Detergents and Surfactants

Introduction

The word "detergent," is derived from the Latin word "*detergere*", which means "to wipe off". Detergent is a surfactant or a mixture of surfactants with cleansing properties in dilute solutions. The surfactants in detergents are usually alkylbenzenesulphonates. Alkylbenzenesulp- onates represent a family of compounds that are similar to soap but are more soluble in hard water, because the polar sulphonate of alkylbenzenesulphonates is less likely than the polar carboxylate of soap to bind to calcium and other ions found in hard water. Detergents are commonly available as powders or concentrated solutions. Detergents, like soaps work because they are amphiphilic, i.e., partly hydrophilic (polar) and partly hydrophobic (non-polar). Their dual nature facilitates the mixing of hydrophobic compounds (like oil and grease) with water. In most household contexts, the term detergent specifically refers to laundry detergent or dish detergent as opposed to hand soap or other types of cleansing agents.

Classification of Detergents

Detergents are classified into four broad classes depending on the electrical charge of the surfactants.

(a) Anionic Detergents

Anionic detergents contain anionic surfactants or mixtures thereof. The most commonly used anionic surfactants are those containing alkyl sulphonates, and sulphate ions. Many alkyl sulphates are used as detergents, but by far the most popular member of this group is sodium lauryl sulphate (SLS) (**Fig. 1.4**). Unlike soaps, SLS is compatible with dilute acid, and calcium and magnesium ions. The lower chain-length compounds, around C12, have better wetting ability, whereas the higher members (C16-C20) have better detergent properties. SLS has been reported to exhibit *in vitro* and *in vivo* antibacterial effects. Some other anionic surfactants include sodium lauryl ether sulphate (SLES) (**Fig. 1.4**), etc.

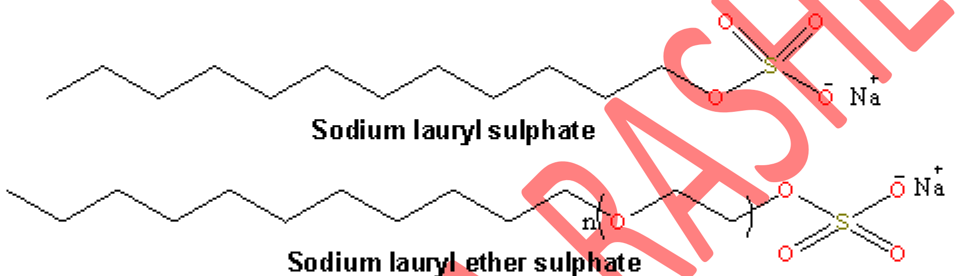


Fig. 1.4: Chemical structures of SLS and SLES.

(b) Cationic Detergents

Cationic detergents contain cationic surfactants or mixtures thereof. Cationic detergents are similar to the anionic ones, but instead of the anionic sulphonate group, the cationic surfactants have positively charged quaternary ammonium as the polar end. However, the use of cationic surfactants is generally limited to antimicrobial preservatives because of their bactericidal activity. Examples of cationic surfactants include, cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (**Fig. 1.5**).

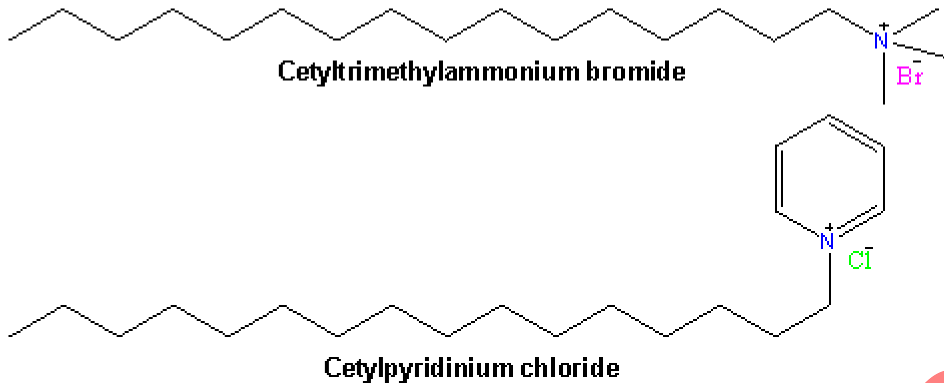


Fig. 1.5: Chemical structures of CTAB and HTAB.

