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Surfactant behavior in Environment

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Abstract—*Surfactants form a unique class of chemical compounds. This review provides basics of surfactant, its types, applications and merit and demerit nature to environment. Surfactant has dual identity of either having environment friendly or polluting globe. Surfactants are discharged into sewage systems or into surface waters and mostly end up dispersed in diverse environmental compartments such as water, soil, etc. The toxic effects of surfactants on various marine organisms are well known. Most surfactants are willingly biodegradable and their proportion can be reduced with another suitable method. The release of wastewater polluted with enormous quantities of surfactants could have serious effects on the ecosystem. It is very important in future to focus on surfactant toxicities and biodegradation and vital to remove highly toxic and non-biodegradable compounds from commercial use and replace them with more environmentally friendly ones.*

1. INTRODUCTION

Surfactants have a unique molecular structure comprising of a group that has very little attraction for water known as the hydrophobic group, together with a group that has a strong attraction for water known as the hydrophilic group. The hydrophobic portion of a surfactant is generally a long hydrocarbon chain often referred to as the 'tail' while the hydrophilic group is polar and is referred to as the 'head'. Hartley introduced the term amphipathy to describe the unusual properties of aqueous solutions of soap and detergent molecules.

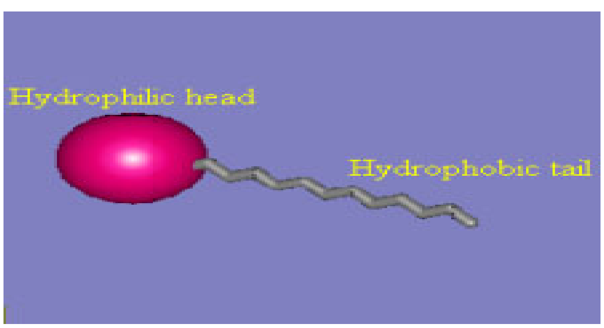

Fig. 1: Schematic representation of a Surfactant molecule

Based on their applications and behavior nature, surfactants can be classified into several categories such as wetting agents, emulsifying agents, foaming agents, antifoaming agents, detergents, solubilizing agents, dispersants etc. They find these and several other roles to play in such varied fields as food industry, agriculture, textile, cosmetic industry, leather and paper industries, mineral extraction, petroleum and oil recovery etc. Thus we can say that surfactants are flexible as far as their function is concerned.

Based on the charge on the polar head group and its molecular structure, they have been classified as anionic, cationic, nonionic and zwitterionic surfactants. [Fig. 2, 3]

Anionic surfactants give rise to a negatively charged surfactant ion and a positively charged counter ion upon dissolution in water. Examples of anionic surfactant groups include sulfonic acid salts, alcohol sulfates, alkyl benzene sulfonates, phosphoric acid esters, and carboxylic acid salts. As per anionic behavior, these surfactants tend to be good solubilizers and are relatively nontoxic. They found application in petroleum oil recovery operations and in contaminant hydrogeology remediation applications. They are the oldest class of surfactant and still used extensively.

Cationic surfactants yield a positively charged surfactant ion and a negatively charged counter ion upon dissolution in water. Cationic surfactants are very important and have commercial potential of their bacteriostatic properties and were recognized by Domagk in 1935. These types of surfactant are generally environment friendly. Nowadays cationic surfactants with antibacterial properties continue to play an important role as sanitizing and antiseptic agents, as components in cosmetic formulations, and as germicides and fungicides. New applications include use in antiseptic agent, textile softeners, corrosion inhibitors, foam depressants, flotation chemicals, and petroleum derivatives.

Quaternary amine type cationic surfactants are very important as fabric softeners. They adsorb on the surface of fibers with their hydrophobic groups oriented away from the fibers. This reduces the friction between fibers and imparts a soft, feathery feel to the fabric.

This same mechanism accounts for the behavior and use of cationic surfactants as hair conditioners. Cationic surfactants are being used in a variety of applications industrially and domestically for a long time. These surfactants are an important ingredient used worldwide as rinse added fabric softeners

Nonionic surfactants are characterized by hydrophilic head groups that do not ionize appreciably in water. Examples include polyoxyethylenated alkyl phenols, alcohol ethoxylates, alkylphenol ethoxylates, and alkanolamides. Nonionic surfactants tend to be good solubilizers and are relatively nontoxic. They are usually easily blended with other types of surfactants and therefore have found widespread use in petroleum and environmental applications. The performance of nonionic surfactants, unlike anionic surfactants, is relatively insensitive to the presence of salts in solution.

Zwitterionic surfactants (amphoteric) are those for which the charge on the polar head group can be either positive or negative depending upon the pH of the solution.

