

Surfactants

Surfactants (or ‘surface active agents’): are organic compounds with at least one lyophilic (‘solvent-loving’) group and one lyophobic (‘solvent-fearing’) group in the molecule. In the simplest terms, a surfactant contains at least one non-polar group and one polar (or ionic) group and is represented in a somewhat stylized form shown in Figure 1.

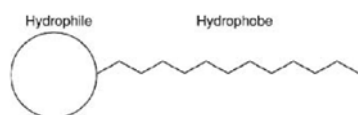


Fig.1 Simplified surfactant structure

For example, in aqueous media, surfactant molecules will migrate to air/water and solid/water interfaces and orientate in such a fashion as to minimise, as much as possible, the contact between their hydrophobic groups and the water. This process is referred to as ‘adsorption’ and results in a change in the properties at the interface.

Likewise, an alternative way of limiting the contact between the hydrophobic groups and the water is for the surfactant molecules to aggregate in the bulk solution with the hydrophilic ‘head groups’ orientated towards the aqueous phase. These aggregates of surfactant molecules vary in shape depending on concentration and range in shape from spherical to cylindrical to lamellar (sheets/layers). The aggregation process is called ‘micellisation’ and the aggregates are known as ‘micelles’. Figure 2 illustrates the various types of micelle described above.

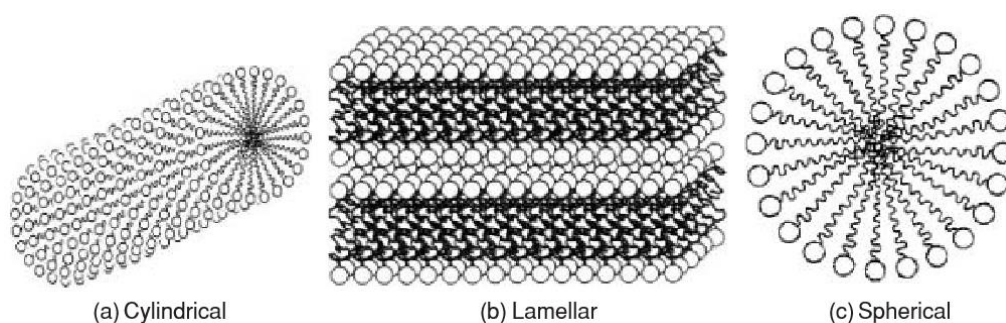


Figure 2 Typical micelle configurations.

The Basic Theory

For a compound to be a surfactant, it should possess three characteristics:

- The molecular structure should be composed of polar and non-polar groups.
- It should exhibit surface activity.
- It should form self-assembled aggregates (micelles, vesicles, liquid crystalline, etc.) in liquids.

1. The critical micelle concentration (CMC)

Self-assembled surfactant aggregates

A surfactant at low concentration in aqueous solution exists as monomers (free or unassociated surfactant molecules). These monomers pack together at the interface, form monolayer and contribute to surface and interfacial tension lowering. Although this phenomenon is highly dynamic (surfactant molecules arrive and leave the interface on a very rapid timescale), molecules at the interface interact with the neighbouring molecules very strongly which enables measurement of the rheological properties of the monolayer.

Micelles and critical micelle concentration

The properties of surfactant at low concentration in water are similar to those of simple electrolytes except that the surface tension decreases sharply with increase in concentration.

At a certain concentration, surfactant monomers assemble to form a closed aggregate (micelle) in which the hydrophobic tails are shielded from water while the hydrophilic heads face water. The critical aggregation concentration is called the critical micelle concentration (CMC) when micelles form in an aqueous medium.

The CMC is a property of the surfactant, it indicates the point at which monolayer adsorption is complete and the surface active properties are at an optimum. Above the CMC, the concentrations of monomer are nearly constant. Hence, there are no significant changes in the surfactant properties of the solution since the monomers are the cause of the surface activity. Micelles have no surface activity and any increase in the surfactant concentration does not affect the number of monomers in the solution but affects the structure of micelles.