(c)Amphoteric Detergents

Amphoteric detergents consist of surfactant molecules with at least one anionic and one cationic group/centre. They have the detergent properties of anionic surfactants and the disinfectant properties of cationic surfactants. Their activity depends on the pH of the media in which they are used. Balanced amphoteric surfactants are reputed to be non-irritant to the eyes and skin, and have therefore, been used in so-called baby shampoos. The most often used amphoterics are betaines, sulphobetaines, imidazolinium derivatives and alkyl aminoacids. Examples of amphoteric surfactants include, N-Oleoylamidopropyl-N,N-dimethylbetaine (**Fig. 1.6**).

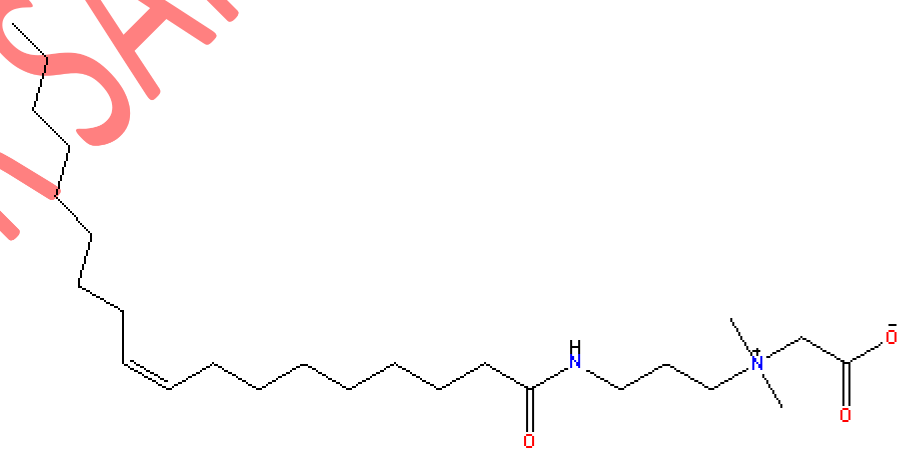


Fig. 1.6: Chemical structure of N-Oleoylamidopropyl-N,N-dimethylbetaine.

(d) Non-ionic Detergents

Non-ionic detergents consist of neutral surfactant molecules. Non-ionic surfactants are advantageous over ionic surfactants in that they are compatible with all other types of media and their properties are minimally affected by pH. Moreover, they are generally less irritant than anionic or cationic surfactants. Non-ionic surfactants are used as emulsifiers, and solubilizing and wetting agents. They have applications in the food, cosmetic, paint, pesticide, and textile industries. Examples of non-ionic surfactants include, octoxynol (Triton X100™) (**Fig. 1.7**).

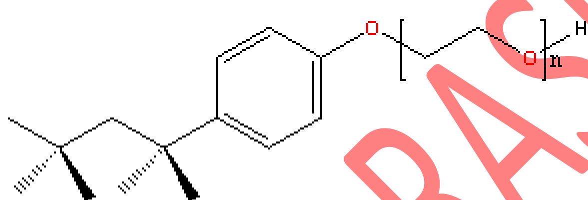


Fig. 1.7: Chemical structure of octoxynol.

