Surfactants

1. Definition and structure

Surface-active molecules are amphiphilic molecules that are used to lower the value of surface tension. They are composed of a hydrophilic head and a hydrophobic tail. Surfactant molecules have a high affinity for water-air and water-oil interfaces. When present at an interface, surfactant molecules decrease the interfacial energy and hence the surface tension. They are used for their properties as wetting agent, foaming agent, detergents, emulsifiers, ...

1.1. concept of HLB

The hydrophilic or hydrophobic character of surfactants depends on their molecular structure. To quantify their predominant nature, the concept of **HLB (Hydrophilic–Lipophilic Balance)** is used. This index provides a numerical estimate of the balance between the hydrophilic and lipophilic portions of a molecule.

The HLB scale ranges from 0 to 40: the higher the value, the greater the solubility of the surfactant in water (i.e., the more hydrophilic it is). Several calculation methods are described in the literature, but the most used one is based on the ratio between the molecular mass of the hydrophilic portion and that of the lipophilic portion:

$$\mathrm{HLB} = 20\mathrm{x}\frac{\text{Molecular mass of hydrophilic part}}{\text{Molecular mass of lipophilic part}}$$

However, the HLB method has limitations. It only considers the chemical structure of the surfactant, without accounting for intermolecular interactions (e.g., Lewis forces, van der Waals interactions, etc.).

1.2. Function of surfactants

Surfactants exhibit different properties and applications depending on their molecular structure and HLB (Hydrophilic–Lipophilic Balance) value:

- Detergents (13 < HLB < 15): Compounds capable of removing dirt or grease from solid surfaces due to their solubilizing power.
- Solubilizing agents (18 < HLB < 20): Above the critical micelle concentration (CMC), surfactant molecules self-assemble into micelles. In these aggregates, the hydrophilic parts remain in contact with water, while the hydrophobic parts form a core that can trap and solubilize otherwise water-insoluble substances.
- Foaming agents (3 < HLB < 8): These surfactants stabilize thin liquid films around air bubbles, enabling the formation and persistence of foam.
- Dispersing agents: They allow the dispersion of hydrophobic solid particles in water by reducing surface tension. Surfactants prevent flocculation (clumping) of particles, which would otherwise aggregate and sediment.
- Emulsifying agents: Surfactants stabilize emulsions between two immiscible liquids by forming an interfacial film around dispersed droplets. Two main types of emulsions exist:
  - O/W (oil-in-water): obtained with surfactants of higher HLB values (HLB > 10).
  - W/O (water-in-oil): obtained with surfactants of lower HLB values (HLB < 6).

1.3. Structure of surfactants

There are four main categories of surfactants classified according to the nature of the hydrophilic part (Figure 1):

- **Anionic:** negatively charged polar head.
- **Cationic:** positively charged polar head.
- **Zwitterionic or amphoteric:** the hydrophilic part has at least one positive charge and one negative charge.
- **Nonionic:** no charge.

Figure 1: categories of surfactants

Surfactants

- Anionic surfactants

They release a negative charge (anion) in aqueous solution. They have a more pronounced hydrophilic tendency with an HLB value between 8 and 18. They can be used to form oil-in-water (O/W) emulsions. These surfactants include soaps (fatty acid salts) with the general formula RCOOM, where R is the hydrocarbon chain length and M is an alkali metal or an organic base; sulfated derivatives (sodium lauryl sulfate) used as emulsifiers or foaming agents, and sulfonated derivatives (sodium dioctyl sulfosuccinate), often characterized by high wetting power.

- Cationic surfactants

They release a positive charge (cation) in aqueous solution. They are often nitrogen-containing products (a positively charged nitrogen atom) such as quaternary ammonium salts. They have bacteriostatic and emulsifying properties.

- Amphoteric surfactants

These contain both acidic and basic groups. At basic pH, they behave like anionic surfactants, and at acidic pH, they behave like cationic surfactants. They have a high HLB and are used as detergents. Examples include betaines (quaternary ammonium and carboxylic acid groups), imidazoline derivatives, and polypeptides. They all have the advantage of being compatible with other types of surfactants.

