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A Concise Review on Surfactants and Its Significance

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Abstract

Surface active agents constitute an interesting class of substances with unique structural features. This review provides an introduction to the nature and physical properties of surfactants, its trade name, types, characteristics and their basic applications. Fundamental of critical micelle concentration (CMC), cloud point, kraft point are mentioned. Surfactant size and shape are vital characteristics and provide unique information during industrial formulation. Surfactant properties play significant roles in industrial and consumer products including detergents, paints, paper products, pharmaceuticals and cosmetics. The last few years show an increased interest in work involving the preparation and study of surfactants based on natural products.

Keywords: Surfactant, cmc, micelles, krafft points, cloud points

INTRODUCTION

The word surfactant is an abbreviation of the term **Surf**ace **act**ive age**nts** having dual characteristics of hydrophilicity and hydrophobicity and it itself suggests the surface active nature of these classes of compounds and their tendency to adsorb at interfaces. The polar portion exhibits a strong affinity or attraction towards polar solvents and it is often called hydrophilic part or hydrophile. The apolar part is called hydrophobe or lipophile having attraction towards oil [Figure 1]. [1-5]

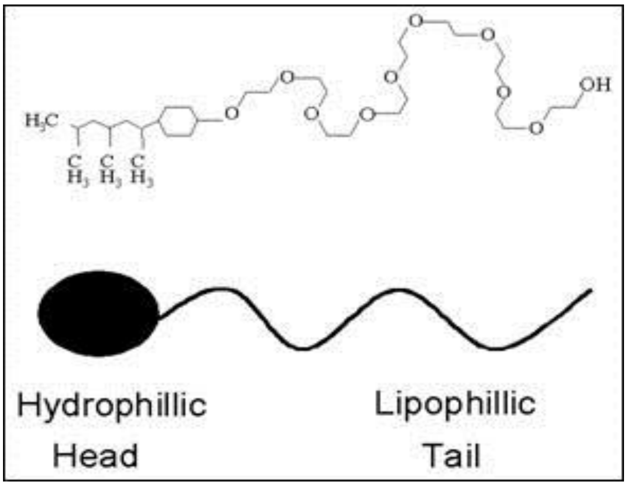


Figure 1: Surfactant Molecule

Surfactants are also known as amphiphiles or tensides. The word amphiphile was coined by Paul Winsor more than 50 years ago. It comes from two Greek roots. Surfactant in French known as "tensioactif", in German it is known by the name "tenside" and in Spanish it is called "tensioactivo". [6, 7]

Etymology

Interesting combination of English, Greek and Latin make sense to understand about history of words, their origins, and how their form and meaning have changed over time [Table 1]. [8]

Table 1: Etymology

English	Greek	Latin
oil	lipo-	oleo-
water	hydro-	aqua-
solvent	lyo-	solvo-
both	amphi-	
affinity	-philic	
lacking of affinity	-phobic	

Technical terms are formed by combinations of these words, such as:

- amphipathic = combining both natures (oil and water)
- amphiphilic = with affinity for both (oil and water)
- hydrophilic = with affinity for water
- lipophilic = with affinity for oil
- lyophilic = with affinity for the solvent
- lyophobic = lack of affinity for the solvent

❖ Categorization of surfactants

Surfactant can be classified into four broad categories: anionic, cationic, amphoteric and nonionic. [Figure 2] [9-15]

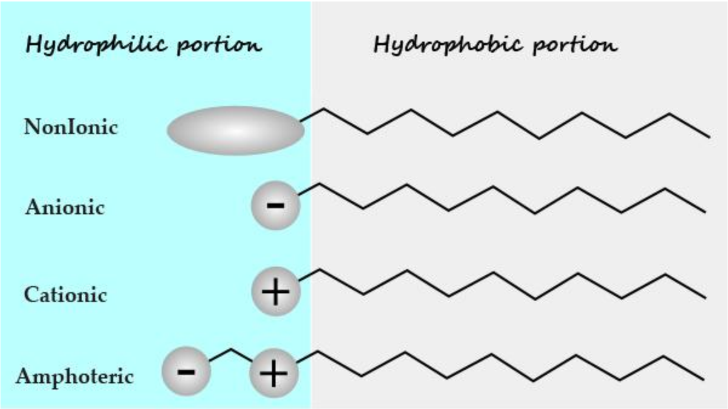


Figure 2: Categorization of surfactants

Anionic surfactants give rise to a negatively charged surfactant ion upon dissolution in water. This is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties. Most of the anionic surfactants are carboxylate, sulfate and sulfonate ions. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps. Anionic surfactants are relatively nontoxic. The straight chain is a saturated/unsaturated C_{12}-C_{18} aliphatic group. The water solubility potential of the surfactant is determined by the presence of double bonds in it. In solution, the head is negatively charged. The surfactant is particularly good at keeping the dirt away from fabrics, and removing residues of fabric softener from fabrics. Figure 3 represent the structure of anionic surfactant, Sodium dodecyl sulfate.

