VIVEKANANDA COLLEGE,THAKURPUKUR

TOPIC:CRITICAL MICELLE CONCENTRATION

COURSE : CELL BIOLOGY

PAPER:CC8

SEMESTER:4

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DEPARTMENT:BIOCHEMISTRY

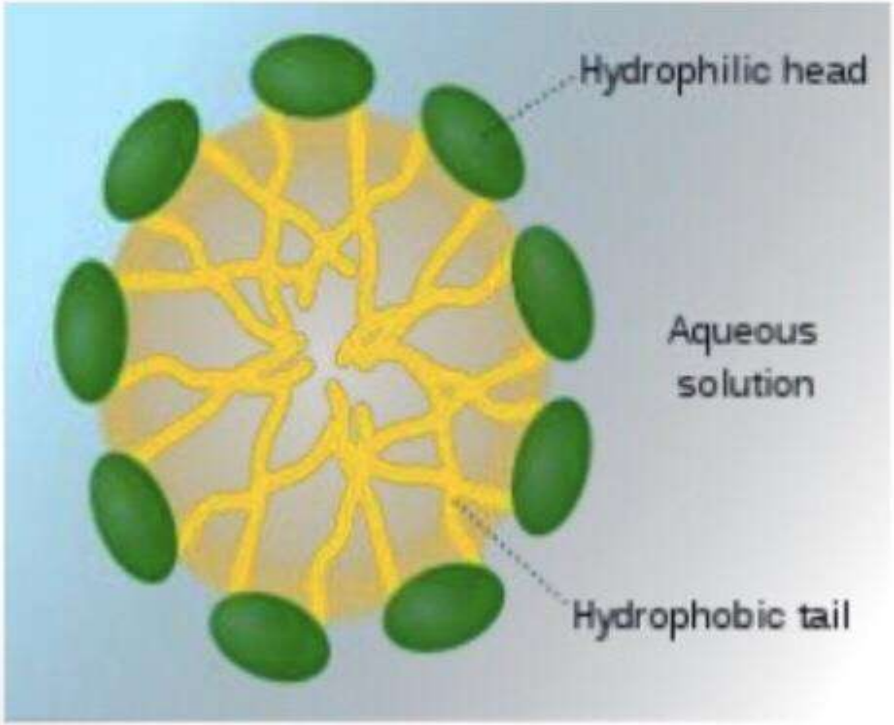
Surfactants and micelle

- Surfactants (tensides) are organic substances, which signifícantly decrease the surface tension of water at relatively low concentrations and are, at least partially, water soluble. Because surfactants are adsorbed mainly on the surface of the solution, creating a thin monolayer, they are called surface active substances.
- When dissolving them, after they reach a certain value of concentration, molecules or ions of surfactants begin to associate and to organize themselves into more complex units, called micelles.

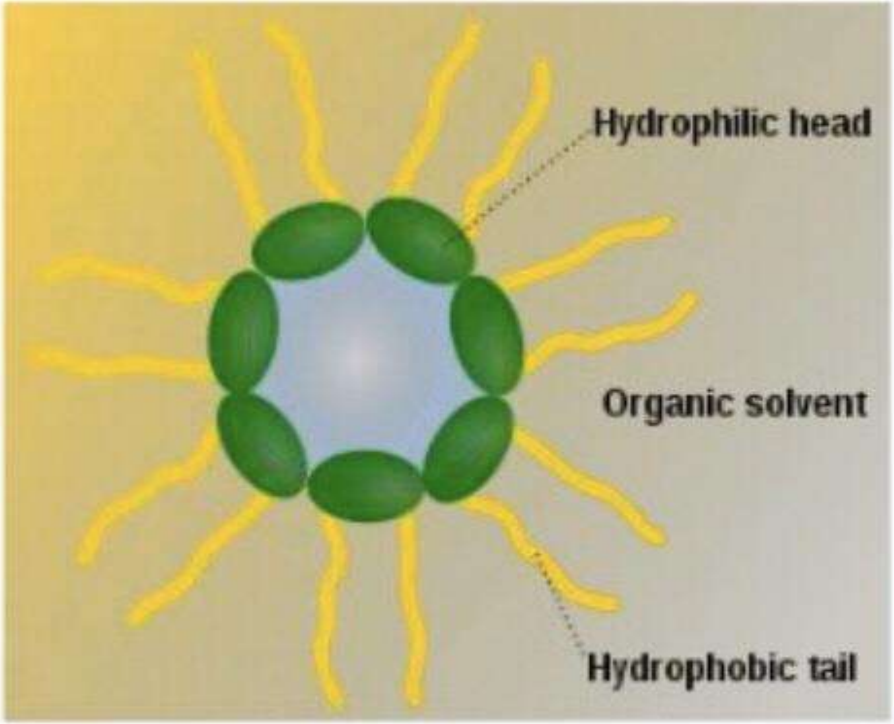
The characteristic concentration value, where the association process begins, is called the critical micelle concentration and it is labeled with symbol c or abbreviation CMC.