- Nonionic surfactants

They have no charge and therefore do not ionize in water.

2. Surfactants' Behavior

2.1 In Aqueous solutions

The hydrophilic part of a surfactant molecule exhibits a strong affinity for water due to van der Waals forces and Lewis-type interactions, including hydrogen bonding. In contrast, the hydrophobic part can interact with water only through weaker van der Waals forces and cannot form hydrogen bonds, resulting in lower affinity for water. Nevertheless, the hydrophobic part still has greater affinity for water than for air, because van der Waals interactions with air molecules are negligible.

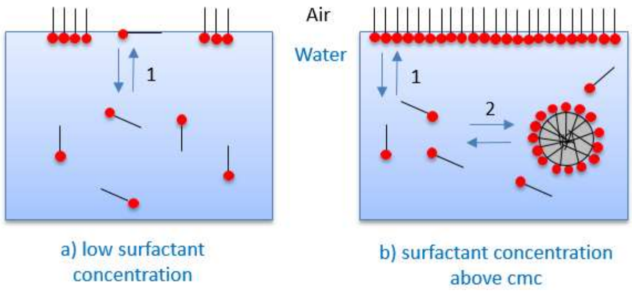

Figure1 : Surfactants in solution at low concentration (a) and high concentration above the CMC (b).

At low surfactant concentrations (Figure 2a), an equilibrium is established between surfactant molecules in the bulk solution and surfactant molecules adsorbed at the water–air interface. Individual surfactant molecules at the surface tend to lie flat to maximize van der Waals interactions with water molecules. As more surfactant molecules accumulate at the interface, they organize into a "brush" structure, aligning their hydrophobic chains to satisfy van der Waals interactions among the fatty chains.

As the concentration of surfactants in water increases, the surface becomes increasingly saturated, and more energy is required for additional surfactant molecules to adsorb. Beyond a certain concentration, the interface reaches full saturation, and the energy barrier for adsorption becomes too high. At this point, surfactant molecules aggregate in the bulk to form **micelles** (Figure 2b). In these micelles, the hydrophilic heads remain in contact with water, while the hydrophobic tails cluster together. This self-assembly is further driven by the incompatibility of water with the fatty chains of the surfactants.

In aqueous solutions, micelles can aggregate several hundred surfactant molecules. The size and geometry of these micelles depend primarily on the surfactant's molecular structure and the surrounding chemical environment [4 ,5].

Above a certain concentration, micelle formation is driven by hydrophobic interactions between surfactant molecules, which become sufficiently strong relative to the hydrophilic interactions to allow spontaneous micellization. When the hydrophilic portion of a surfactant is larger relative to its hydrophobic portion, the tendency to form micelles is stronger, resulting in a lower critical micelle concentration (CMC).

Surfactants

Certain factors can inhibit micelle formation. These include interactions that favor the monomolecular solubilization of surfactants in water, such as solvation effects of the polar group. The higher the polarity of the hydrophilic group, the lower the tendency to form micelles, and thus the higher the CMC. Repulsive electrostatic interactions between the hydrophilic heads can also hinder micellization; if these repulsions are too strong, the molecules cannot approach closely enough for hydrophobic interactions between the fatty chains to occur. This explains why ionic surfactants with charged hydrophilic groups form micelles less readily than nonionic surfactants with uncharged hydrophilic groups. For surfactants with the same hydrophilic group, the CMC of ionic surfactants is typically 100 to 1,000 times higher than that of nonionics.

Thus, the CMC can be considered a quantitative measure of a surfactant's overall affinity for the aqueous phase.

2.2 in Fatty or oily environment

When dissolved in oil, surfactants are not repelled toward the surface (Figure 3). The hydrophobic tails are compatible with the oil, while the hydrophilic heads have lower affinity for air, due to the absence of van der Waals interactions with air molecules. Nevertheless, the hydrophilic heads can form hydrogen bonds with each other, allowing surfactant molecules to aggregate and achieve a more energetically favorable state.

