Chemistry and Technology of Surfactants

- **To understand what is needed to achieve effective cleaning, it is helpful to have a basic knowledge of soap and detergent chemistry.**
- **Water, the liquid commonly used for cleaning, has a property called surface tension. In the body of the water, each molecule is surrounded and attracted by other water molecules.**
- **However, at the surface, those molecules are surrounded by other water molecules only on the water side.**
- **A tension is created as the water molecules at the surface are pulled into the body of the water.**
- **This tension causes water to beat up on surfaces (glass, fabric), which slows wetting of the surface and inhibits the cleaning process. You can see surface tension at work by placing a drop of water onto a counter top.**
- **The drop will hold its shape and will not spread.**

In the cleaning process, surface tension must be reduced so water can spread and wet surfaces.

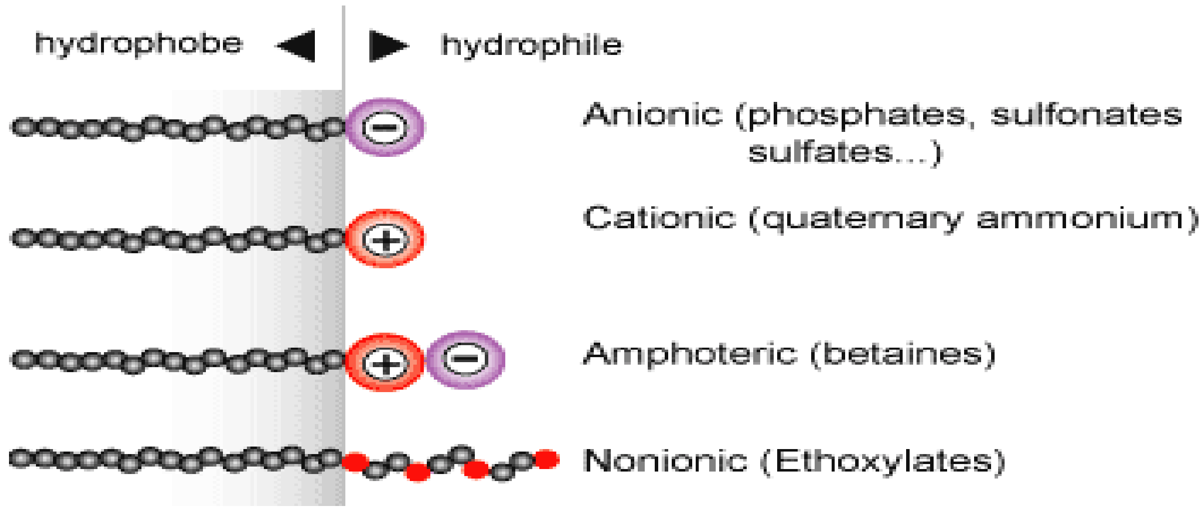
Chemicals that are able to do this effectively are called surface active agents, or surfactants. They are said to make water "wetter."

Surfactants perform other important functions in cleaning, such as loosening, emulsifying (dispersing in water) and holding soil in suspension until it can be rinsed away. Surfactants can also provide alkalinity, which is useful in removing acidic soils.

Surfactants are classified by their ionic (electrical charge) properties in water:

- Anionic (negative charge)
- nonionic (no charge)
- cationic (positive charge)

- Amphoteric (either positive or negative charge).



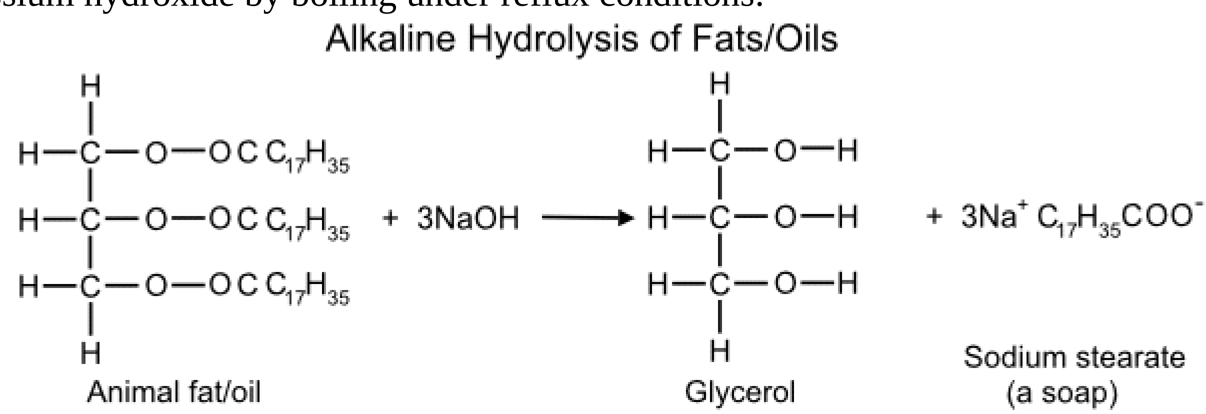
Soap is an anionic surfactant. Other anionic as well as nonionic surfactants are the main ingredients in today's detergents. Now let's look closer at the chemistry of surfactants.

Soaps

Soaps are water-soluble sodium or potassium salts of fatty acids. Soaps are made from fats and oils, or their fatty acids, by treating them chemically with a strong alkali.

Making Soaps

Soaps are formed by the alkaline hydrolysis (breaking up) of fats and oils by sodium or potassium hydroxide by boiling under reflux conditions:



Fats and Oils

The fats and oils used in soap making come from animal or plant sources. Each fat or oil is made up of a distinctive mixture of several different triglycerides.

In a triglyceride molecule, three fatty acid molecules are attached to one molecule of glycerin. There are many types of triglycerides; each type consists of its own particular combination of fatty acids.

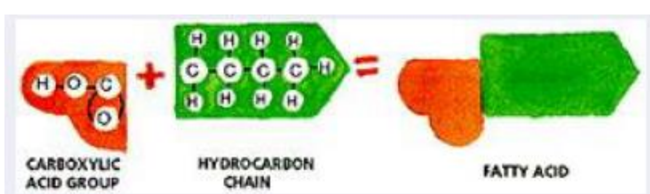
Fatty acids are the components of fats and oils that are used in making soap. They are weak acids composed of two parts:

A carboxylic acid group consisting of one hydrogen (H) atom, two oxygen (O) atoms, and one carbon (C) atom, plus a hydrocarbon chain attached to the carboxylic acid group. Generally, it is made up of a long straight chain of carbon (C) atoms each carrying two hydrogen (H) atoms.

Alkali

An alkali is a soluble salt of an alkali metal like sodium or potassium. Originally, the alkalis used in soap making were obtained from the ashes of plants, but they are now made commercially. Today, the term alkali describes a substance that chemically is a base (the opposite of an acid) and that reacts with and neutralizes an acid.