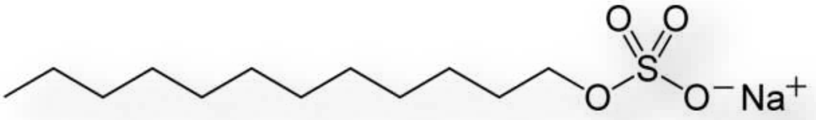


Figure 3: Sodium dodecyl sulfate

Cationic surfactants In solution, the head is positively charged. They are good emulsifying agents. These surfactants have also been found to be good bactericides and some find use as topical antiseptics. Their germicidal properties make them especially useful in bathroom and hand sanitizers. Cationic surfactants are attracted to negatively-charged sites; they can bind to these sites and provide the fabric with a soft, comfortable feel. Due to this reason, they are often used as fabric softeners. CTAB is suitable example of cationic surfactant and is shown in Figure 4.

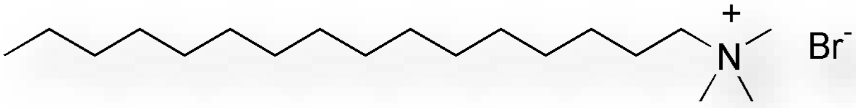
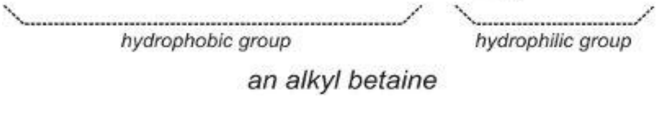


Figure 4: Cetyl trimethylammonium bromide (CTAB)

Zwitterionic surfactants also known as amphoteric surfactants have both cationic and anionic centers attached to the same molecule. Zwitterionic surfactants are less common than anionic, cationic and non ionic ones. These surfactants are very mild, making them particularly suited for use in personal care and household cleaning products. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis. These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties. Typical example of zwitterionic surfactant is alkyl betaine and lecithin which is shown in Figure 5.



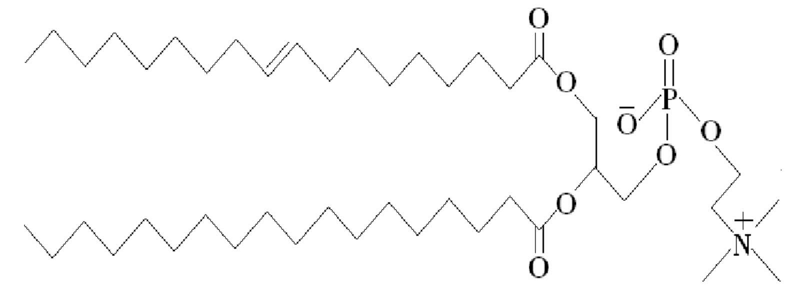

Lecithin

Figure 5: Alkyl betaine and lecithin

Nonionic surfactants

Surfactants that do not ionize in aqueous solution, due their hydrophilic group are of a non-dissociable type, such as alcohol, phenol, ether, ester, or amide. These surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. They are excellent grease removers that are used in laundry products, household cleaners and hand dishwashing liquids. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. Non ionic surfactants are probably the ones used most frequently in drug delivery applications. The nonionic surfactant can be of polyol esters, polyoxyethylene esters, and poloxamers or pluronics. Polyoxyethylene esters majorly include polyethylene glycol (PEGs). [Figure 6]. The most commonly used nonionic surfactants are ethers of fatty Alcohol. Non-ionic surfactants contribute to making the surfactant system less hardness sensitive.