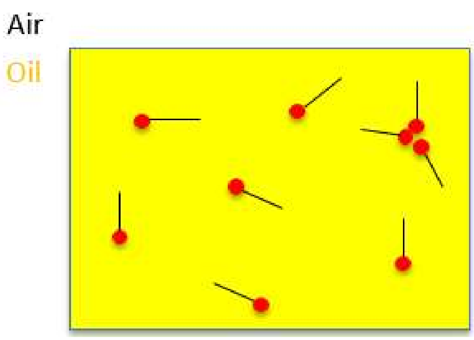

Figure2 : Surfactants in a fatty medium.

2.3 In Water/oil environment

When two immiscible phases, such as water and oil, come into contact, surfactant molecules can partition between the two phases and adsorb at the water–oil interface. Depending on the surfactant's structure and hydrophilic–lipophilic balance (HLB), it may preferentially associate with one phase, resulting in low interfacial adsorption. Additionally, micelles can facilitate solubilization of the oil phase, leading to the formation of oil-in-water emulsions.

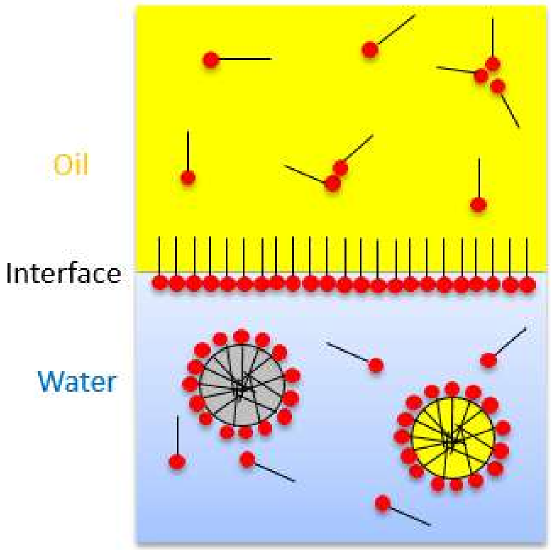

Figure3 : Distribution of surfactants in Water/oil environment

3. Factors influencing CMC

The behavior of surfactants and the formation of micelles are influenced by various factors. In general, the presence of solutes primarily affects ionic surfactants, while temperature has a more pronounced effect on nonionic surfactants.

3.1 Effect of solutes

Solutes in the aqueous phase can modify the interactions that either promote or inhibit micellization. The addition of electrolytes reduces the solubility of substances in water, thereby decreasing the solvation of the surfactant's hydrophilic groups. Electrolytes also increase the local ion concentration near micelle surfaces, producing a **screening effect** that reduces electrostatic repulsion between the hydrophilic head groups. These two effects facilitate micelle formation and generally lead to a **decrease in the CMC**.

This effect is particularly pronounced for **ionic surfactants**, where electrostatic screening dominates. For **nonionic and amphoteric surfactants**, the decrease in CMC is mainly

Surfactants

due to reduced solvation of the hydrophilic group and enhanced interactions between the hydrophobic tails and the aqueous phase.

Alcohol is commonly used as co-surfactants and generally decreases the CMC. This effect arises from the formation of mixed surfactant–alcohol micelles, in which the incorporation of alcohol molecules reduces the repulsive forces between the hydrophilic head groups [6-9].

3.2 Effect of temperature

Temperature has two opposing effects on the hydrophilic character of nonionic surfactants. An initial increase in temperature, up to around 50 °C, reduces the hydration of the hydrophilic group. Hydrogen bonding depends on the structured network of water molecules, and as temperature rises, increased molecular agitation makes hydrogen bond formation more difficult. This reduction in hydration can lead to the **cloud point** of nonionic surfactants and promotes micellization, resulting in a **decrease in CMC**.

Conversely, higher temperatures also disrupt the organization of water molecules around the hydrophobic moiety, reducing the hydrophobic–hydrophilic antagonism. This effect discourages micelle formation, causing the **CMC to increase**. Thus, temperature exerts a competing influence on micellization in nonionic surfactants.