Types of micelle

1. Oil in water type



2. Water in oil type



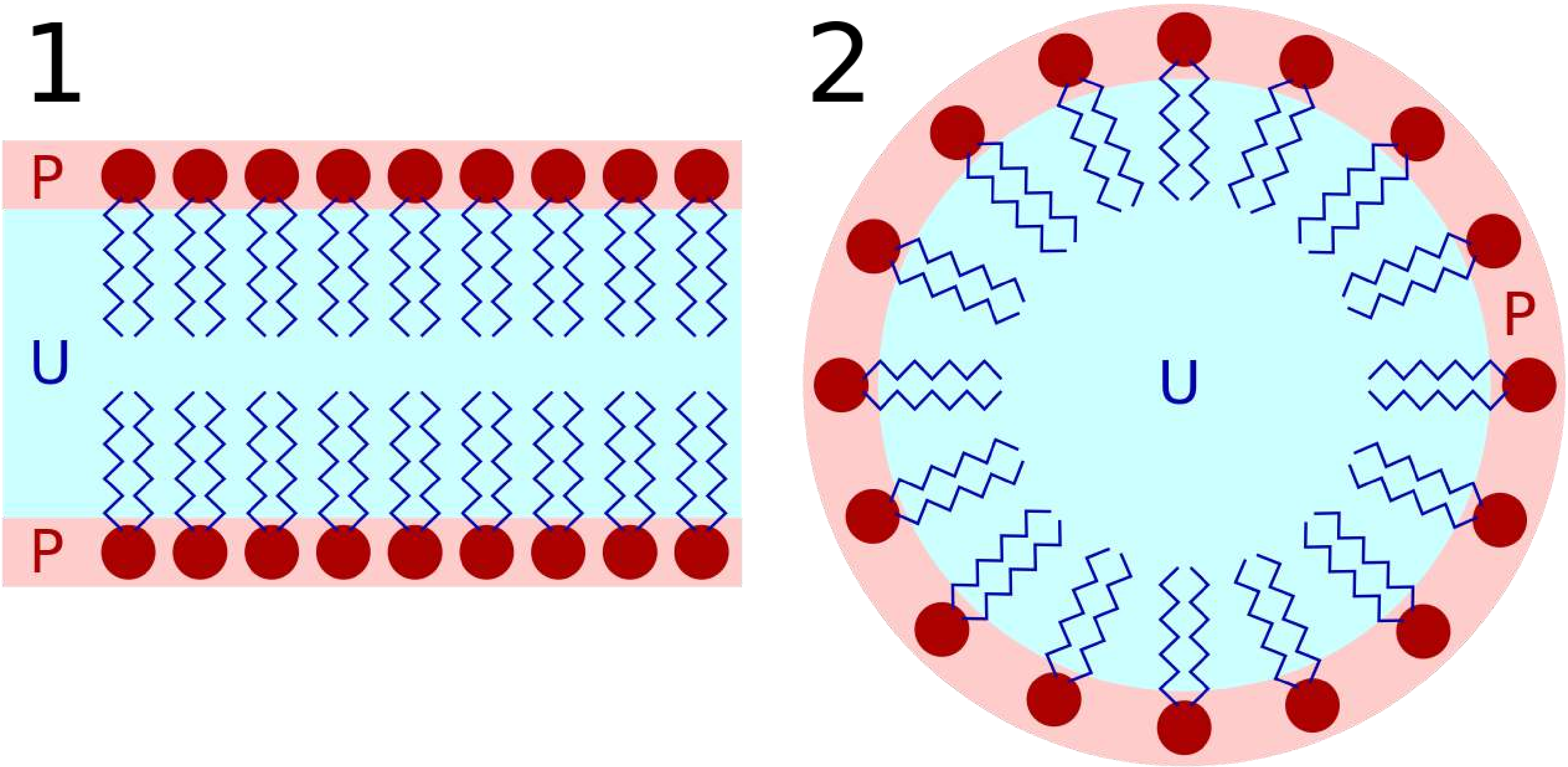
The CMC is one of the most useful physicochemical characteristics of many biologically active substances and drugs. From the chemical point of view, surfactants are mostly low-molecular compounds, so when dissolved, they form a true solutions in concentration ranges below the CMC.