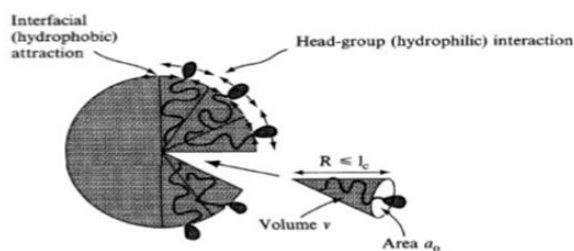
Surfactant packing parameter

Conceptual framework that relates molecular parameters (head group area, chain length and hydrophobic tail volume) and intensive variables (temperature, ionic strength etc.) to surfactant microstructures

- Critical Packing Parameter / Packing Parameter

$$CPP \text{ or } P = \frac{v}{l \cdot a_0}$$

v : volume of hydrocarbon core
 l : hydrocarbon chain length
 a_0 : effective head group area




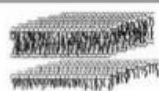









Aggregate structures and shapes

A theory for the aggregate structure was developed based on the area occupied by the hydrophilic and hydrophobic groups of surfactant. For a stable formation of a surfactant aggregate structure in an aqueous system, the internal part of the aggregate should contain the hydrophobic part of the surfactant molecule while the surface of the aggregate should be made up of the hydrophilic heads. The polar head groups in water, if ionic, will repel each

other because of same charge repulsion. The larger the charge, the greater the repulsion and the lower the tendency to form aggregates.

1. Spherical micelles are formed where the value of surfactant packing parameter is less than $1/3$ (single chain surfactants with large head group areas such as anionic surfactants). The spherical aggregates are extremely small and their radius is approximately equal to the maximum stretched out length of the surfactant molecule.
2. Cylindrical micelles are formed where the surfactant packing parameter is between $1/3$ and $1/2$ (single chain surfactants with small head group areas such as non-ionic surfactants and ionic surfactants in high salt concentration). Any change in solution properties which causes a reduction in the effective size of hydrophilic head groups will change the aggregate size and shape from spherical to cylindrical form.
3. As the packing parameter approaches unity, the lamella becomes flat and planar (double chain anionic surfactants in high salt concentration).

Surfactant shape	Surfactant packing parameter ($v/l_c a_0$)	Surfactant aggregates		
	$< 1/3$			
Truncated cone				
	$1/3 - 1/2$			
	$1/2 - 1$			

Increase of the critical packing parameter of a system with a single straight-chain ionic surfactant can be accomplished in the following ways:

- (1) Change of a surfactant to one with a longer hydrocarbon chain.
- (2) Change of a surfactant to one with a branched hydrocarbon chain.
- (3) Use of surfactants with two hydrocarbon chains.
- (4) Addition of a long-chain alcohol, amine or other hydrophobic amphiphilic molecule.
- (5) Addition of a hydrophobic non-ionic surfactant.
- (6) Addition of a small amount of surfactant with opposite charge.
- (7) Addition of salt.

Increase of the critical packing parameter of a system with a single straight chain non-ionic surfactant can be achieved in the following ways:

- (1) Change of a surfactant to one with a longer hydrocarbon chain.
- (2) Change of a surfactant to one with a branched hydrocarbon chain.
- (3) Use of surfactants with two hydrocarbon chains.
- (4) Change of a surfactant to one with a shorter polyoxyethylene chain.
- (5) Increase of temperature.
- (6) Addition of salt.

Adsorption of surfactants at surfaces

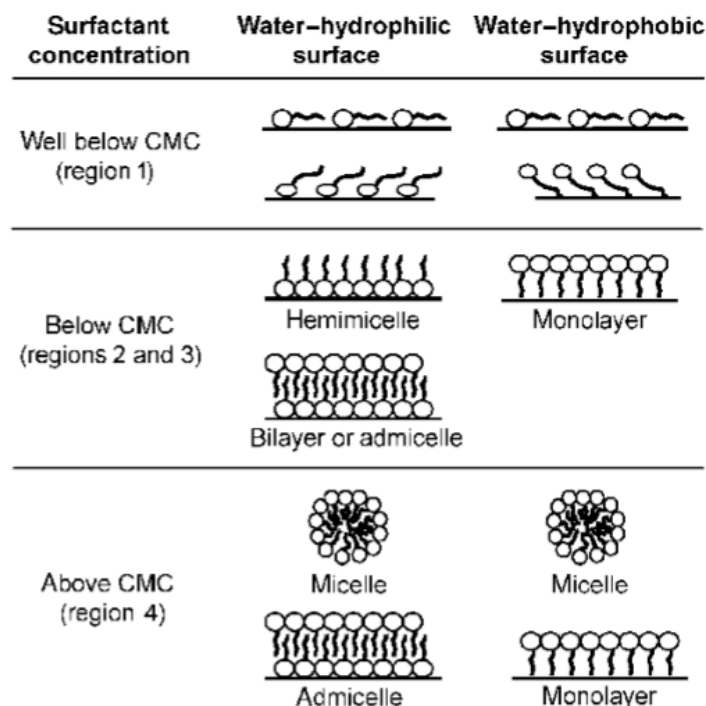
The adsorption mechanisms of surfactant at interfaces have been extensively studied in order to understand their performance in many processes such as dispersion, coating, emulsification, foaming and detergency. These interfaces are liquid–gas (foaming), liquid–liquid (emulsification) and liquid–solid (dispersion, coating and detergency).