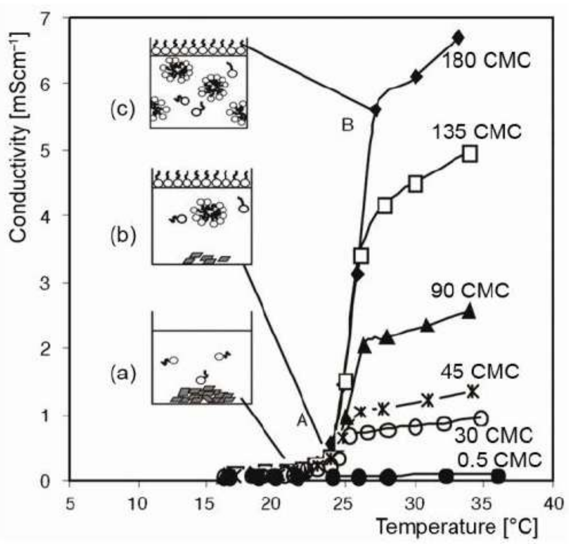

Figure4 : Conductivity of CTAB solutions at concentrations below and above the CMC as a function of temperature [10].

Temperature also affects the solubility of ionic surfactants in solution. As temperature increases, their solubility rises gradually (Figure 5). Above a certain threshold, known as the Krafft temperature, solubility increases sharply. This transition reflects a change in the surfactant's solubilization mode—from monomolecular solubilization to micellar solubilization.

The Krafft temperature corresponds to the point at which the surfactant's solubility reaches the CMC. Below this temperature, the surfactant is insufficiently soluble to achieve the concentration needed for micelle formation. The Krafft temperature is influenced by all factors affecting the CMC, such as hydrophobic chain length, polarity, and molecular structure. The effect of electrolytes on the Krafft temperature is more complex, as they can simultaneously influence both the CMC and solubility [11].

References

1. Griffin, W.C., *Classification of Surface-Active Agents by "HLB."* Journal of the Society of Cosmetic Chemists, 1949.**1** : p. 311.
2. ICI Americas, i., *The HLB System: A Time-saving Guide to Emulsifier Selection*. 1984: ICI Americas, Incorporated.
3. Kruglyakov, P.M., *Hydrophile Lipophile Balance of Surfactants and Solid Particles: Physicochemical aspects and applications*. 2000: Elsevier Science.
4. Rosen, M.J., *Surfactants and Interfacial Phenomena*. 2004: Wiley.
5. Mittal, K.L. and A.C. Society, *Micellization, solubilization, and microemulsions*. 1977: Plenum Press.
6. Leung, R. and D.O. Shah, *Dynamic properties of micellar solutions: I. Effects of short-chain alcohols and polymers on micellar stability.* Journal of Colloid and Interface Science, 1986.**113** (2): p. 484-499.
7. Yiv, S., et al., *Effect of alcohol on the properties of micellar systems: II. Chemical relaxation studies of the dynamics of mixed alcohol + surfactant*

Surfactants

micelles. Journal of Colloid and Interface Science, 1981.80 (1): p. 224-236.

8. Zana, R., et al., *Effect of alcohol on the properties of micellar systems: I. Critical micellization concentration, micelle molecular weight and ionization degree, and solubility of alcohols in micellar solutions.* Journal of Colloid and Interface Science, 1981.80 (1): p. 208-223.
9. Almgren, M. and S. Swarup, *Size of sodium dodecyl sulfate micelles in the presence of additives i. alcohols and other polar compounds.* Journal of Colloid and Interface Science, 1983.91 (1): p. 256-266.
10. Manojlovic, J., *The Krafft temperature of surfactant solutions.* Thermal Science, 2012.16 (2): p. 631.
11. Vautier-Giongo, C. and B.L. Bales, *Estimate of the Ionization Degree of Ionic Micelles Based on Krafft Temperature Measurements.* The Journal of Physical Chemistry B, 2003.107 (23): p. 5398-5403.