Surfactants

- Surfactants are one of many different compounds that make up a detergent.
- They are added to remove dirt from skin, clothes and household articles particularly in kitchens and bathrooms.
- They are also used extensively in industry.

- The term surfactant comes from the words surface active agent.

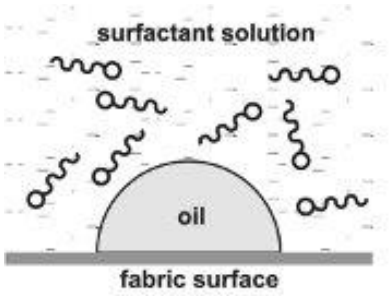
- **Surfactants function by breaking down the interface between water and oils and/or dirt.**

- **They also hold these oils and dirt in suspension, and so allow their removal.**

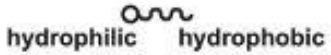
- **They are able to act in this way because they contain both a hydrophilic (water loving) group, such as an acid anion, (-CO_2^- or SO_3^-) and a hydrophobic (water hating) group, such as an alkyl chain.**

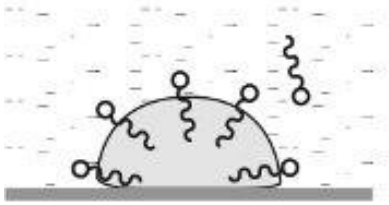
- **Molecules of water tend to congregate near the former and molecules of the water-insoluble material congregate near the latter.**

- Action of a surfactant

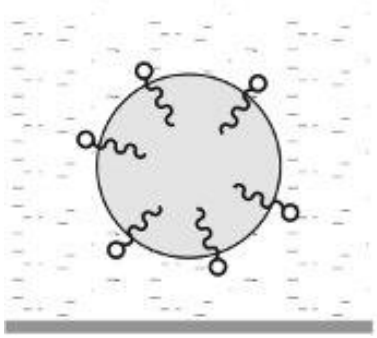


The surfactant contains molecules with hydrophilic and hydrophobic portions.



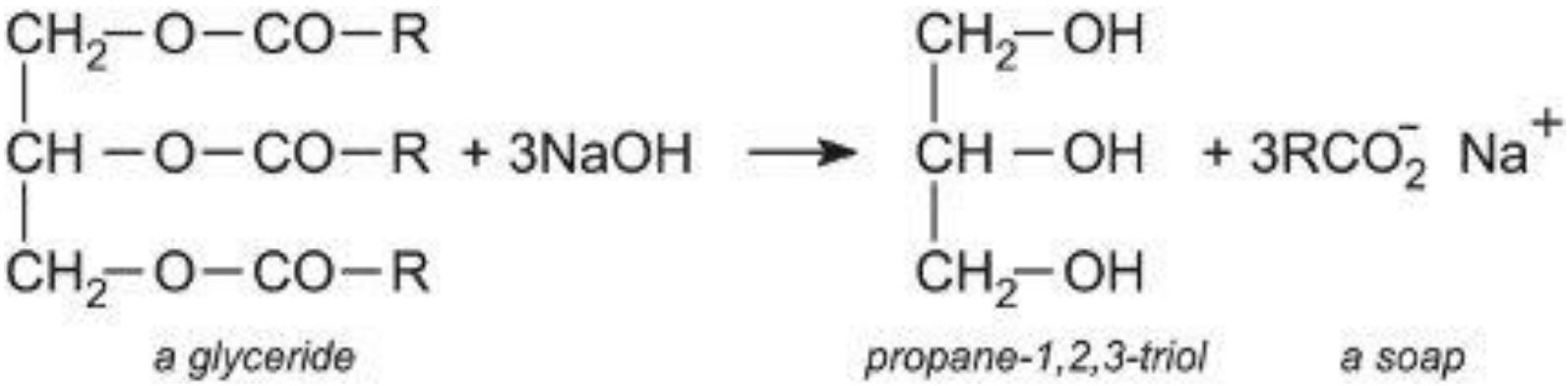


Surfactant molecules are absorbed into the surface of the oil and so remove it from the fabric surface.



The surfactant molecules remain surrounding the oil once it has been removed, so helping to prevent its redeposition onto the cleaned surface.