The modern detergent formulations available in market contain several ingredients in addition to surfactants. The main ingredients include builders and bleaches, among others. Builders are also referred by the names, complexing or sequestering agents. They act as water softeners. They soften water through chelation or ion exchange of calcium and magnesium ions present in hard water. Some of the builders used in modern day detergent formulations are chelators such as citric acid, gluconic acid and EDTA (ethylenediaminetetraacetic acid), and ion exchange agents such as zeolites. The bleaches used in detergent formulations are primarily stable adducts of hydrogen peroxide such as sodium perborate and sodium percarbonate. Basically, these agents are inactive in solid form but react with water to produce hydrogen peroxide, which then performs the bleaching action. Some detergents also include bleach activators including tetraacetylethylenediamine. These activators react with hydrogen peroxide to form peracetic acid, which is a more effective bleaching agent. Bleaches help in the removal of oxidisible organic stains, which are typically of vegetable origin, e.g., chlorophyll, anthocya-

nin dyes, tannins, humic acids and carotenoid pigments. Certain detergent types are also added with some enzymes such as proteases (for protein stains), lipases (for fat stains) and amylases (for carbohydrate stains). Generally, the amount of enzyme added can be up to about 2% by weight of the product. The enzymes ensure the degradation of recalcitrant stains composed of proteins, fats, or carbohydrates.

Some other ingredients/additives are also added to detergent formulations depending on the desired application. Certain additives adjust the foaming properties of detergents either by stabilization or counteraction of foam. Some other ingredients are used to increase or decrease viscosity of the detergent solutions, or for the solubilization of other ingredients. Corrosion inhibitors, dye transfer inhibitors and anti-redeposition agents are used for counteracting damage to washing equipment, preventing dyes from one article from colouring other items and preventing fine soil particles from re-attaching to the product being cleaned, respectively.Several ingredients are added to enhance the aesthetic properties of the items to be cleaned or the detergent itself before or during use. Ingredients such as optical brighteners, fabric softeners, colourants and perfumes are added provided they are compatible with the other components and do not affect the colour of the cleaned item.

Biodegradable Detergents

•The term "biodegradable detergent" refers to detergents with a straight hydrocarbon chain.

•Unbranched chains can biodegrade more easily. So, pollution is prevented.

An example of biodegradable detergent

•Sodium lauryl sulfate is an example of a biodegradable detergent.

Nonbiodegradable detergents

•Non-biodegradable detergents are described as those with a branched hydrocarbon chain.

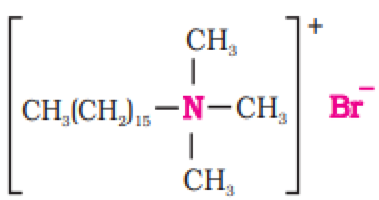
•These are classified as non-biodegradable because microbes cannot degrade them.

•These are one of the pollution sources.

Example of nonbiodegradable detergent

•Non-biodegradable substances include cetyl trimethyl ammonium bromide.