The common alkalis used in soap making are sodium hydroxide (NaOH), also called caustic soda; and potassium hydroxide (KOH), and also called caustic potash.



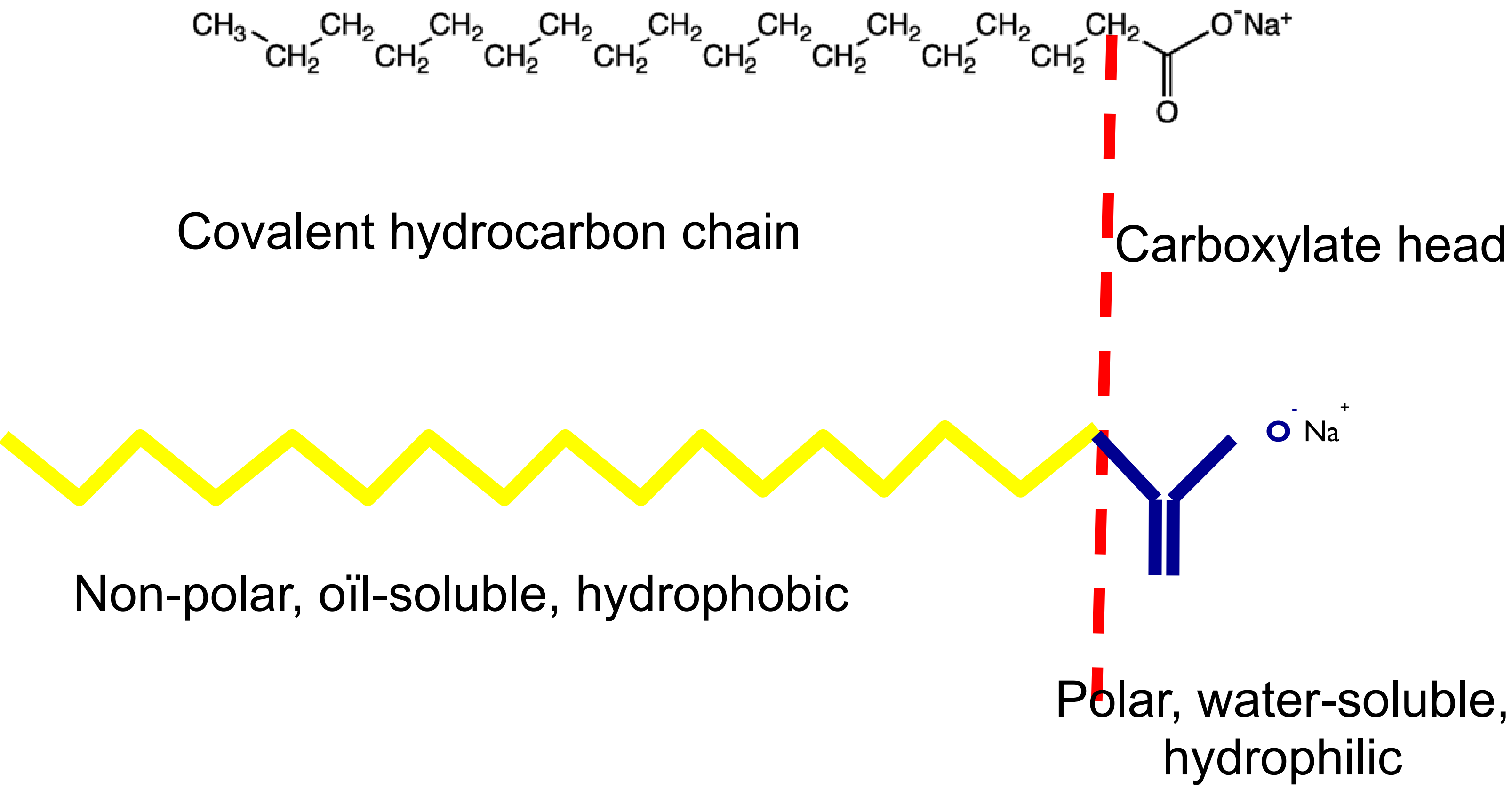
- Hydrolysis of esters such as fats/oil produces glycerol and fatty acids. Fats and oils are triglycerides meaning they are esters which contain 3 molecules of fatty acid condensed to 1 molecule of the trihydric alcohol, glycerol. So during hydrolysis, three molecules of soap are made per molecule of glycerol. (3:1 ratio of fatty acid: glycerol)

- The hydrolysis is carried out using alkalis (NaOH or KOH) as catalyst and the fatty acids formed are changed into sodium or potassium salts (soaps) the soaps are ionic and water-soluble.
- The long covalent hydrocarbon chain that makes up the tail section of a soap structure can be represented in a number of ways, either in the shorthand notation shown below or as a bond-stick representation, shown at the bottom of the page. The charged carboxylate group represents the head section of the soap structure.

The structure of soap

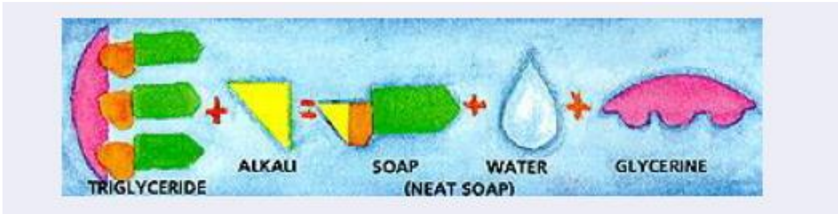
The long covalent hydrocarbon chain gives rise to the hydrophobic (water hating) and oil-soluble (non-polar) properties of the soap molecule (represented in yellow). The charged carboxylate group (represented in blue) is attracted to water molecules (hydrophilic). In this way, soaps are composed of a hydrophilic head and a hydrophobic tail:

In solution a soap molecule consists of a long non-polar hydrocarbon tail (e.g. C17H35-) and a polar head (-COO-).



How Soaps are made

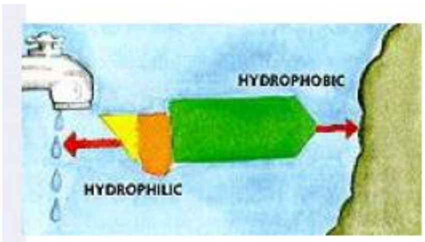
Saponification of fats and oils is the most widely used soap making process. This method involves heating fats and oils and reacting them with a liquid alkali to produce soap and water (neat soap) plus glycerine.



