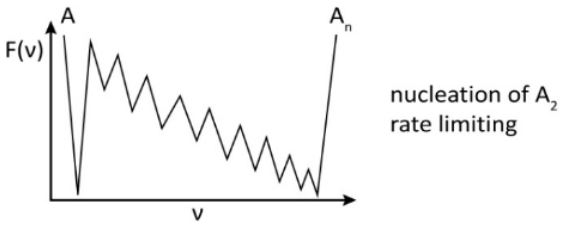
$$\frac{s^n}{1 + s^n} \tag{19.1.7}$$

This similarity indicates that a cooperative model exists for micelle formation in which the aggregation number reflects the number of cooperative units in the process. Cooperativity can be obtained from models that require surmounting a high nucleation barrier before rapidly adding many more molecules to reach the micelle composition.The simplest description of such a process would proceed in a step-wise growth form (a zipper model) for n copies of monomer A assembling into a single micelle A_n.

$$nA \rightleftharpoons A_2 + (n+2)A \rightleftharpoons A_3 + (n-3)A \rightleftharpoons \ldots \rightleftharpoons A_n \tag{19.1.8}$$

$$K_n = \prod_{i=1}^{n-1} K_i \qquad K_i = \frac{k_f(i \rightarrow i+1}{k_r(i+1 \rightarrow i} \tag{19.1.9}$$

Examples of how the energy landscape looks as a function of oligomerization number v are shown below. However, if you remove the short-range correlation, overall we expect the shape of the energy landscape to still be two-state depending on the nucleation mechanism.



This picture is overly simple though, since it is not a one-dimensional chain problem. Rather, we expect that there are equilibira connecting all possible aggregation number clusters to form larger aggregates. A more appropriate description of the free energy barrier for nucleating a micelle is similar to classical nucleation theory for forming a liquid droplet from vapor.

D. H. Boal, Mechanics of the Cell, 2nd ed. (Cambridge University Press, Cambridge, UK, 2012), p. 250.

This page titled 19.1: Micelle Formation is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by Andrei Tokmakoff via source content that was edited to the style and standards of the LibreTexts platform.