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Surfactant innovations: A journey from ancient Bharat to modern Bharat

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Abstract:
Surface-active agents, or surfactants, are a unique class of chemical compounds with both hydrophilic and hydrophobic properties. Also known as amphiphiles or tensides, they are widely used for cleaning, wetting, dispersing, emulsifying, foaming, acting as bactericides, and as drug delivery agents. Surfactants find applications across industries such as soaps and detergents, agriculture, pharmaceuticals, oil recovery and nanotechnology. Historical records indicate that soap-like materials have been used since 2800 BC in ancient Babylon. In India, plant-based surfactants were traditionally employed, and modern soaps were introduced during the colonial period. The Godrej Group produced the first Indian soap under the brand name "Key" during the Swadeshi movement in order to promote self-reliance and reduce dependence on foreign goods. The Indian surfactant industry flourished during the 19th and 20th centuries. Despite their widespread use, conventional surfactants are poorly biodegradable, prompting a shift toward environmentally friendly green surfactants in present days.

Keywords: Green & biodegradable surfactants, history, industrial application

Introduction of Surfactants:

Surfactant is contraction of "surface-active agent", has a thousands of years history however it is defined scientifically only in the last century. Surfactant is scientifically defined as amphiphilic substance consists of two parts water insoluble hydrophobic moiety (i.e. nonpolar chains) and water-soluble hydrophilic moiety (i.e. polar heads). The schematic representation of surfactant molecule is shown in Fig. 1.

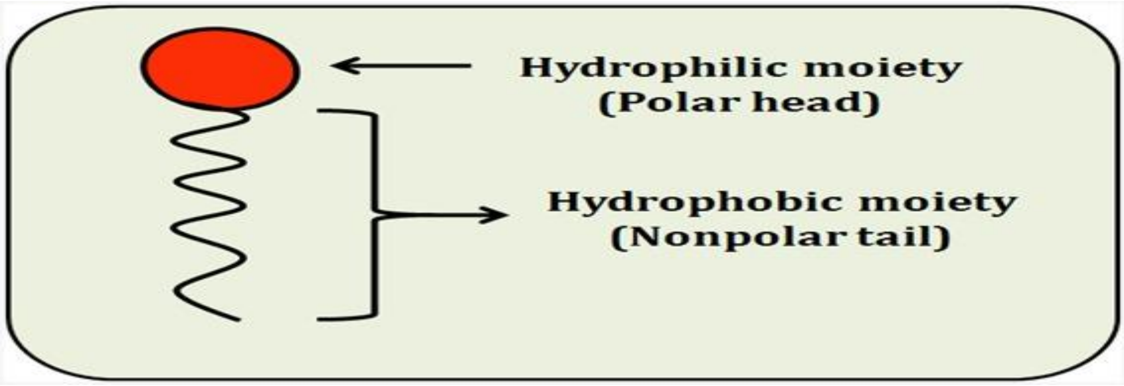

Fig. 1: A Schematic representation of a surfactant molecule.

The polar head of surfactant molecule have strong affinity to interact water molecules and immersed in water via dipole or ion-dipole interactions while hydrophobic part stays away from water. Surfactant adsorb at the surface (air-water interface) until saturation is reached, when the surfactant molecules are packed close together at the surface/interface, they undergo cooperative self-association in the bulk resulting in the formation of micelles and this process is termed as **Micellization** and this concentration is called **Critical Micelle Concentration (CMC)**. In the micelle, the nonpolar chains are directed towards the interior of the aggregate called 'core' and polar heads are directed towards the aqueous media called 'shell'. The systematic representation of adsorption and micellization of surfactant in aqueous solution showed in Fig. 2.

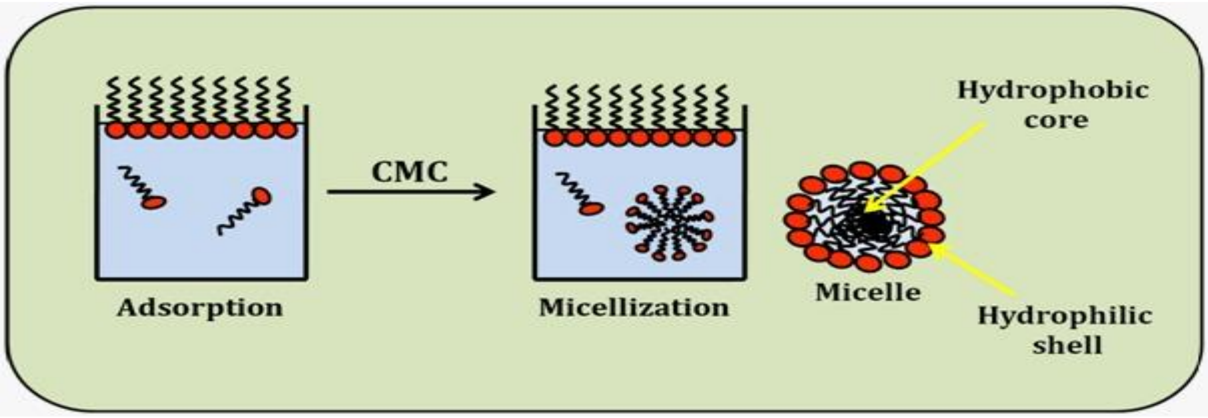

Fig. 2: Adsorption and Micellization of surfactants in aqueous solution.