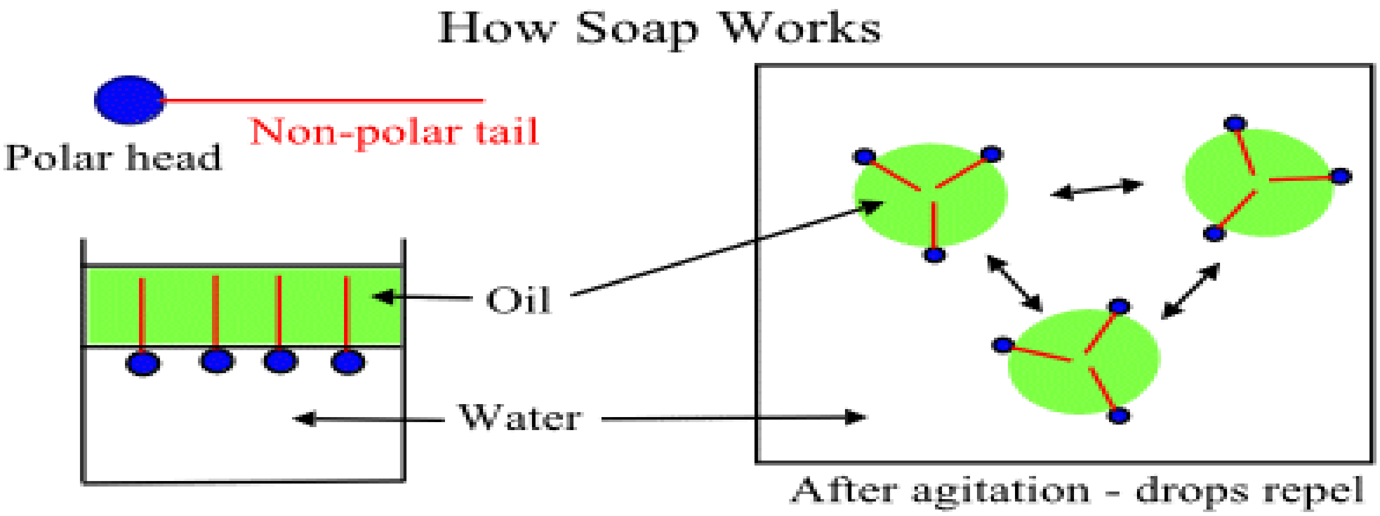
The other major soap making process is the neutralization of fatty acids with an alkali. Fats and oils are hydrolyzed (split) with a high-pressure steam to yield crude fatty acids and glycerine. The fatty acids are then purified by distillation and neutralized with an alkali to produce soap and water (neat soap).

When the alkali is sodium hydroxide, a sodium soap is formed. Sodium soaps are "hard" soaps. When the alkali is Potassium hydroxide, a potassium soap is formed. Potassium soaps are softer and are found in some liquid hand soaps and shaving creams.

The carboxylate end of the soap molecule is attracted to water. It is called the hydrophilic (water-loving) end. The hydrocarbon chain is attracted to oil and grease and repelled by water. It is known as the hydrophobic (water-hating) end.



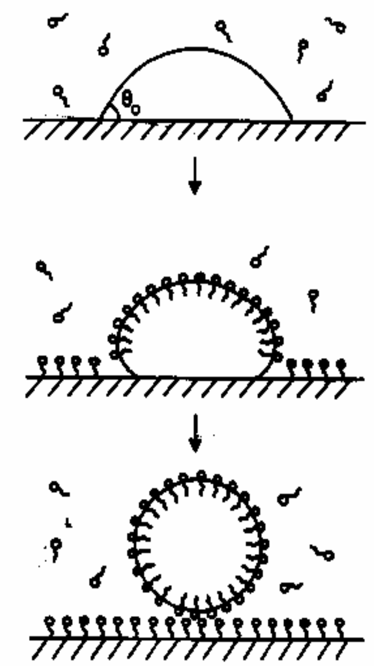
How a soap works



MECHANISM OF STAIN/DIRT REMOVAL

Roll-up mechanism

- The hydrophobic tails ‘burrow’ into the droplet of oil or grease.
- The hydrophilic heads are left to face the surrounding water.
- This results in the formation of a ball-like structure (a micelle).
- The non-polar substances, such as oil or grease, are held inside the ball and suspended in water, to be washed away.



How Water Hardness Affects Cleaning Action

Although soap is a good cleaning agent, its effectiveness is reduced when used in hard water. Hardness in water is caused by the presence of mineral salts - mostly those of calcium (Ca) and magnesium (Mg), but sometimes also iron (Fe) and manganese (Mn). The mineral salts react with soap to form an insoluble precipitate known as soap film or scum.

Soap film does not rinse away easily. It tends to remain behind and produces visible deposits on clothing and makes fabrics feel stiff. It also attaches to the insides of bathtubs, sinks and washing machines.

Some soap is used up by reacting with hard water minerals to form the film. This reduces the amount of soap available for cleaning. Even when clothes are washed in soft water, some hardness minerals are introduced by the soil on clothes. Soap molecules are not very versatile and cannot be adapted to today's variety of fibers, washing temperatures and water conditions.

Soapless detergents

- When soap is used in hard water, a white solid precipitate we call scum forms. This is because charged calcium and magnesium ions present in the hard water react with soap to form an insoluble substance.
- Like soap, detergent molecules have a long chain of carbon and hydrogen atoms, but at the end of the molecule there is this group $-SO_3^-$ called sulphonate instead of the $-COO^-$ carboxylate group present in soap.
- The calcium salt of a sulphonate is soluble in water unlike the calcium salts of the carboxylate.

Emulsions

- An emulsion contains small droplets of one liquid dispersed in another liquid.
- Emulsions in Food
  - Emulsions in food are mixtures of oil and water. To prevent oil and water components separating into layers, a soap-like molecule known as an emulsifier is added. Emulsifiers for use in food are commonly

made by reacting edible oils with glycerol to form molecules in which either one or two fatty acid groups are linked to a glycerol backbone rather than the three normally found in edible oils. The one or two hydroxyl groups present in these molecules are hydrophilic whilst the fatty acid chains are hydrophobic.

Surfactants in Detergents

A detergent is an effective cleaning product because it contains one or more surfactants.

Because of their chemical makeup, the surfactants used in detergents can be engineered to perform well under a variety of conditions.

Such surfactants are less sensitive than soap to the hardness minerals in water and most will not form a film.

Detergent surfactants were developed in response to a shortage of animal and vegetable fats and oils during World War I and World War II. In addition, a substance that was resistant to hard water was needed to make cleaning more effective.

At that time, petroleum was found to be a plentiful source for the manufacture of these surfactants.

Today, detergent surfactants are made from a variety of petrochemicals (derived from petroleum) and/or oleochemicals (derived from fats and oils).