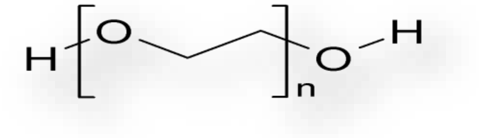


Figure 6: Polyethylene glycol

❖ Physicochemical properties of surfactants

Fundamental property of surface active agents is that monomers in solutions tend to form aggregates, called micelles or in other words, in aqueous solution, molecules having both polar and non polar regions form aggregates called micelles. [16] In a micelle, polar heads form an outer shell in contact with water, while non polar tails are sequestered in the interior. Hence, the core of a micelle, being formed of long non polar tails. Structure of micelle formation is shown in Figure 7. [17]

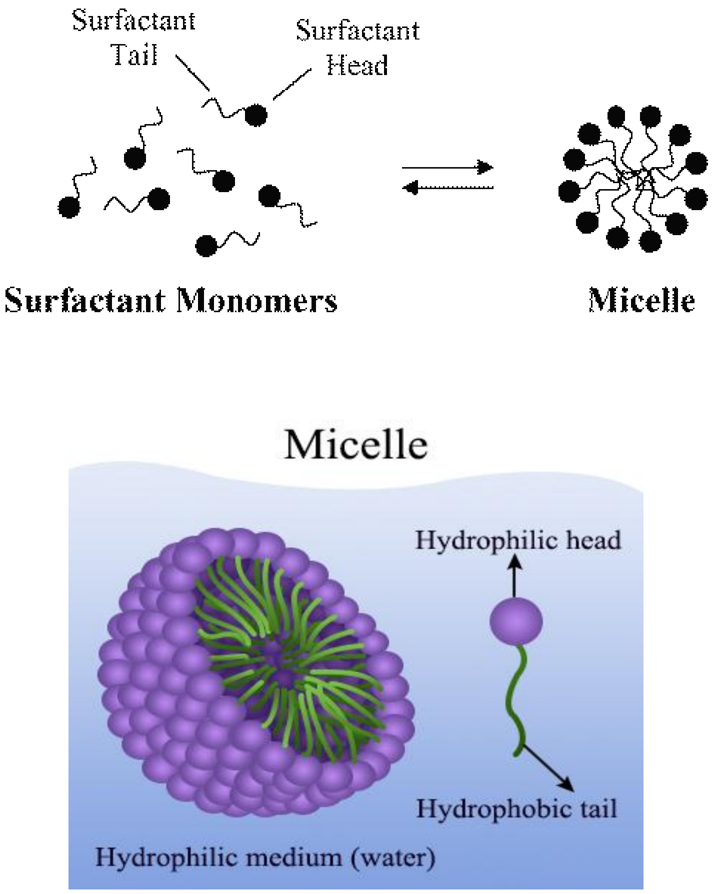


Figure 7: Micelle formation

The concentration at which micelles start to form is called critical micelle concentration (CMC). It is an important phenomenon since surfactant molecules behave very differently depending on whether they are present in micelles or as free monomers. The micelles influence the solubility of organic hydrocarbons and oils in aqueous solution and also influence the important property called viscosity. The size of the micelle is measured by the aggregation number which is the number of surfactant molecules associated with a micelle. Only surfactant monomers contribute to surface and interfacial tension lowering. Wetting and foaming are governed by the concentration of free monomers in solution. It was suggested by Adam [18] and Hartley [19] that micelles are spherical in shape. In general the shape of the micelle is dependent on the structure of the surfactant, typically the relative size of the head group and tail group. Ionic surfactant form smaller micelles (aggregation number ~10-70) than nonionic surfactants ($N_{agg} \geq 100$). This is because the electrostatic repulsion between ionic head-groups is greater than the steric repulsion between non-ionic head groups. The structure of a micelle could be of various shapes, spherical to rod- or disc- like to lamellar. [20-25] In concentrated solution (much above the CMC); lamellar micelles form, such that water molecules occupy the region between parallel sheets of surfactant. [Figure 8]