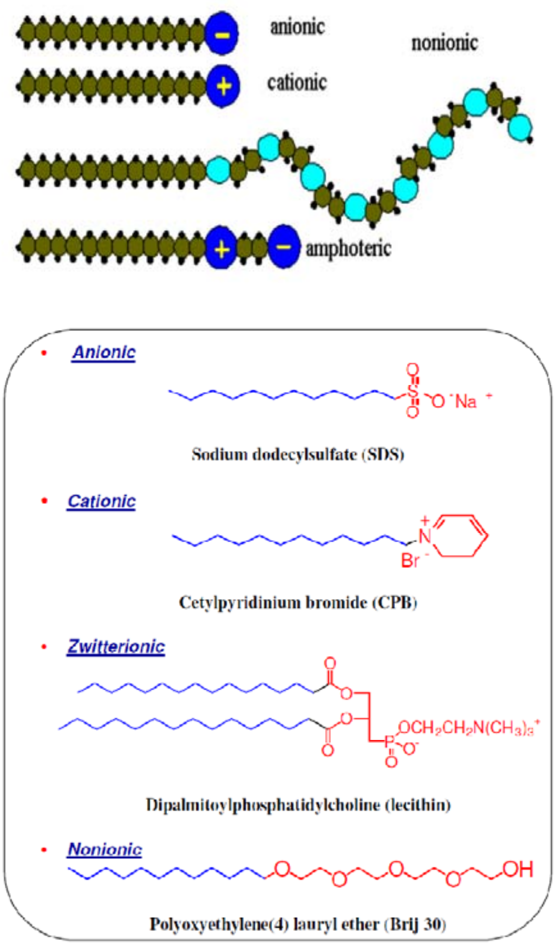

Fig. 2, 3: Schematic representation of different type of Surfactant molecules

Amphoteric surfactants have not been studied to a great extent. The best known and well studied example of amphoteric surfactants are amine oxides (AOs). AOs are exothermic, second-order reaction products of tertiary amines and hydrogen peroxide. As a rule, AO precursor is a C_{12}-C_{18} alkyldimethyl amine and the nature of tertiary amine may be aliphatic, aromatic, heterocyclic, or alicyclic.

AOs are used in textile industry as anti-static agents, in rubber industry as foam stabilisers and polymerisation catalysts, and in deodorant bars as antibacterial agents. They are skin-compatible and usually used with other surfactants. Due to zwitterionic nature, they are compatible with anionic surfactants and can in fact produce a synergistic effect in such formulations.

2. CHEMISTRY OF SURFACTANTS

When surfactant dissolved in water at low concentrations, surfactant molecules exist as monomers. At higher concentrations, surfactant molecules aggregate into micelles (Sizes of micelles range from 2 nm to 20 nm, depending on composition and concentration and shape may be either spherical, wormlike, cylindrical etc.) [Fig. 4, 5], reducing the system's free energy. The threshold concentration at which this occurs is known as the critical micelle concentration (CMC).

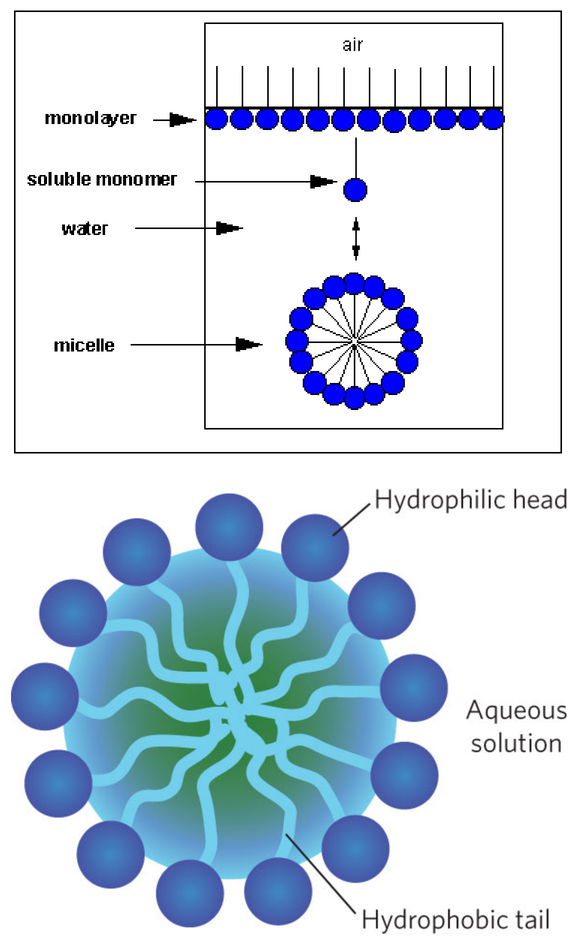

Fig. 4, 5: A schematic of a monomer, spherical micelle of surfactant molecules in aqueous solution

Nonionic surfactants have lower CMC levels compare to both anionic and cationic surfactants. This essential ability to form micelles gives surfactants their detergency and solubilisation properties. At concentrations above CMC, surfactants solubilise more hydrophobic organic compounds than would dissolve in water alone. CMC also seems to define surfactant's antibacterial properties. Surfactants with lower CMC exhibited higher germicidal activity

3. APPLICATIONS OF SURFACTANTS

Surfactants are involved in countless applications few of them are in the production of many common food items and can be found in the extraction of cholesterol, solubiliztion of oils, liquor emulsification, prevention of component separation, and solubiliztion of essential nutrients. One popular example is ice cream, a partially frozen foam that is 40–50% air (by volume).