Classification of surfactants:

According to the charge on the polar head group upon dissolution in water and its molecular structure, surfactants are mainly classified as anionic, cationic, nonionic and zwitterionic as shown in Fig.3.

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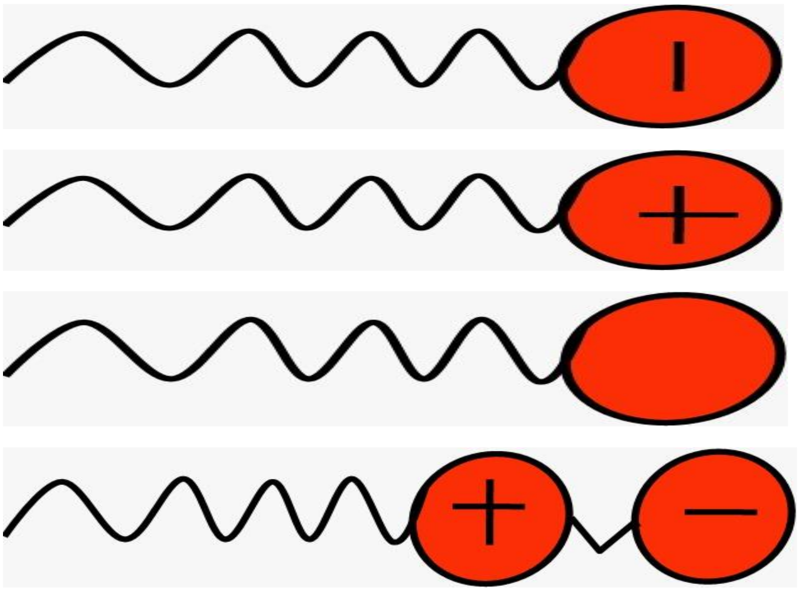


Anionic surfactant

Cationic surfactant

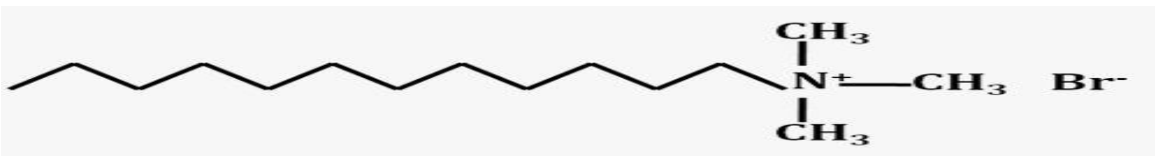
Nonionic surfactant

Zwitterionic surfactant

Fig. 3: Representation of different type of surfactant molecules.

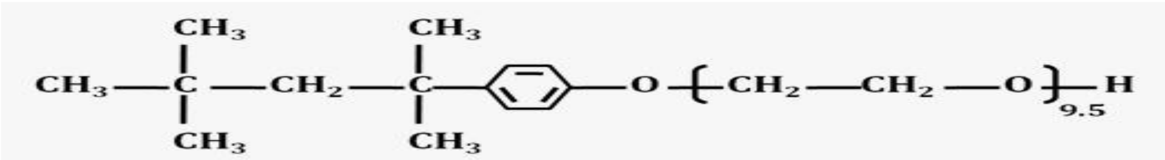
Anionic surfactants: These surfactants having negatively charged polar head and a positively charged counterion upon dissolution in aqueous solution. Anionic surfactant head groups include carboxylates, sulphates, sulphonates, alkyl benzene sulfonates, phosphates, etc. for example Sodium dodecyl sulphate (SDS).

Cationic surfactants: These surfactants having positively charged polar head and a negatively charged counterion upon dissolution in aqueous solution. Cationic surfactant head groups include long chain amines, quaternary amine and quaternary phosphonium etc., for example Dodecyl trimethylammonium bromide (DTAB).

