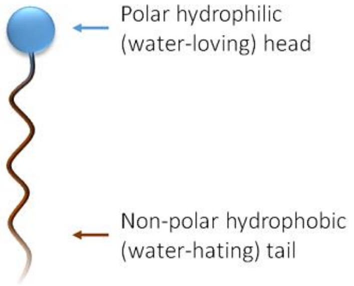
# Surfactants

**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.

If the solvent in which the surfactant is to be used is water or an aqueous solution, then the respective terms 'hydrophilic' and 'hydrophobic' are used. 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 stylised form shown in Figure.




**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 minimize, 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. Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.

### The Basic Theory

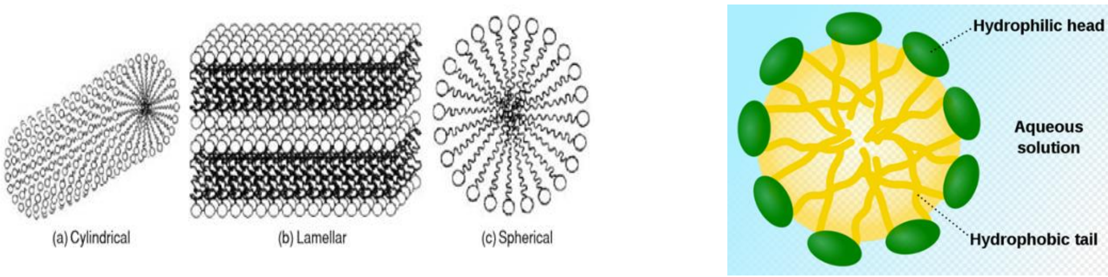
For a compound to be a surfactant, it should possess three characteristics:

- 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.

## Structure of surfactant phases in water

In the bulk aqueous phase, surfactants form aggregates, such as micelles, where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with the surrounding liquid. Other types of aggregates can also be formed, such as spherical or cylindrical micelles or lipid bilayers. The shape of the aggregates depends on the chemical structure of the surfactants, namely the balance in size between the hydrophilic head and hydrophobic tail. 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'.

Micelles begin to form at a distinct and frequently very low concentration known as the ‘critical micelle concentration’ or ‘CMC’. Figure 1 illustrates the various types of micelle described above.




Schematic diagram of a micelle – the lipophilic tails of the surfactant ions remain inside the oil because they interact more strongly with oil than with water.

**Figure 1 Typical micelle configurations.**

# 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 monomers 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.

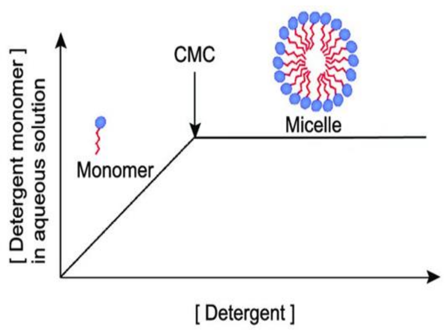



**Figure 2 Equilibrium between detergent monomers and micelles depending on the detergent concentration. Critical micelle concentration (CMC)**

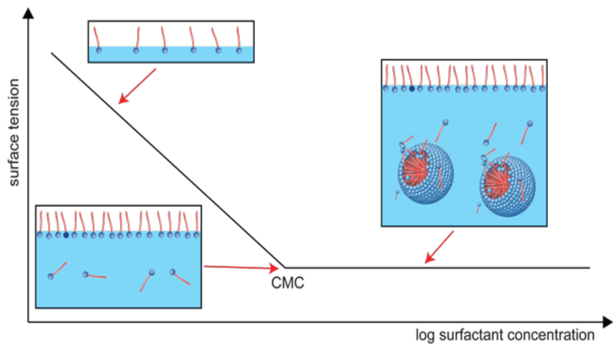



**Figure 3 Surface tension as a function of the surfactant concentration**

## Surfactant packing parameter

The critical packing parameter (CPP) is the most important the parameter to determine the self-assembly behavior of amphiphilic molecules in micelles. Estimating this critical packing parameter (CPP) enables the determination of the surfactant molecular packing and formed preferred structure such as micelles, cylindrical micelles, bilayers, inverted micelles, etc. as shown in Fig 2 as determined by their respective critical packing parameter (CPP).