- The structure of cetyltrimethyl ammonium bromide is as follows:-

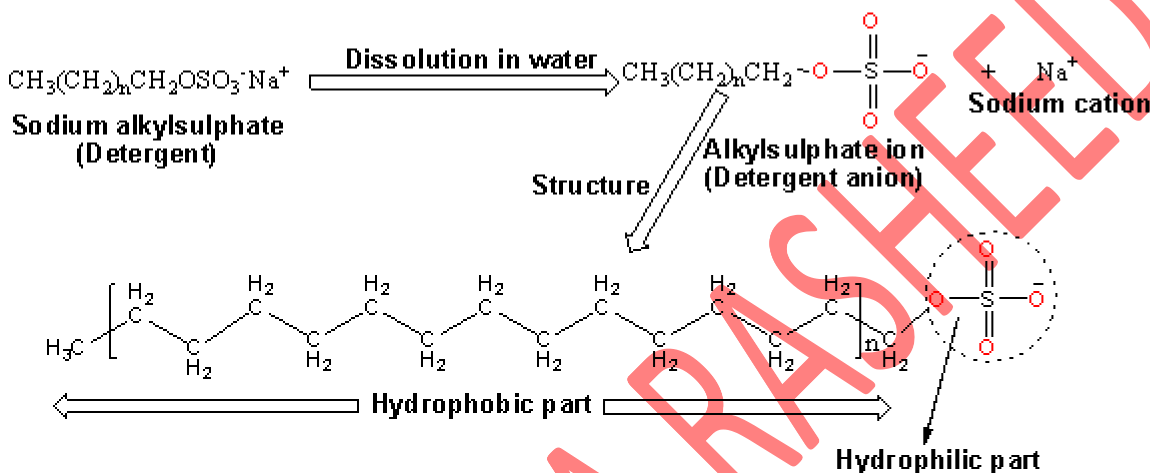


Cetyltrimethyl ammonium bromide

Washing action of Detergents/ Mechanism of Action

Detergents work in a similar fashion as do soaps. For understanding the mechanism of action of detergents, the rule of nature, "similia simlibus solvuntur” which means “like dissolves like" applies. The cleansing action of detergents is due to their ability to lower the surface tension of water, to emulsify oil or grease and to hold them in a suspension in water. The reduced surface tension of water enables a thorough wetting of the cloth.

When a detergent is dissolved in water, it forms detergent anions (surfactants) and sodium cations. Let us consider the ionization of sodium alkylsulphates in water (**Scheme 1.3**).



Scheme 1.3: General schematic representation of the dissociation of an anionic detergent molecule in water.

The dissociation of a detergent molecule in water produces anions of the detergent surfactants and the sodium cations. A detergent molecule has both hydrophilic (polar head) and a hydrophobic (hydrocarbon tail). The non-polar hydrophobic tails of detergent are lipophilic (oil loving) and thus, embed into the grease and oils that help dirt and stains adhere to surfaces. The hydrophilic heads, however, remain surrounded by the water molecules to which they are attracted. As more and more detergent molecules embed into a greasy stain, they eventually surround and isolate little particles of the grease and form structures called micelles that are lifted into solution. In a micelle, the tails of the detergent molecules are oriented towards and into the grease, while the heads face outwards into water, resulting in an emulsion of grease particles suspended in water.

With agitation, the micelles are dispersed into water and removed from the previously dirty surface. In essence, detergent molecules partially dissolve the greasy stain to form the emulsion that is kept suspended in water until it can be rinsed away (**Fig. 1.8**).