Adsorption at liquid–gas and liquid–liquid interfaces

Surfactant has a tendency to adsorb at interfaces since the polar head group has a strong preference for remaining in water while the hydrocarbon tail prefers to avoid water. The surfactant concentration affects the adsorption of surfactants at interfaces. Surfactant molecules lie flat on the surface at very low concentration. Surfactant molecules on the surface increase with increasing surfactant concentration in the bulk and surfactant tails start to orient towards gas or non-polar liquid since there is not enough space for the surfactant molecules to lie flat on the surface. Surfactant molecules adsorb at the interface and form monolayer until the surface is occupied at which point surfactant molecules start forming self-assembled structures in the liquid.

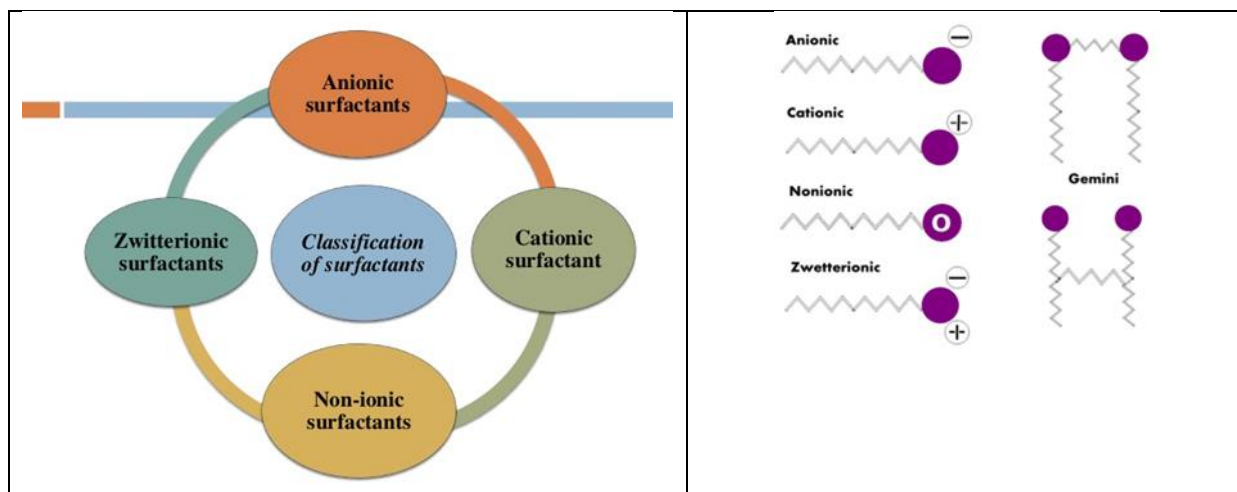
Adsorption at liquid–solid interface

Surfactants adsorb on solid surfaces due to hydrophobic bonding, electrostatic interaction, acid–base interaction, polarization of π electrons and dispersion forces. Hydrophobic bonding occurs between the hydrophobic surfactant tail and the hydrophobic solid surface (tail down adsorption with monolayer structure) or between the hydrophobic tails of the surfactant adsorbed on the hydrophilic solid surface and the hydrophobic tails of the surfactant from the liquid phase (head down adsorption with bilayer structure).



Classification of surfactants

The "tail" of most surfactants are fairly similar, consisting of a hydrocarbon chain, which can be branched, linear, or aromatic. Fluorosurfactants have fluorocarbon chains. Siloxane surfactants have siloxane chains.



Anionic

Sulfate, sulfonate, and phosphate esters.

Anionic surfactants contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate, and carboxylates. Prominent alkyl sulfates include ammonium lauryl sulfate, sodium lauryl sulfate (sodium dodecyl sulfate, SLS, or SDS), and the related alkyl-ether

sulfates sodium laureth sulfate (sodium lauryl ether sulfate or SLES), and sodium myreth sulfate.

Reference

1. **Richard J. Farn**, “Chemistry and Technology of Surfactants” 2006 by Blackwell Publishing Ltd.