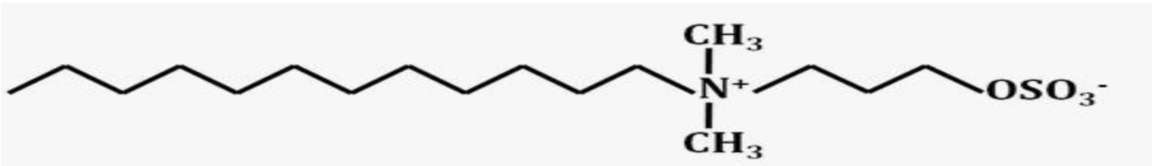


Nonionic surfactants: These surfactants having no charge upon dissolution in aqueous solution. Generally, nonionic surfactants possess hydroxyl group (R-OH) or ether group (R-

O-R') as a polar head [1, 3, 4] that do not ionize in water, for example p-tert-octylphenoxy polyethylene (9.5) ether (Triton X-100).



Zwitterionic surfactants: These surfactants possess both cationic and anionic charge on polar head and sometimes charge on the polar head group can be either positive or negative depending upon the pH of the solution. Example: N-Dodecyl N,N-dimethyl-3-ammonio-1-propanesulfonate (DPS). [1-9]



History of Surfactants:

History reveals that surfactants date back to around 2800 BC in ancient Babylon. A specific soap formula was inscribed on a Babylonian clay tablet and included water, alkali (potash), and cassia oil. Babylonian medical texts suggest that these mixtures were used as sanitizers for cleaning wounds[10]. The Ebers Papyrus (1500 BC), one of the oldest, longest, and most comprehensive medical papyri of ancient Egypt, describes how Egyptians regularly bathed using a mixture of animal fats, vegetable oils, and alkaline salts. According to Roman legend (31 BC–AD 476), surfactants were primarily used for laundering clothing and medicinal applications, and toward the end of the empire were increasingly used for personal hygiene [11].

India has a long and unique history of surfactant use dating back to before 1900. Indian civilization extensively used natural, plant-based surfactants such as soapnut (reetha), shikakai, Jatropha leaves, and other saponin-rich plants for personal hygiene and textile cleaning during ancient and traditional periods. These natural materials functioned as effective surfactants and were fully biodegradable, highlighting an early alignment with sustainable practices. Soap was introduced to India during the colonial period. The British brought hard soaps for laundry and bathing, which initially existed only in small-scale artisanal or elite use. Gradually, Indians began producing natural soaps using local vegetable oils, alkalis, and ash-based ingredients. Alkalis such as soda ash (Na_2CO_3) and caustic soda (NaOH) were initially imported from Britain. Later, these alkalis were manufactured in India during the "Swadeshi movement" to promote self-reliance and boycott foreign goods. Eventually, the Godrej Group produced the first soap made from vegetable oils instead of animal fats and launched it under the brand name "Chhavi" in 1897. They were soon followed by the Sarabhai Group's Swastik Oil Mills, Hindustan Lever's (HLL) *Surf*, Tata Oil Mills Company (TOMCO), Nirma, Galaxy Surfactants Limited, and many other companies. After independence in 1947, the Indian soap industry began to flourish. Rising demand for efficient cleaning and processing agents led to rapid industrial growth. Synthetic surfactants were introduced to meet this demand, marking a significant transition from traditional surfactants to petroleum-derived synthetic surfactants. These synthetic surfactants are man-made amphiphilic chemical compounds produced primarily from petroleum-based raw materials. They are widely used in household cleaning, personal care and cosmetic products, as well as in agriculture, paints and coatings, oil and gas, food, textile, pharmaceutical industries, and nanotechnology.

Applications of Surfactants

Soap & Detergent

Soap and Detergents are efficient cleaning products composed of one or more surfactants along with other auxiliary chemicals. Its primary function is to remove dirt from clothes, skin, and household articles, particularly in kitchens and bathrooms. Surfactants act by reducing the interfacial tension between oil and water, thereby holding dirt and oil in suspension and allowing their easy removal. This action is possible because surfactant molecules contain both hydrophilic and hydrophobic groups. Surfactants alone are not practically effective; therefore, soaps and detergents contain additives such as builders, brighteners, anti-redeposition agents, and co-surfactants. Alkyl benzene sulfonates are commonly used with other surfactants in laundry detergent powders such as Surf, Daz, and Ariel. Alkyl sulfates are widely used in detergent products, especially in liquid detergents, and are also used in toothpaste formulations [12-14]. Nonionic surfactants do not react with hardness-causing ions such as calcium and magnesium and are therefore effective in hard water. They are more efficient in removing organic dirt and oil compared to anionic surfactants. Nonionic surfactants are widely used in fabric-washing detergents, emulsion polymerization, agrochemical formulations, and various industrial processes. Amphoteric surfactants are mild in nature and are widely used in shampoos and cosmetics owing to their pH-balancing characteristics.

Food

Surfactants are crucial in the food industry for stabilizing oil-and-water mixtures, improving texture, enhancing shelf life, and processing efficiency. They act as emulsifiers, foaming agents, and dispersants in products like bread, ice cream, margarine, and beverages. Non ionic surfactants have most common type of surfactant used in food industries as food emulsifier.