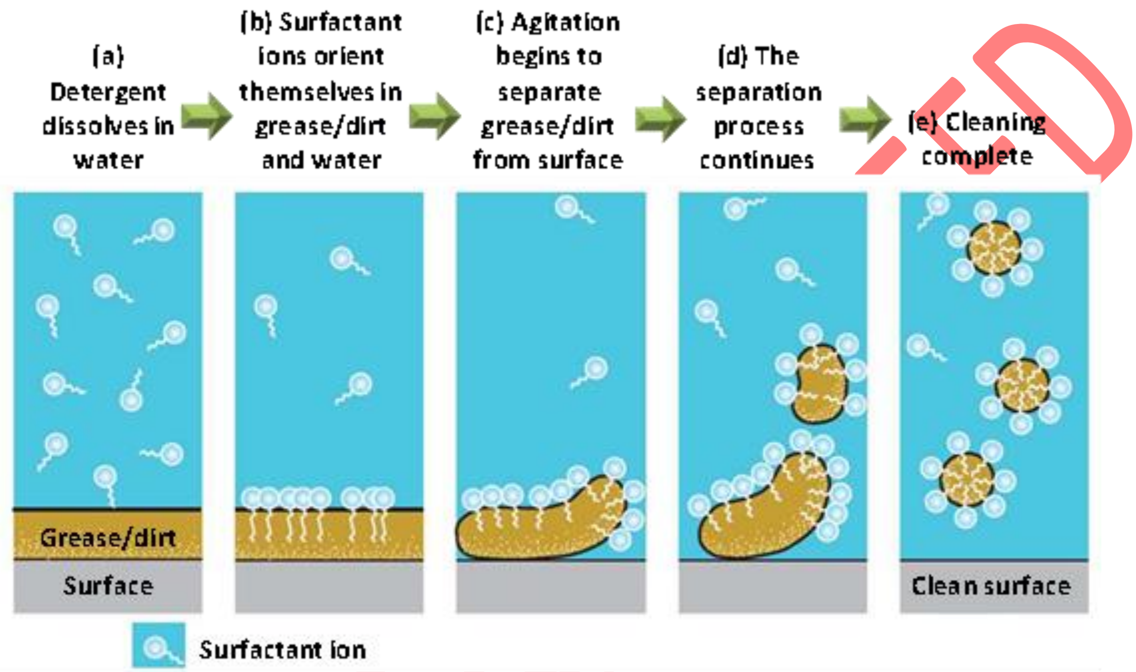


Fig. 1.8: A general representation of the mechanism of action of detergent.

Detergents have better cleansing properties than soaps. For example, they work well in hard water containing calcium and magnesium ions, because the calcium and magnesium salts of detergents (calcium and magnesium sulphonates) are water soluble and therefore, do not precipitate and fall out of solution.

What Are Surfactants?

Surfactants are a category of chemical compounds that are used in lowering the surface tension (or interfacial tension) between different compounds such as two liquids or between a gas and a liquid or it can also be between a liquid and a solid. Surfactants are categorized as organic compounds and are amphiphilic in nature. What it basically means is that it contains both hydrophobic and hydrophilic groups.

In other words, a surfactant has both a water-insoluble component as well a water-soluble component. One of the common properties of surfactants is that they will diffuse in water and adsorb at interfaces between air and water. It can also adsorb at the interface between oil and water where water is mixed with oil. The water-insoluble group can extend out of the bulk water phase and move into the air or oil phase. On the other hand, the water-soluble head group usually stays in the water phase.

The word surfactant has been derived from the word surface active agent and was coined in the year 1950. In any case, surfactants today are found in many products that we use today. They are found in detergents, wetting agents, foaming agents, emulsifiers and dispersants. Surfactants are one of the important components in detergents that help to eliminate dirt from clothes, skin and household utensils mainly in bathrooms and kitchens. Besides, they are extensively used in industries.

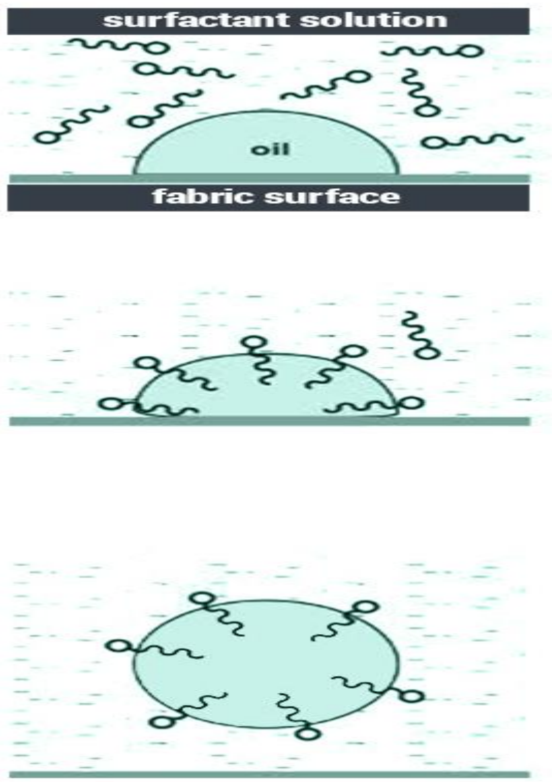
Soaps are the foremost surfactants mostly obtained from fats called glycerides that were mainly esters formed by trihydric alcohol, glycerol with fatty acids having lengthy chain carboxylic acids. Glycerides are hydrolyzed by heating with a solution of sodium hydroxide to make soaps, sodium salts of acids and propane 1,2,3 triol. This process is called saponification.

How do Surfactants Work?