- **Soaps were the earliest surfactants and are obtained from fats which are known as glycerides because they are esters formed by the trihydric alcohol, propane-1,2,3-triol (glycerol), with long chain carboxylic acids (fatty acids).**
- **The glycerides are hydrolyzed by heating with sodium hydroxide solution to form soaps.**
- **The sodium salts of the acids, and propane-1,2,3-triol. The process is known as saponification.**



Manufacture

- **The glycerides used to make surfactants contain saturated and unsaturated carboxylic acids which have an even number of carbon atoms, generally within the range 12-20, for example, octadecanoic acid (stearic acid), $CH_3(CH_2)_{16}CO_2H$.**

- **Synthetic surfactants have one very important advantage over soaps. Because soaps form insoluble calcium and magnesium salts with the calcium and magnesium ions in hard water. However, this is avoided when using a synthetic surfactant. For example, in the anionic surfactants, the carboxylate group in soap is replaced by a sulfonate or sulfate group as the hydrophilic component.**
- **The corresponding calcium and magnesium salts are more soluble in water than the calcium and magnesium salts of carboxylic acids.**
- **Surfactants are classified based upon the nature of the hydrophilic "head-groups" as:**
- **anionics cationics**
- **nonionics**
- **amphoterics**

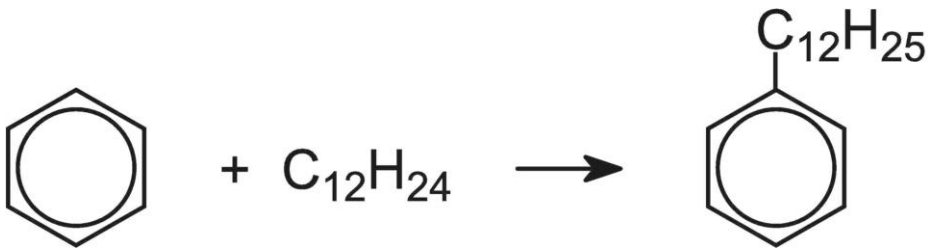
Anionic surfactants

- **In these surfactants the hydrophilic group is negatively charged.**
- **They are the most widely used type of surfactants for laundering, dishwashing liquids and shampoos.**
- **They are particularly good at keeping the dirt, once dislodged, away from fabrics.**
- **Four anionic surfactants are used:**
- **a) alkylbenzene sulfonates**
  b) alkyl sulfates
- **c) alkyl ether sulfates**
- **d) soaps**

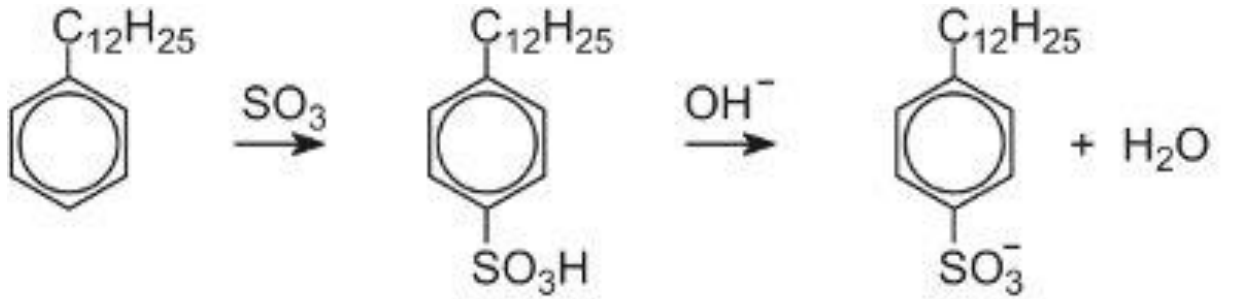
(a) Alkylbenzene sulfonates

The most common of the synthetic anionic surfactants are based on the straight chain alkylbenzene sulfonates.

Benzene, in slight excess, is mixed with an alkene or chloroalkane in the presence of an acid catalyst, usually a solid zeolite (ion exchange), aluminium chloride ($AlCl_3$) or hydrofluoric acid (HF), to produce an alkylbenzene (sometimes called detergent alkylate).

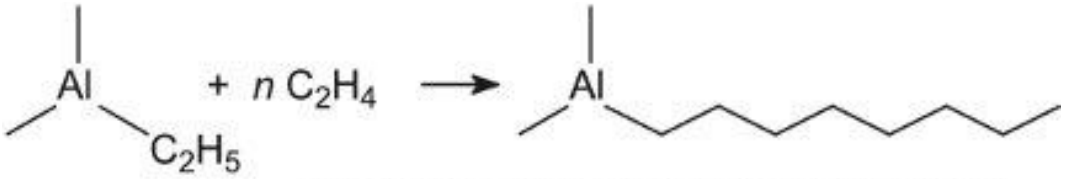


- **The alkylbenzene varies in average molecular mass, depending upon the starting materials and catalyst used and is often a mixture in which the length of the alkyl side chain varies between 10 and 14 carbon atoms.**
- **Historically these included branches in the side chains with the result that they biodegrade very slowly and lead to foaming in rivers and sewage plants. By law, in most countries today, the surfactant must have side chains which are not branched so they degrade more rapidly.**
- **The alkylate is sulfonated using an air/sulfur trioxide mixture, and the resulting sulfonic acid is then neutralised with an aqueous solution of sodium hydroxide, for example:**