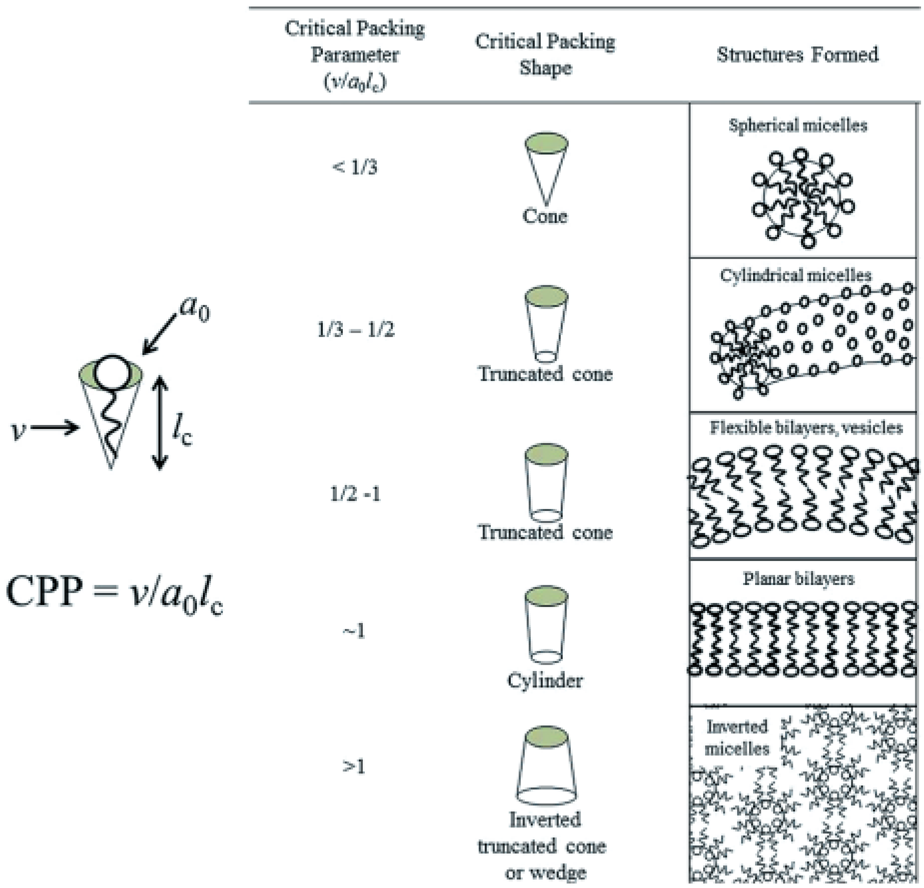
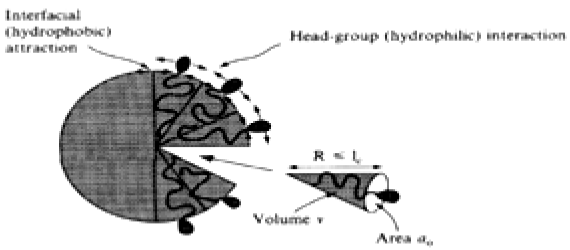
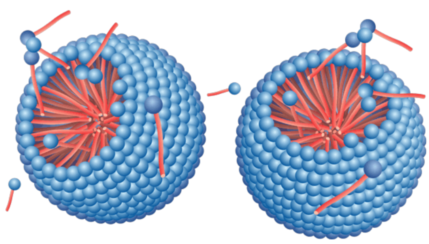



**Figure 4 Molecular shapes and critical packing parameter (CPP) of surfactants and lipids and the structures formed (here, v = volume of hydrocarbon core, $a_o$ =effective head group area, $l_c$ = hydrocarbon chain length).**