Micelles are aggregates of a larger number of simple molecules or ions of surfactants (e.g. several dozens), so the resulting size of such structures is in the colloidal range. For this reason the micelle solutions of surfactants are regarded as association colloids. The molecular structure of surfactants is amphiphilic (biphilic), it consists of both non polar (hydrophobic, lipophilic) and polar (hydrophilic) parts -

Micelle and bilayer

The preferred structure of lipids in aqueous solutions are usually a bilayer sheet of lipids rather than spherical micelles. This is because the two fatty acid chains are too big and bulky to fit into the interior of a micelle. Therefore, micelles usually have one hydrocarbon chain instead of two. Lipid bilayers" form rapidly and spontaneously in an aqueous media and are stabilized by hydrophobic interactions, Van der Waals attractive forces, and electrostatic interactions.

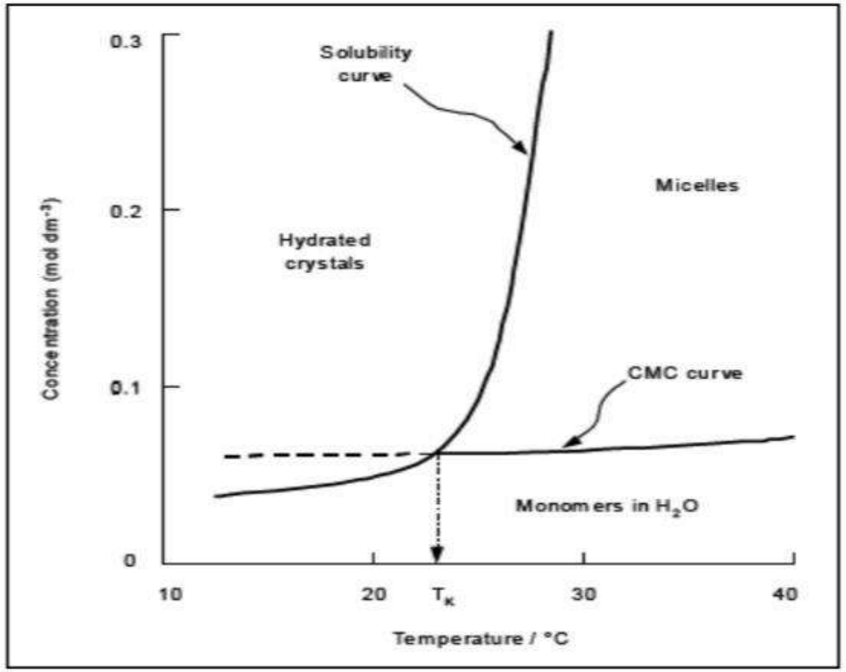
The function of the lipid bilayer is to form a barrier between the two sides of the membrane. Due to the fact that the lipid bilayer consists of hydrophobic fatty acid chains, ions and most polar molecules have trouble passing through the bilayer.