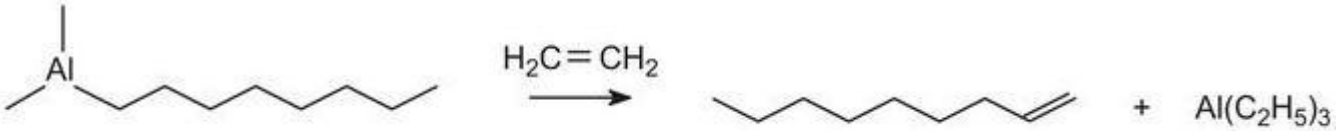
an alkylbenzene sulfonate

- **Straight chain alkenes for this process can be produced from ethene using a Ziegler catalyst (triethyl aluminium). Triethyl aluminium reacts with ethene at *ca* 400 K and 100 atm to form aluminium alkyls, for example:**



This reaction will take place at all three ethyl groups.
For clarity, only one is shown.

When heated in excess ethene, straight chain alkenes, with the double bond at the end of the chain (an a-alkene), are produced:

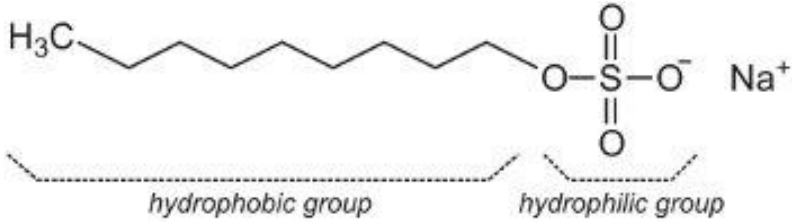


The mixture is then separated into fractions by distillation, the fraction of alkenes containing 10 to 14 carbon atoms being used to make the surfactants.

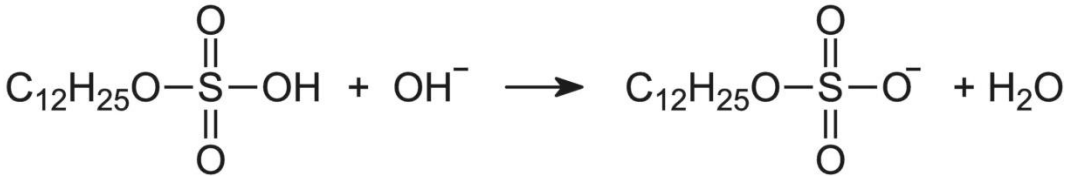
These are used together with other surfactants in powder and liquid laundry detergents such as Ariel, Daz, Persil and Surf.

(b) Alkyl sulfates

- **Many detergent products, particularly liquids, contain other synthetic anionic surfactants such as alkyl sulfates, esters of linear alcohols (C_{10}-C_{18}) and sulfuric acid. The alkyl sulfates are also used in personal care products such as toothpaste and are manufactured by treating the alcohol with sulfur trioxide. The product is then neutralised with aqueous sodium hydroxide solution to form a sodium alkyl sulfate:**



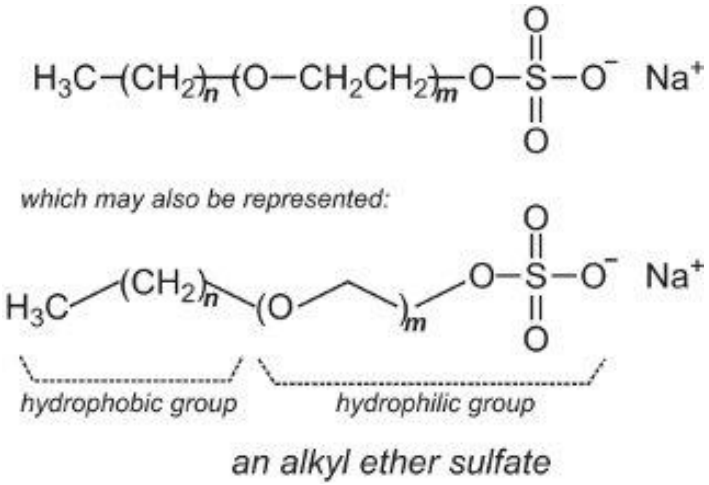
an alkyl sulfate



The alcohols are either produced from carboxylic acids obtained from oils, obtained naturally, for example from palm kernel oil or coconut oil, or alternatively from long-chain alkenes, manufactured from ethene.