Petrochemicals and Oleochemicals

Like the fatty acids used in soap making, both petroleum and fats and oils contain hydrocarbon chains that are repelled by water but attracted to oil and grease in soils. These hydrocarbon chain sources are used to make the water-hating end of the surfactant molecule.

Other Chemicals

Chemicals, such as sulphur trioxide, sulfuric acid and ethylene oxide, are used to produce the water-loving end of the surfactant molecule.

Alkalis

As in soap making, an alkali is used to make detergent surfactants. Sodium and potassium hydroxide are the most common alkalis.

How Detergent Surfactants Are Made

Surfactants come in four different types:

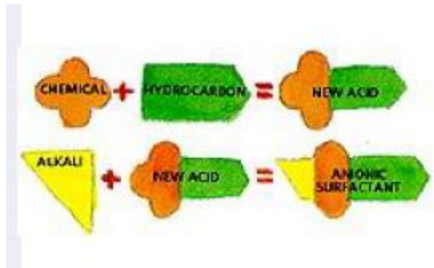
- Anionic
- non-ionic
- cationic
- amphoteric/ Zwitterionic

Once you understand the differences between these different surfactant types, as well as how to classify them by their names, choosing the right cleaning products should be a snap.

Anionic Surfactants

The chemical reacts with hydrocarbons derived from petroleum or fats and oils to produce new acids similar to fatty acids.

A second reaction adds an alkali to the new acids to produce one type of anionic surfactant molecule.



Probably the most commonly used surfactants in carpet cleaning chemistry are anionic surfactants.

Anionic surfactants possess a negative charge on their hydrophilic end. This charge helps the surfactant molecules to interact with both the carpet fibres and soil particles, lifting and suspending soils in "bubble-like" arrangements called micelles.

Anionic surfactants possess other benefits that make them ideal for certain carpet applications. Generally, they make a lot of foam when agitated. Also, they tend to be flaky or powdery when dry, not sticky like other surfactants.

Anionic surfactants, therefore, are the most common type of surfactant found in low moisture carpet cleaners, like traditional shampoos and encapsulation products. However, these detergents tend to not be as good at emulsifying oily soils as some other detergent types.

When reading the ingredients list on your cleaning products, you can identify anionic surfactants as those that have the following in their names:

· Sodium

· Ammonium

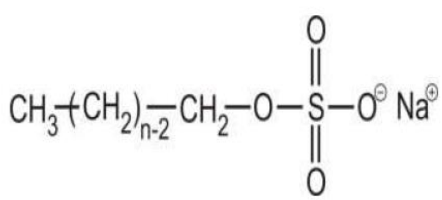
· Magnesium

· Sulphate

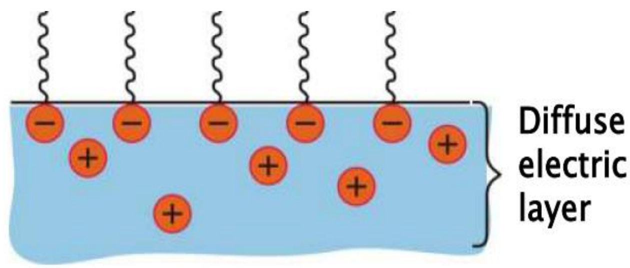
· Sulfonate

· Gluconate

(For example, sodium laurel sarcosinate, magnesium laurel sulphate, and sodium gluconate.)



sodium dodecyl sulfate



Salts of higher fatty acids (soaps)

Sodium dodecyl sulphate (SDS) (Sodium lauryl sulphate (SLS))

(Widely used to produce oil in water o/w emulsions).

Sodium glycocholate

Sodium taurocholate

Alkyl benzene sulfonates (detergents)

Sodium Oleate:

$CH_3\ (CH_2)_7CH{=}CH\ (CH_2)_7COO^-\ Na^+$

Sodium Dodecyl sulphate:

$CH_3\ (CH_2)_{11}SO_4^-\ Na^+$

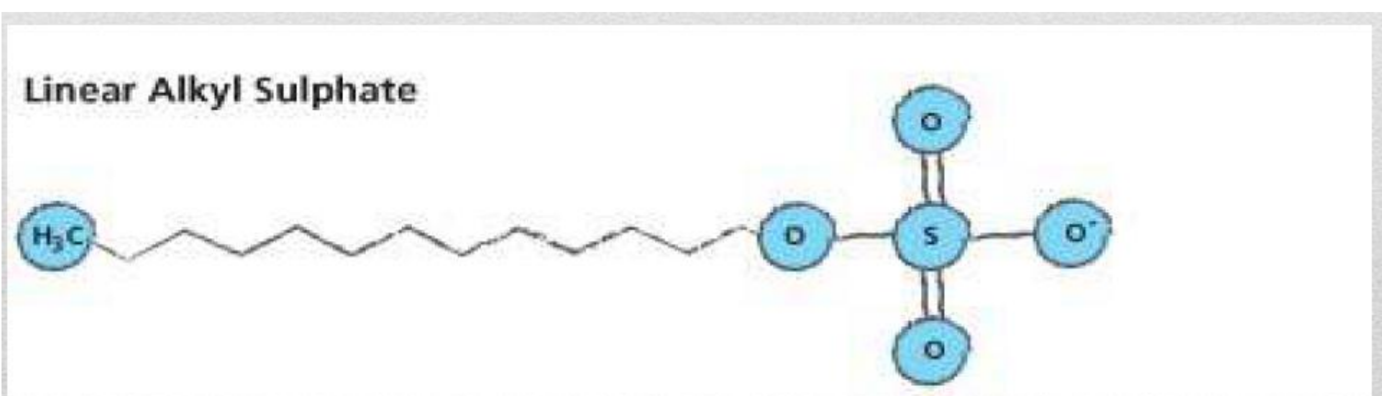
Sodium Dodecylbenzenesulphonate:

$CH_3\ (CH_2)_{11}C_6H_4SO_3^-\ Na^+$

Sodium Stearate:

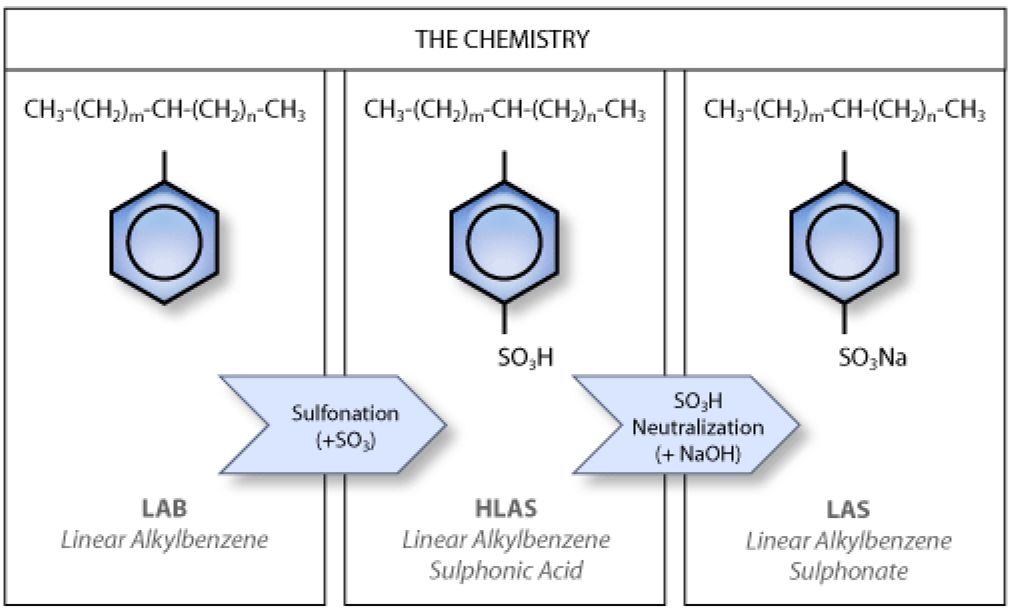
$CH_3\ (CH_2)_{16}COO^-\ Na^+$

The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps. Most of the anionic surfactants are carboxylate, sulfate and sulfonate ions .The straight chain is a saturated /unsaturated C12-C18 aliphatic group. The water solubility potential of the surfactant is determined by the presence of double bonds.



LAS Anionic surfactant:

LAS is an anionic surfactant developed from Linear Alkylbenzene (LAB). Approximately 99% of the LAB produced worldwide is transformed into LAS through a sulphonation process. LAS, in turn, is almost exclusively used as a surfactant ingredient in detergents. In most cases LAS is used as a sodium derivative. For some special applications other derivatives are also produced.



m+n = 7-10

One of the biggest attractions of LAS is that it can be used together with all types of detergent ingredients, because of its high compatibility.

Both HLAS (Linear Alkylbenzene Sulphonic Acid) and LAS are highly stable chemicals which can be stored and transported using standard materials and logistic facilities.

The performance of LAS in cleaning products compares favourably with other surfactants on the market, and is at times significantly better. Furthermore, its environmental and human safety profile is unmatched by any other surfactant.

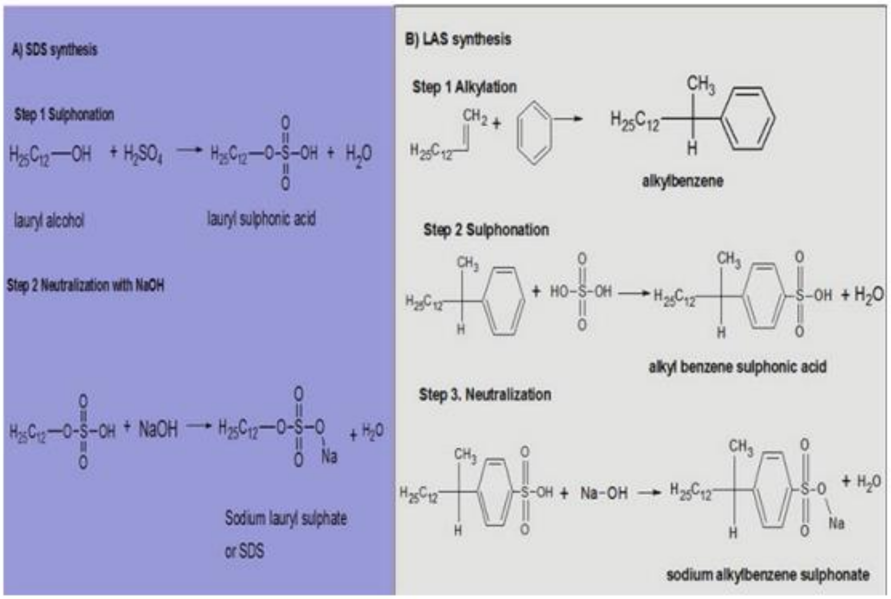
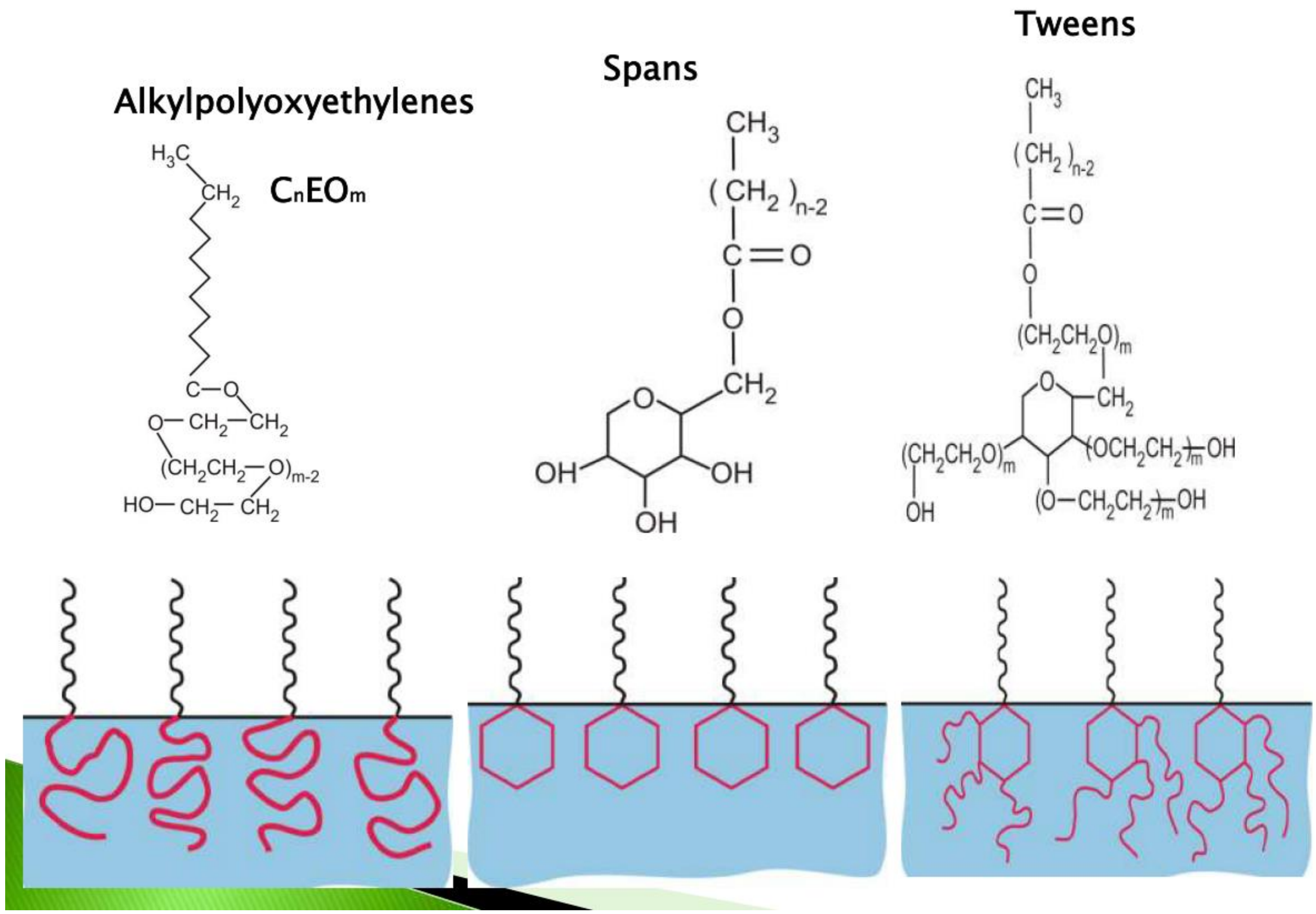