When a sufficient amount of surfactant molecules are added to a solution they start combining together. During this, they form structures or aggregates called micelles in the bulk aqueous phase. As the micelle starts to form, the surfactant heads (hydrophilic heads) remain exposed to water or with the surrounding liquid. The tails (hydrophilic heads) come together at the centre of the structure and remain protected from water. Different types of aggregates such as spherical or cylindrical micelles or lipid bilayers can also be formed. Furthermore, the shape of the aggregates mostly depends on the chemical structure of the surfactants (balanced size between the hydrophilic head and hydrophobic tail).

In any case, surfactants work by breaking down the interface between oils, water or dirt. The oils and dirt are also held in suspension making it easy to remove them.

Action Of Surfactants



1. Surfactants consist of hydrophobic (water-hating) and hydrophilic (water-loving) groups.
2. The molecules of surfactant are adsorbed by the oil and hence it is removed from the surface.
3. The molecules of surfactant surround the oil after it has been removed and prevents it from depositing again.

Manufacture

The glycerides which are used in making surfactants contain unsaturated and saturated carboxylic acids that consist of an even number of carbon atoms in the range of 12-20 such as stearic acid, $CH_3(CH_2)16CO_2H$. Synthetic surfactants hold one major edge over soaps. Since soaps form insoluble magnesium and calcium salts with magnesium and calcium ions in hard water and clays that exist in the dirt where a lot of soap goes in vain in making an insoluble scrum. However, this can be avoided by using a synthetic surfactant. For instance, in anionic surfactants, the carboxylate group is replaced by sulfonate as the hydrophilic component. The corresponding magnesium and calcium salts are soluble in water more than salts of carboxylic acids.

Types of Surfactants

There are several types of surfactants that are classified according to the polar head group. The hydrophobic tails are seen to be often similar. Let's quickly go through the below.

Anionic

If the charge on the head group (hydrophilic end) is negative, the surfactant is called anionic. It contains anionic functional groups at its head, such as sulfate, sulfonate, phosphate, and carboxylates. A few examples of anionic surfactants include sulfates, sulfonates, and gluconates.Cationic

Similarly, if the head group (hydrophilic end) has a positive charge it is called cationic. Alkyl ammonium chlorides are common examples of cationic surfactants.

Zwitterionic

Zwitterionic also known as amphoteric surfactants have both positive and negative charges on their hydrophilic end. They have both cationic and anionic centres attached to the same molecule. It basically has a net charge of zero. Betaines and amino oxides are examples of this type of surfactant.

Non-ionic

Nonionic surfactants are mostly neutral and no charge is present on their hydrophilic end. Non-ionic surfactants have covalently bonded oxygen-containing hydrophilic groups, which are bonded to hydrophobic parent structures. They can be used to emulsify oils and seem to do a better job than anionic surfactants at removing organic soils. Non-ionic surfactants are less sensitive to water hardness than anionic surfactants, and they foam less strongly. Some common examples of nonionic surfactants are ethoxylates, alkoxylates and cocamide.

Uses Of Surfactants

A vast range of surfactants like Emulsifiers, foaming agents and wetting agents are utilized based on the areas of use. Surfactants minimize the surface tension with respect to the phase and hence lie at the heart of interfacial chemistry.

- Surfactants play an important role in cleaning, wetting, dispersing, emulsifying, foaming and anti-foaming agents.
- Used in agrochemical formulations such as herbicides (some), insecticides, biocides (sanitisers), and spermicides.
- Personal care products such as cosmetics, shampoos, shower gel, hair conditioners, and toothpaste.
- Surfactants are used in firefighting and pipelines (liquid drag-reducing agents). Alkali surfactant polymers are also used to mobilize oil in oil wells.
- Surfactants are sometimes added to car engine lubricants which greatly help to keep particles from sticking to engine parts.
- Surfactants are also commonly used in corrosion inhibition in ore flotation.
- corrosion inhibition, to promote oil flow in porous rocks, and to produce aerosols.