The commercially used surfactants are listed in the below table-1; includes an E-number, which is a reference number assigned to food additives that have passed safety tests and are approved for use throughout the European Union and Switzerland. [15]

Table-1 : Most common food surfactants/emulsifiers used in the food industries.

Name of Food surfactant/Emulsifier	Code name	E-Number
Lecithins	Lecithins	E 322
Polyoxyethylene sorbitan esters	Polysorbates/Tweens	E 432 – 436
Mono- and diglycerides of fatty acids	MDG/ Monoglycerides	E 471
Acetic acid esters of MDG	ACETEM	E 472 a
Lactic acid esters of MDG	LACTEM	E 472 b
Citric acid esters of MDG	CITREM	E 472 c
Mono- and diacetyl tartaric acid esters of MDG	DATEM	E 472 e
Sucrose esters of fatty acids	Sucrose esters	E 473
Polyglycerol esters of fatty acids	Polyglycerol esters	E 475
Polyglycerol polyricinoleate	PGPR	E 476
Propane-1,2-diol esters of fatty acids	Propylene glycol esters	E 477
Sodium stearoyl-2-lactylate	SSL	E 481
Calcium stearoyl-2-lactylate	CSL	E 482
Sorbitan fatty acid esters	Spans	E 491 – 495

Table-1 has taken from Reference No. 15

Agriculture

The surface tension of herbicide, pesticide, and fungicide spray solutions is reduced by the use of surfactants, allowing closer contact between the spray droplets and plant surfaces. This enhances the effectiveness of pesticides by bringing them into direct contact with the leaf surface, thereby protecting crops more efficiently. Common surfactants used in pesticides include ethoxylated alcohols, alkylphenols, alkylamines, and sorbitans. Organosilicone surfactants are also employed in commercial sprays for improved performance. [16]

Nanotechnology

Nanotechnology is the deliberate design, characterization, production, and application of materials, structures, devices, and systems by precisely controlling their size and shape at the nanoscale. [17]. Mixtures of surfactants that reduce surface tension can be used in the preparation of nanoparticles, which have wide applications in cosmetics, pharmaceuticals, agriculture, and many other fields. [18]

Oil recovery

Anionic surfactants are the most commonly used in oil recovery processes. The three main classes of anionic surfactants are carboxylates, sulfates, and sulfonates. Sulfonate surfactants, such as petroleum sulfonates, internal olefin sulfonates, synthetic sulfonates, and alkoxy sulfonates, are among the most widely used. Sulfate surfactants used in oil recovery include alcohol propoxy sulfates, alkyl ether sulfates, tristyrylphenol alkoxysulfates, and dodecyl alkyl sulfates. Carboxylate surfactants are stable at high temperatures under both alkaline and acidic conditions. Ethylene carboxylates, in particular, exhibit good salt tolerance, thermal stability, and high-water solubility. [19-21]

Pharmaceutical

Surfactants play a crucial role in the development of pharmaceutical formulations. Their amphiphilic nature enables them to interact with both hydrophilic and hydrophobic substances, thereby enhancing drug solubility, stability, and bioavailability. [22]

Limitations of petroleum-based surfactants:

Surfactants derived from non-renewable resources such as petroleum are often slowly biodegradable, resulting in environmental persistence and potential toxicological effects. These surfactants have been associated with adverse impacts on terrestrial and aquatic ecosystems, including increased mortality of flora and fauna, risks to human health, and overall environmental pollution [23-29].

As a result, there is a growing demand for biodegradable products developed through green chemistry to reduce environmental pollution. Biosurfactants, derived from microbial or plant sources, offer several advantages, including high biodegradability, low toxicity, ready availability of raw materials, and ease of application. For this reason, they are often referred to as “green surfactants.” The shift from petrochemical-based surfactants to those derived from renewable materials has been driven by environmental concerns, legislation, and restrictions on toxic detergents, making green surfactants suitable and sustainable alternatives. These products are more biocompatible and biodegradable and align with rising consumer demand for mild, effective, and environmentally friendly products. Green surfactants are biobased amphiphilic molecules obtained naturally or synthesized from renewable raw materials and are sometimes used synonymously with biosurfactants [30, 31].

Conclusion:

In India, surfactants have evolved from traditional soaps to synthetic compounds that are widely used in pharmaceuticals, personal care, agriculture, and household products. However, petrochemical-based surfactants pose environmental challenges due to poor biodegradability and associated toxicity. This has driven the adoption of green surfactants, or biosurfactants, derived from renewable microbial and plant sources. These sustainable alternatives are biodegradable, less toxic, and align with India’s environmental regulations and growing consumer demand, marking an important shift toward eco-friendly and responsible practices in the chemical industry.

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