Fig. 5.2 Chemical synthesis of anionic surfactants (**a**) sodium dodecyl sulfate (SDS) synthesis involving sulfonation and subsequent neutralisation (**b**) linear alkyl benzene sulfonate (LAS) synthesis by alkylation, sulfonation and subsequent neutralisation (Constructed based on Behler et al. 2001)

Non-ionic Surfactants

Non-ionic surfactant molecules are produced by first converting the hydrocarbon to an alcohol and then reacting the fatty alcohol with ethylene oxide.

These non-ionic surfactants can be reacted further with sulfur-containing acids to form another type of anionic surfactant.



The non ionic surfactant can be classified as

• Polyol esters ,

• polyoxyethylene esters ,

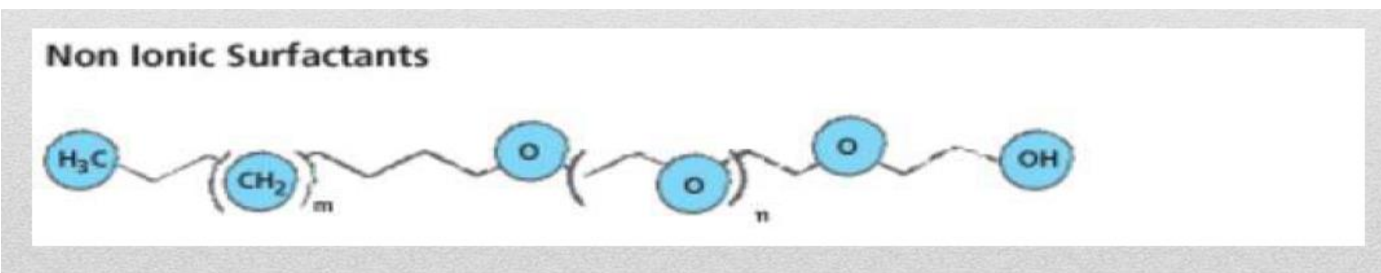
• poloxamers .

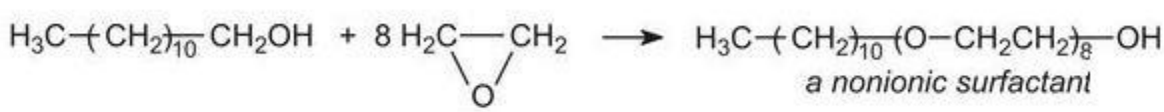
- The Polyol esters includes glycol and glycerol esters and sorbitan Derivatives.
- Polyoxyethylene esters includes polyethylene glycol (PEG 40, PEG -50 , PEG- 55).
- The most commonly used non-ionic surfactants are ethers of fatty Alcohols.

Non-ionics: Can be tailored to specific applications (e.g. detergency, wetting agent)

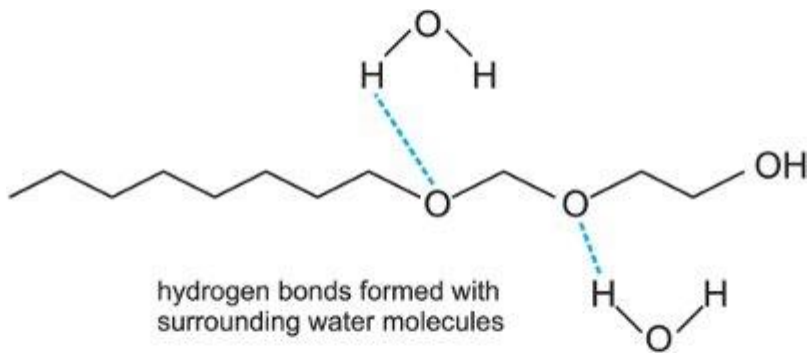
Non-Ionic Surfactants:

- Those surfactants do not have any electrical charge, which makes them resistant to water hardness deactivation.
- They are less irritant than other anionic or cationic surfactants.
- The hydrophilic part contains the polyoxyethylene, polyoxypropylene or polyol derivatives.
- The hydrophobic part contains saturated or unsaturated fatty acids or fatty alcohols
- They are excellent grease/oil removers and emulsifiers.





Although they do not contain an ionic group as their hydrophilic component, hydrophilic properties are conferred on them by the presence of a number of oxygen atoms in one part of the molecule which are capable of forming hydrogen bonds with molecules of water.



As the temperature of the surfactant solution is increased the hydrogen bonds gradually break causing the surfactant to come out of solution. This is commonly referred to as the cloud point and is characteristic for each nonionic surfactant. Nonionics are more surface active and better emulsifiers than anionics at similar concentrations. They are less soluble than anionics in hot water and produce less foam. They are also more efficient in removing oily and organic dirt than anionics. Depending on the type of fibre, they can be active in cold solution and so are useful in countries which lack hot water supplies and in developed countries where there is a desire to lower the wash temperatures either to save energy or because of the type of fabric being washed. Nonionics are used in fabric washing detergents (both powders and liquids), in hard surface cleaners and in many industrial processes such as emulsion polymerization and agrochemical formulations.

What are PEGs?