(c) Alkyl ether sulfates

- **More widely used than simple alkyl sulfates are various types of sodium alkyl ether sulfates (SLES).**
- **Alkyl alcohol (from a synthetic or natural source and typically a blend based around dodecanol) is first ethoxylated with 1 to 3 molar equivalents of epoxyethane**
- **The product is then sulfated using sulfur trioxide and neutralized with alkali to form the alkyl ether sulfate:**

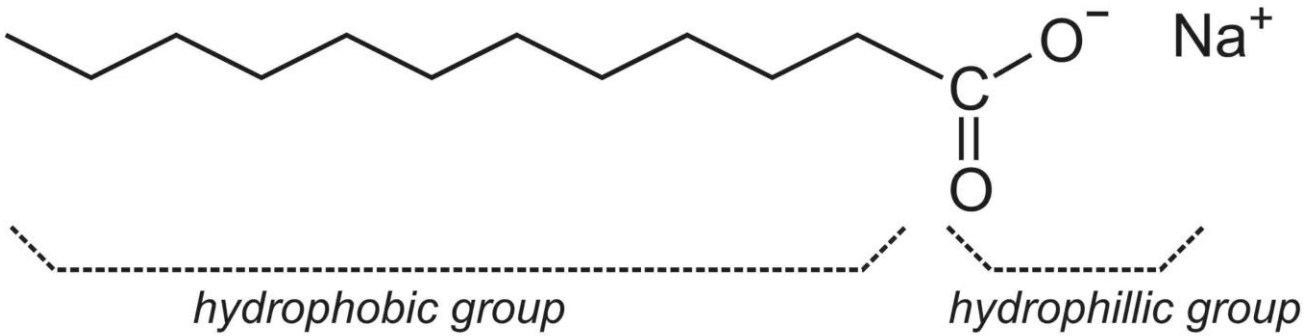


an alkyl ether sulfate

These materials are preferred by product formulators for many applications (dishwashing liquids, shower gels, shampoo, etc) because they are milder to the skin than alkyl sulfates. They also generate less foam which is an advantage in the formulation of laundry machine products.

(d) Soaps

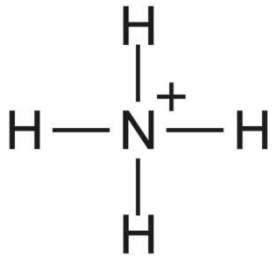
- Soaps are anionic detergents:



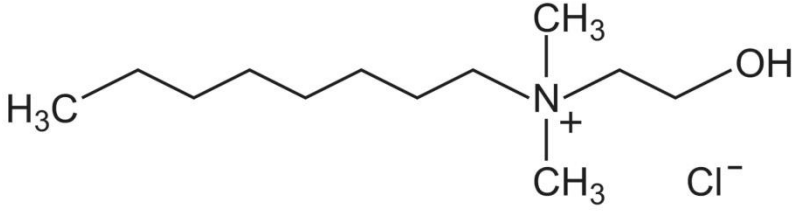
a soap

Cationic surfactants

- **With these surfactants, the hydrophilic head is positively charged.**
- **Although they are produced in much smaller quantities than the anionics.**
- **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:**

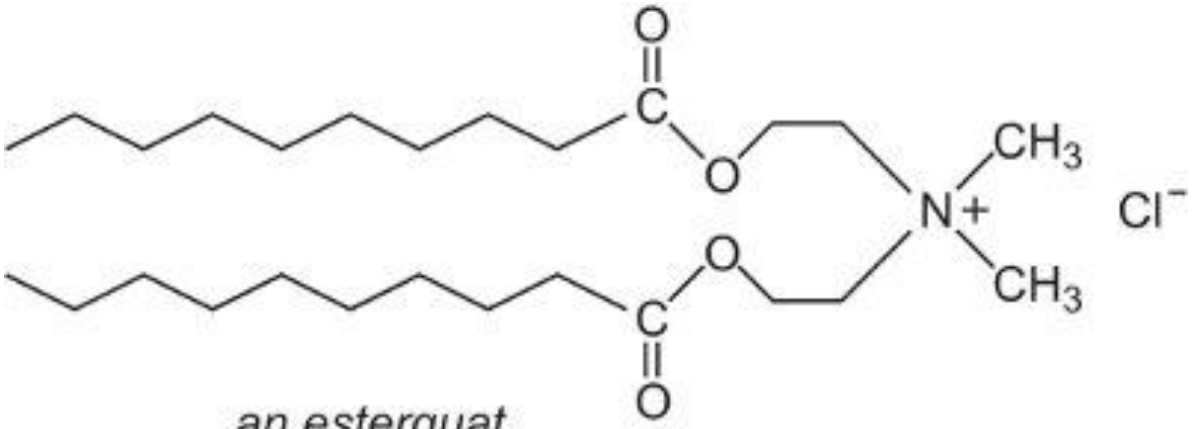


an alkyl quaternary system

- **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 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.**