Surfactants can also useful in crop protection. Crop protection products relate with pesticides, herbicides, fungicides and insecticides. The current focus in crop protection is towards products which are more effective, safer to user, having less impact on the environment, more convenient to use and improved efficiency.

Generally cationic surfactants are being used in various applications industrially and domestically. Pyridium salts shows antimicrobial activity with no toxicity, when used in recommended concentration. They are quite stable and do not contain any phenol, iodine, active chlorine, mercury, or other heavy metals. Their activity restricts the growth of various microorganisms such as bacteria, viruses, fungi, protozoa etc.

The antimicrobial activity of alkylpyridium salts generally increases with the length of the alkyl chain. Pyridium salts are effectively used to inhibit the corrosion of ferrous surfaces in highly acidic medium. Quaternary pyridium salts are employed in preparation of asphalt emulsions. They are used in highway construction, since they improve the adhesion of asphalt to acidic aggregate and road becomes more resistant to water. These emulsions can be applied on roads, while it is raining. Various many more applications of cationic surfactants are:

i) Dye removal from waste water

ii) Drug delivery

iii) Electrolytes for lithium batteries

iv) Textile processing

v) Gene delivery

vi) Modification of membranes

vii) Used as antimicrobialagents in medical, sanitizers, cosmetics and surgical applications.

4. BIODEGRADATION OF SURFACTANTS

In the environment, surfactants are primarily degraded through microbial activity, and in sewage treatment plants. Biodegradation mostly depends on surfactant's chemical structure and physicochemical conditions of its environmental medium. It is well known that salinity hardly affected decomposition of sodium dodecylbenzene sulphonate in seawater, but that higher temperature increased the degradation rate.

The presence of sediment also enhanced the biodegradaton rate, probably because sediments accumulate both surfactants and bacteria. A study on biodegradation of alkyl sulphate surfactants in water sediments suggests that surfactants adsorb onto the river sediment and stimulate bacteria to attach to them. Generally, nonionic surfactants are readily biodegradable under aerobic conditions.

5. ECOTOXICITY OF SURFACTANTS

Surfactants show a noticeable biological activity. Anionic surfactants can unite to bioactive macromolecules such as peptides, enzymes, and DNA. Binding to proteins and peptides may change the folding of the polypeptide chain and the surface charge of a molecule. This may modify biological function. Nonionic surfactants exert antimicrobial activity by binding to various proteins and phospholipid membranes. Such binding increases the permeability of membranes and vesicles, causing leakage of low molecular mass compounds. This can result in cell death or damage through loss of ions or amino acids.

Concerns about ecotoxicity of surfactants arise from their tremendous exploitation in everyday life. A major proportion of surfactants are degraded in wastewater treatment plants, but some amount ends up in surface waters, soil, or sediment. There is also a concern about surfactant accumulation in the sewage sludge treatment. High concentrations of accumulated surfactants can inhibit sewage sludge microorganisms and compromise the way in which a wastewater treatment plant removes pollutants and breaks down sewage.

The serious issue is about extreme use of any type of surfactants and their disposal in the environment, particularly in marine bodies, could fatally affect the ecosystem. Hence the amounts of anionic, non-ionic, and cationic surfactants released in sewage and aquatic recipient are monitored and regulated. Precaution taken that the concentrations of surfactants allowed in aquatic recipients are below the effective toxicity concentrations to aquatic organisms. Dilution in surface waters should minimise toxic effects on aquatic organisms. Cationic surfactants are recognised as the greatest hazard, and their limits are the lowest.

Various toxicity effects are:

i) Toxicity to bacteria

ii) Toxicity to aquatic plants

iii) Toxicity to invertebrates

iv) Toxicity to vertebrates

6. FUTURE PROSPECTS

One has to understand the dual behavior of surfactant towards our environment and effect on ecosystem. Future studies of surfactant toxicities and biodegradation are necessary to eliminate highly toxic and non-biodegradable compounds from commercial use and replace them with more environmentally friendly ones.

7. CONCLUSIONS

The surfactants can some time environment friendly and reduce harmful effect that cause our globe to be pollute but it also led to toxic effects on environments and various aquatic organisms, but their ecotoxicity profile is still incomplete. Most of the surfactants are readily biodegradable and their amount is very much reduced with alternative treatment in wastewater treatment plants. It is already confirmed that cationic surfactants are being used in a variety of applications in both domestically and industrially.

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