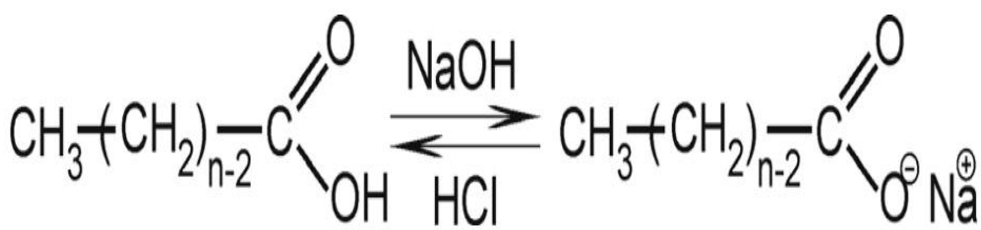
You have probably noticed that many of cosmetics and personal care products you use have different types of PEGs among ingredients. PEG, which is the abbreviation of polyethylene glycol, is not a definitive chemical entity in itself, but rather a mixture of compounds, of polymers that have been bonded together. Polyethylene is the most common form of plastic, and when combined with glycol, it becomes a thick and sticky liquid.

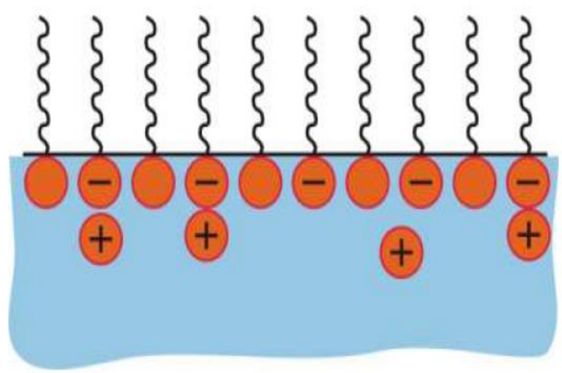
PEGs are almost often followed by a number, for example PEG-6, PEG-8, PEG-100 and so on. This number represents the approximate molecular weight of that compound. Typically, cosmetics use PEGs with smaller molecular weights. The lower the molecular weight, the easier it is for the compound to penetrate the skin. Often, PEGs are connected to another molecule. You might see, for example, PEG 100 stearate as an ingredient. This means that the polyethylene glycol polymer with an approximate molecular weight of 100 is attached chemically to stearic acid.

In cosmetics, PEGs function in three ways: as emollients (which help soften and lubricate the skin), as emulsifiers (which help water-based and oil-based ingredients mix properly), and as vehicles that help deliver other ingredients deeper into the skin.

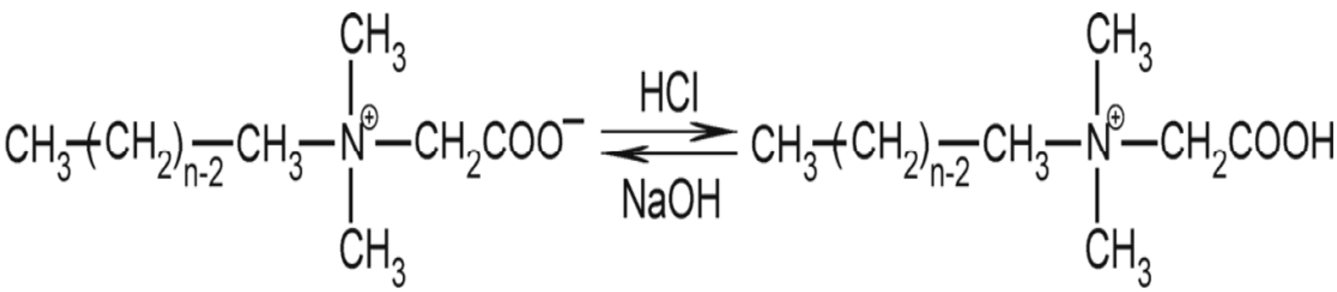
Amphoteric surfactants

(a) Natural soaps (alkylcarboxylates), Lipids





(b) Betaines



- These surfactants are very mild, making them particularly suited for use in personal care preparations over sensitive skins.
- They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water.
- Those surfactants may contain two charged groups of different sign.
- Whereas the positive charge is almost always ammonium but 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.

Cationic Surfactants:

In solution, the head of the cationic surfactant is positively charged. Cationic surfactants are quaternary ammonium compounds and they are mostly used for their disinfectant and preservative properties as they have good bactericidal properties. They are used on skin for cleansing wounds or burns. Mostly used cationic surfactants are cetrimide which has tetradecyl trimethyl ammonium bromide with minimum amount of dodecyl and hexadecyl compounds. Other cationic surfactants are benzalkonium chloride,cetylpyridinium chloride etc.

Cationic surfactants are less common in cleaners, and almost always absent from carpet products. Cationic have positively charged ends, which makes them ideal in antistatic formulas like fabric softeners and automobile “cheater waxes.” Also, cationic surfactants have antimicrobial characteristics, and they are found in hard-surface disinfectants and cleaners.

However, cationic surfactants have been shown to damage the mill-applied protectants on carpet, and are therefore strictly verboten in carpet products.

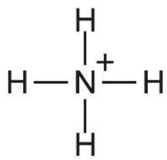
Formulas containing cationic surfactants cannot be mixed with those containing oppositely charged anionic surfactants. The molecules would interact with each other, producing a gooey mess that drops out of solution. When reading the ingredients list, look for the words “chloride” or “bromide” (as in alkylbenzene ammonium chloride) to identify cationics.

With these surfactants, the hydrophilic head is positively charged.

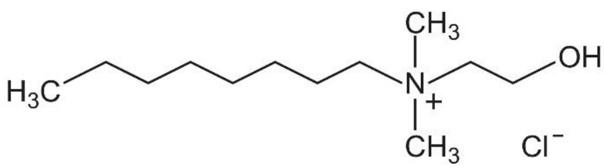
Although they are produced in much smaller quantities than the anionic, there are several types, each used for a specific purpose.

(a) Mono alkyl quaternary systems

The simplest quaternary system is the ammonium ion:



An alkyl quaternary nitrogen system has alkyl groups attached to the nitrogen atom. An example is:



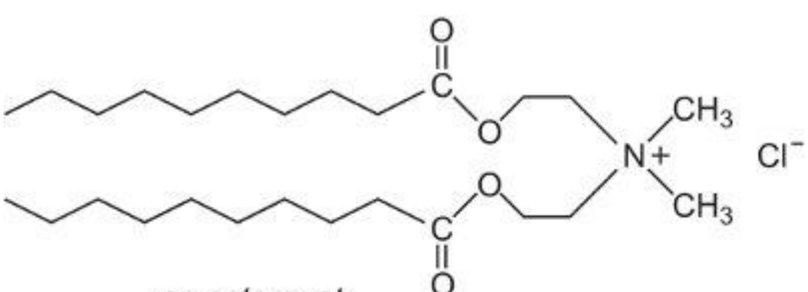
an alkyl quaternary system

They are used as fabric softeners with anionic surfactants, helping them to break down the interface between the dirt/stain and the water.