Bilayer and micelle

Micelle formation

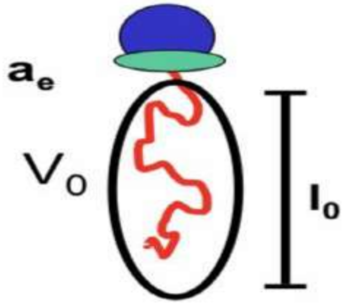
- The CMC is the concentration above surfactant when micelles will form spontaneously. The higher the concentration, the more micelles there are. Micelle formation also depend on the Krafft temperature. This temperature is when surfactants will form micelles. If the temperature is below the Krafft temperature, then there is no spontaneous formation of micelles. As the temperature increases, the surfactant will turn into a soluble form and be able to form micelles from a crystalline state.



Binary phase diagram surfactant/water

- Solubility of surfactants highly T dependent
- Solubility is usually low at low T, rising rapidly in narrow range
- No micelles possible above a certain temperature
- The point where solubility curve meets CMC curve is the Krafft point, which defines the T_{krafft}..
- The Krafft temperature can be regarded as a „melting point“

Critical packing parameter



$P = V_0/(a_e\, l_0)$

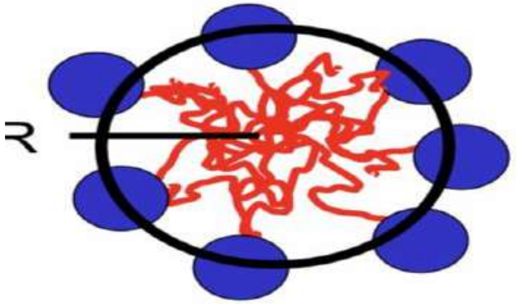
V_0 **surfactant tail volume**

a_e ***equilibrium*** **area per molecule at the aggregate interface**

l_0 **tail length**

Common surfactants:
v_0/l_0 = const. = 0.21 nm^2 (single tail)

Example: Spherical micelle with aggregation number g



$$\left.\begin{array}{l} V_{core} = g\, V_0 = 4\pi R^3/3 \\ A \quad\;\; = g\, a_e = 4\pi R^2 \end{array}\right\} \quad R = 3\, V_0/a_e$$

With $R \leq l_0$ ➡ $0 \leq V_0/(a_e\, l_0) \leq 1/3$

Prediction of the shape of self-assembled structures in solution

Table 1. Geometrical Relations for Spherical, Cylindrical, and Bilayer Aggregates[a]

variable	sphere	cylinder	bilayer
volume of core $V = gv_0$	$4\pi R^3/3$	πR^2	$2R$
surface area of core $A = ga$	$4\pi R^2$	$2\pi R$	2
area per molecule a	$3v_0/R$	$2v_0/R$	v_0/R
packing parameter v_0/al_0	$v_0/al_0 \leq 1/3$	$v_0/al_0 \leq 1/2$	$v_0/al_0 \leq 1$
largest aggregation number g_{max}	$4\pi l_0^3/3v_0$	$\pi l_0^2/v_0$	$2l_0/v_0$
aggregation number g	$g_{max}(3v_0/al_0)^3$	$g_{max}(2v_0/al_0)^2$	$g_{max}(v_0/al_0)$

Common surfactants:
v_0/l_0 = const. = 0.21 nm^2
(single tail)

- **Only the headgroup controls the equilibrium aggregate structure via the headgroup area a_e**
- **The tail does not have any influence on the shape and size of the aggregate**

- Micelles only form above critical micelle temperature.

For example, the value of CMC for sodium dodecyl sulfate in water (no other additives or salts) at 25 °C, atmospheric pressure,
is $8x10^{-3}$ mol/L.