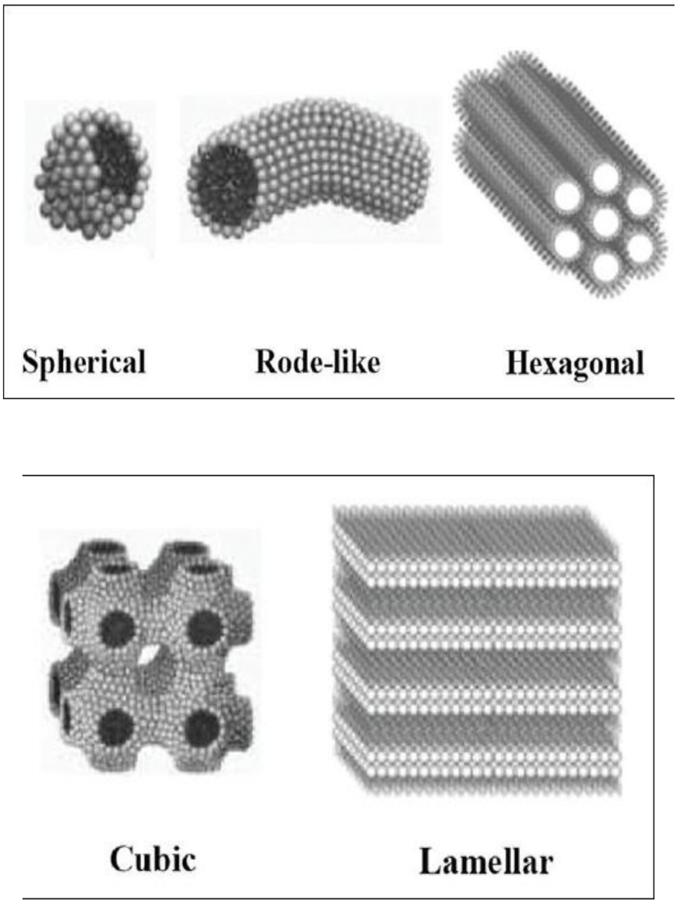


Figure 8: Different shapes surfactant aggregates

Krafft point and Cloud Point

The solubility of micelle forming surfactants shows a strong increase above a certain temperature, termed the Krafft point (KP). The Krafft point of ionic surfactant may be defined as the temperature at which the solubility of surfactant becomes equal to its CMC. Krafft point represents the temperature at which the alkyl chains melt resulting in the dissolution of surfactant crystals into micelles and monomers as illustrated in Figure 9.

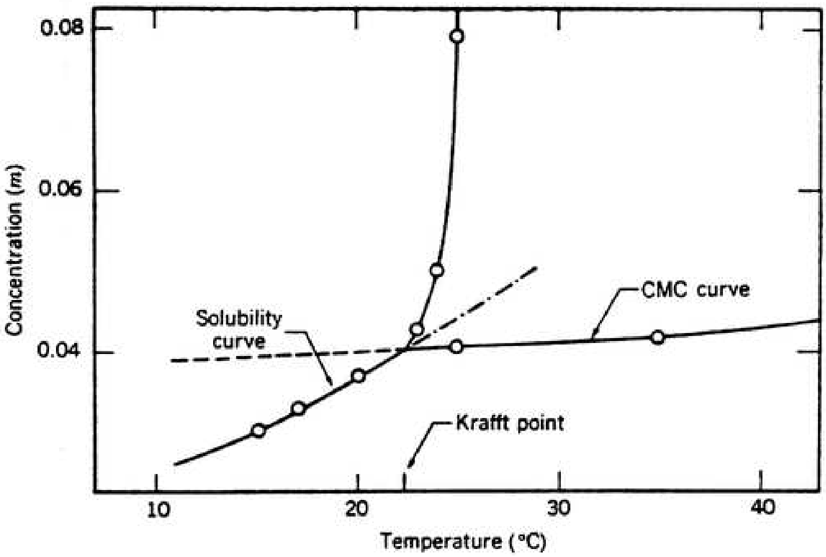


Figure 9: Krafft point phenomena

The Krafft temperature is an essential parameter that must be known for a surfactant before putting it into use. Since micelles form only at temperature above the Krafft point, a surfactant is often required to possess a KP value lower than the temperature at which it is used. Nonionic surfactants often do not exhibit Krafft points. Instead, the solubility of nonionic surfactants decreases with increasing temperature and these surfactants may begin to lose their surface active properties above a transition temperature referred to as Cloud point.

CONCLUSIONS

Over the past two decades, new surfactant molecules have been appearing at a relatively rapid pace. Scientific curiosity has also driven surfactant science research to focus on surfactant molecules having interesting fabricated shapes and structures. Fundamental knowledge of surfactant is very essential although surfactant science is now very well established discipline and there is still room for new molecules designed for specific purposes and new applications.

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