(b) Esterquats

The directly quaternised fatty acid surfactants described above have been replaced for laundry applications by more complicated structures in which there is an ester linkage between the alkyl chains and the quaternary head-group as these are more biodegradable and less toxic. They are known as esterquats.

An example is:



an esterquat

Esterquats give detergents their fabric softening qualities.

Mechanism of Action

Surfactants can work in three different ways:

Roll-up, Emulsification and Solubilisation.

(a) Roll-up mechanism: The surfactant lowers the oil/solution and fabric/solution interfacial tensions and in this way lifts the stain of the fabric.

(b)Emulsification: The surfactant lowers the oil solution interfacial tension and makes easy emulsification of the oil.

(c)Solubilisation: Through interaction with the micelles of a surfactant in a solvent (water), a substance spontaneously dissolves to form a stable and clear solution.

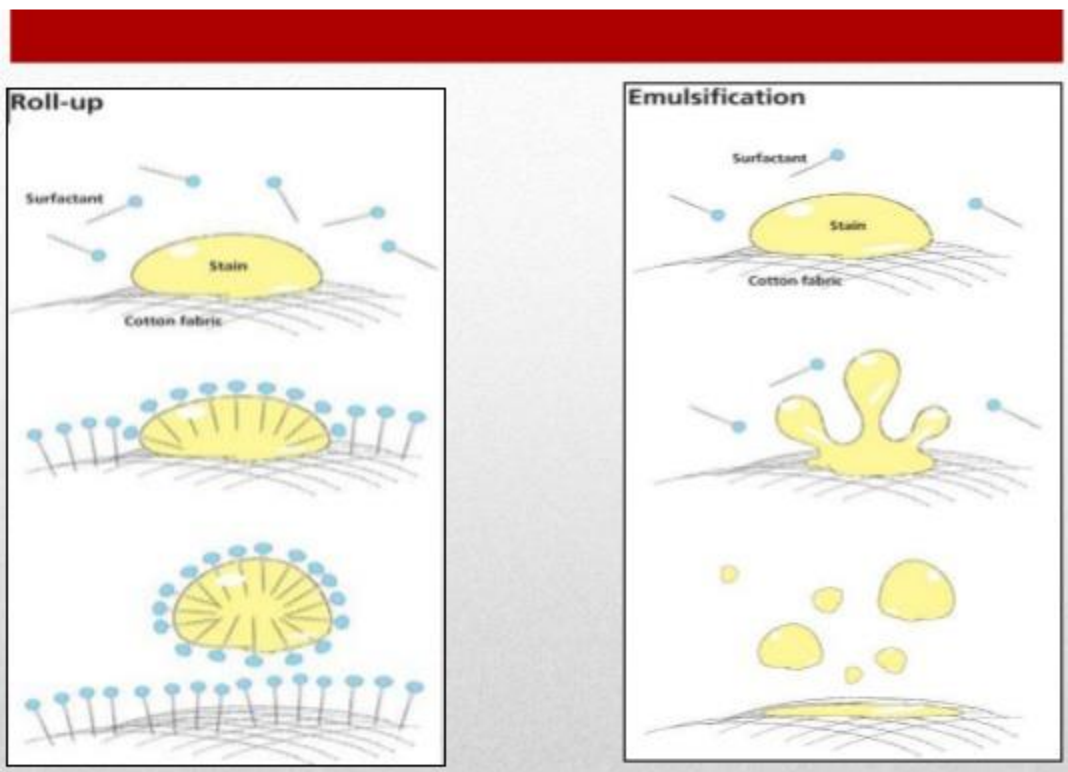
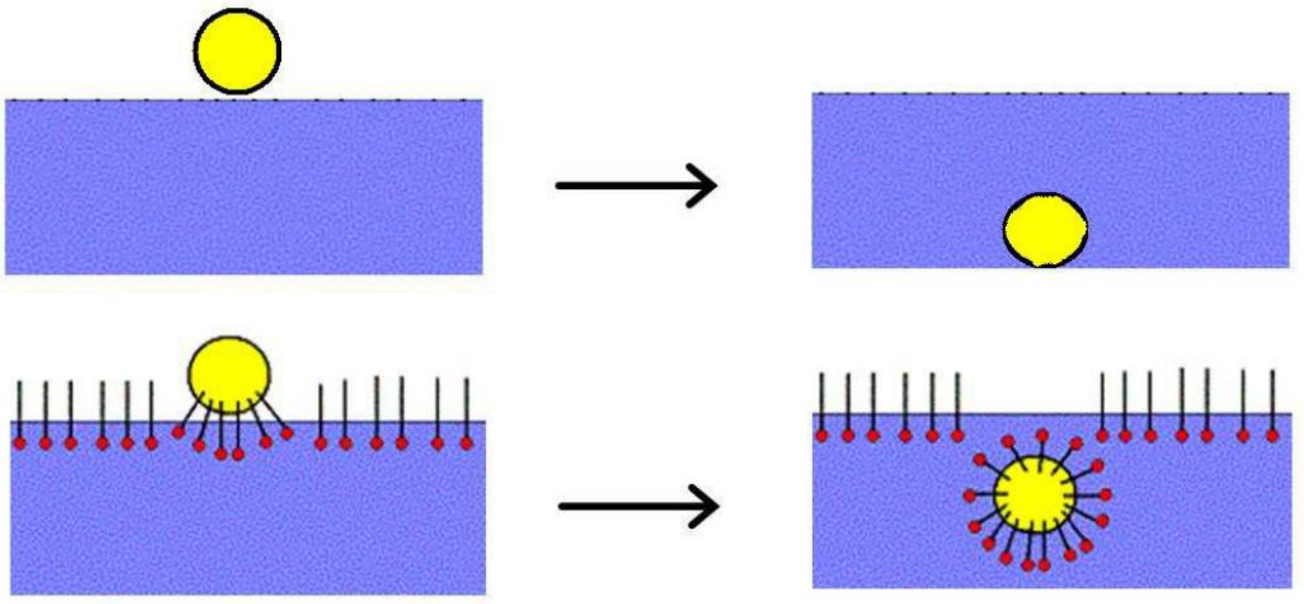


Fig. Surfactant mechanism of action in stain removal from fabric

The mechanism for solubilization



Solubilization is the process of incorporation of the solubilizate into or onto the micelles.

Additives in detergent

Additives	Function
Biological enzymes	to remove protein stains such as blood
Fragrances	to add fragrance to both the detergent and fabrics
Whitening agents	to convert stains into colourless substances
Suspension agents	to prevent the dirt particles removed from redepositing onto cleaned fabrics
Foam control agents	to control foaming in detergent
Builder	to enhance the cleaning efficiency of detergent by softening the water