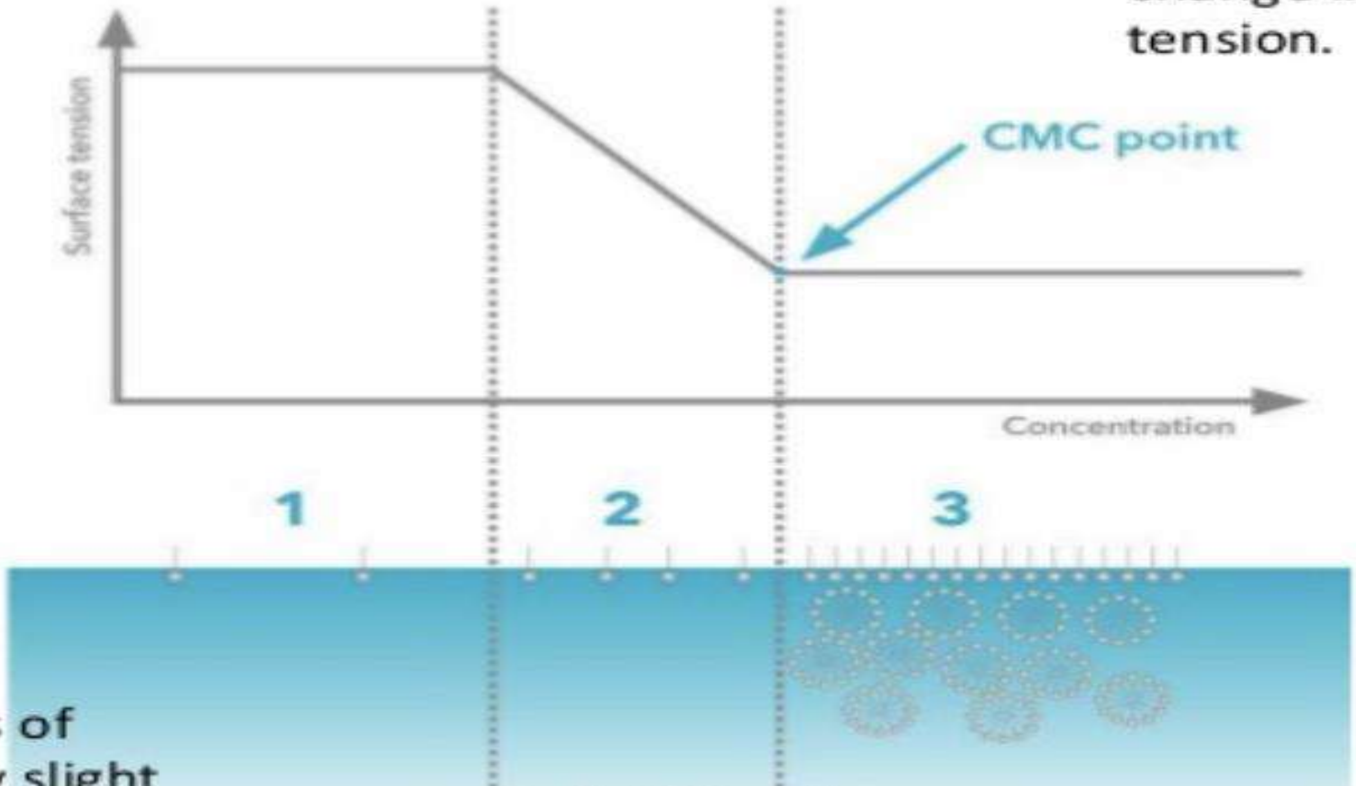
- Upon introduction of surfactants (or any surface active materials) into the system, they will initially partition into the interface, reducing the system free energy by:

1. lowering the energy of the interface (calculated as area times surface tension), and
2. removing the hydrophobic parts of the surfactant from contact with water.

- Subsequently, when the surface coverage by the surfactants increases, the surface free energy (surface tension) decreases and the surfactants start aggregating into micelles, thus again decreasing the system's free energy by decreasing the contact area of hydrophobic parts of the surfactant with water.
- Upon reaching CMC, any further addition of surfactants will just increase the number of micelles (in the ideal case).

1. SURFACE TENSION

3.Surface becomes fully loaded, no further change in surface tension.



1. At very low concentrations of surfactant only slight change in surface tension is detected.

2. Additional surfactant decreases surface tension

- CONDUCTIVITY

- Below the CMC, the addition of surfactant to an aqueous solution causes an increase in the number of charge carriers and consequently, an increase in the conductivity.
- Above the CMC, further addition of surfactant increases the micelle concentration while the monomer concentration remains approximately constant (at the CMC level).
- Since a micelle is much larger than a monomer it diffuses more slowly through solution and so is a less efficient charge carrier.