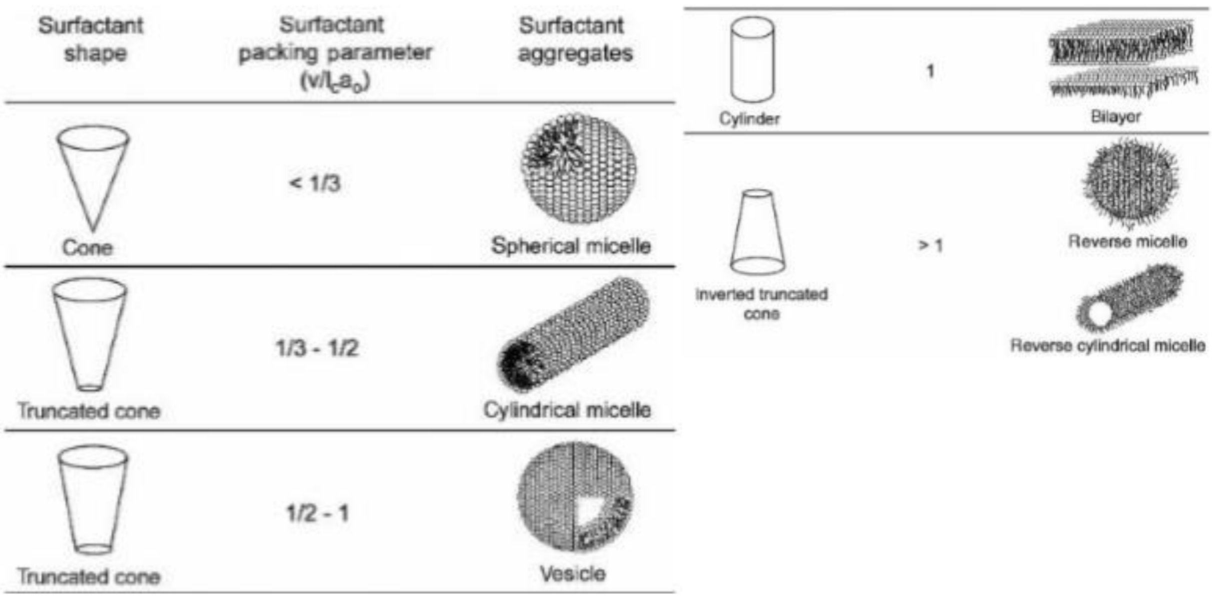


## Aggregate structures and shapes

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 a 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 and1/2(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).




**Classification of surfactants**

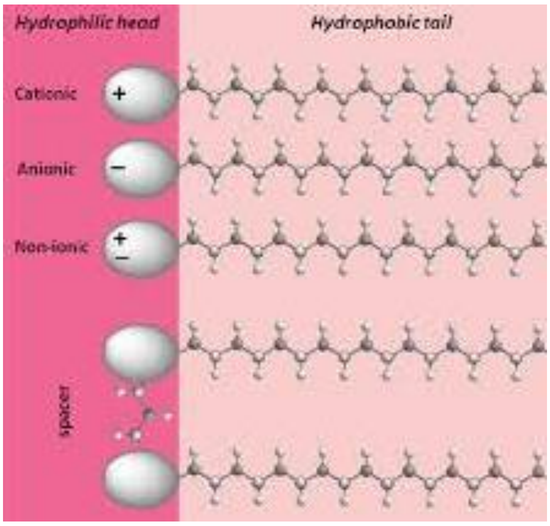
1. Low molecular mass surfactants
- Nonionic
- Ionic
- Amphoteric

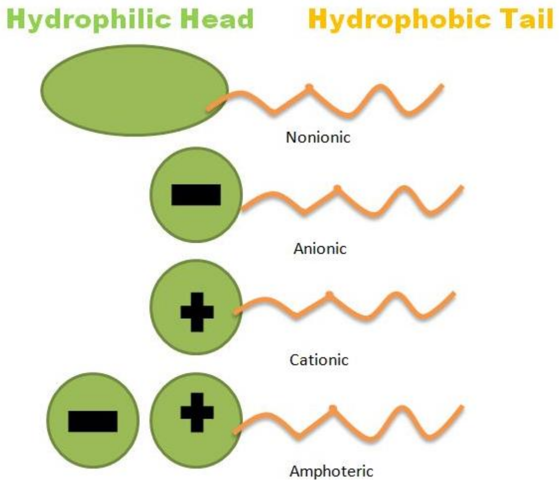
2. Polymeric surfactants
- Synthetic
- Natural

3. Particles as surfactant species

- Spherical vs. non-spherical
- Hydrophilic vs. hydrophobic

Surfactant classification according to the composition of their head: nonionic, anionic, cationic, amphoteric. Most commonly, surfactants are classified according to polar head group. A non-ionic surfactant has no charged groups in its head. The head of an ionic surfactant carries a net positive, or negative charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.




# Reference

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