Soaps and Detergents

Dr Ruchi Saxena
Associate Professor
Department of Chemistry
Nari Shiksha Niketan (P. G.)College
Mona Chandrawati Marg, Kaiser Bagh, Lucknow

Soaps and Detergents

One of the organic chemical reactions known to human beings since 2800 BC in ancient Babylonwas the preparation of soaps through a reaction called saponification.Natural soaps are sodium or potassium salts of fatty acids, originally made by boiling lard or other animal fat together with lye (NaOH) or potash (potassium hydroxide).

Soaps and synthetic detergents concentrate at the surface of the solution forming surface films and reduce the surface tension of the solution to remove the dirt by emulsifying are called surface active agents or **surfactants**.These surfactants or soaps are used for washing, bathing, and housekeeping. In industrial settings, they are used as thickeners, components of some lubricants, and precursors to catalysts.

Chemically soap is defined as a sodium and potassium salt of mixture of various naturally occurring higher fatty acids like stearic acid, palmitic acid and oleic acids. They are obtained by the hydrolysis of oils and fats with aqueous alkalis(NaOH/ KOH).Soaps have the general formula $(RCO_2^-)_nM^{n+}$ (Where R is an alkyl, M is a metal and n is the charge of the cation).

Classification of Soaps:

The classification of soaps is determined by the identity of the metal-M^{n+}.

1. Toilet Soap: M is Na or K, the soaps are called toilet soaps and are used for handwashingand bathing with KOH or NaOH
2. Shaving Soap: M is Na or K with KOH
3. Industrial Soap M is Li, the result is lithium soap (e.g., lithium stearate), which is used in high-performance lubricating grease

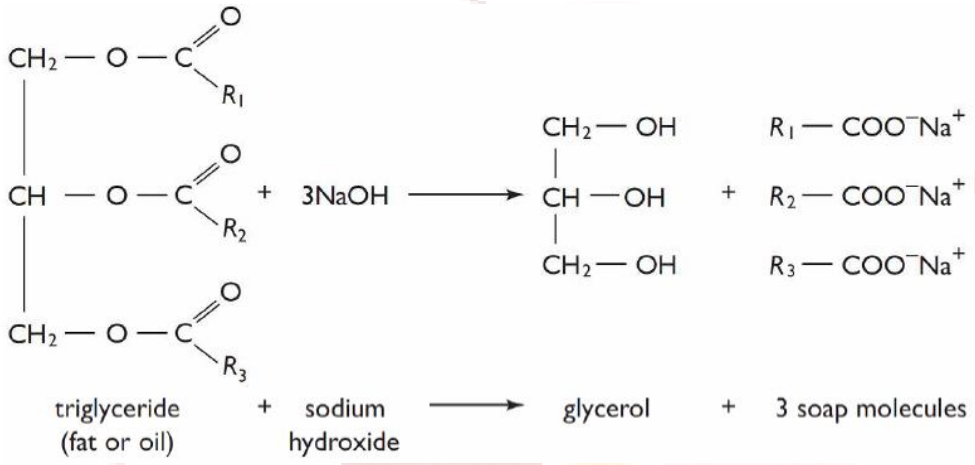
On the basis of the saponification reaction soaps are divided into:

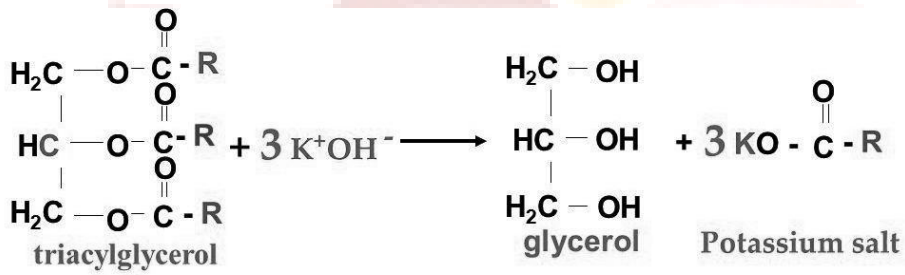
- **Hard Soap**: Hard soap is made using sodium hydroxide (NaOH) or lye. Hard soaps are especially good cleansers and used as toilet and laundry soaps
- **Soft Soap**: Soft soap is made using potassium hydroxide (KOH) in place of sodium hydroxide (NaOH). These soaps are characterized by weaker intermolecular forcesthus having lower melting points and also dissolving readilyin water.KOH is

used in making shaving soaps, liquid soaps, shampoos and cosmetics (e.g. Ethanolamine soaps).

Preparation of Soap and the Saponification Reaction

Saponification is the base catalysed hydrolysis of an ester whereby an alcohol and salt of the acid is formed. The process involves the reaction of a metallic alkali (base), such as NaOH or KOH with that of a fat or oil to form soap.





Traditionally soap is prepared by vegetable oils and animal fats which are chemically fatty esters in the form of triglycerides are added to the base (NaOH/KOH) which cleaves the ester bond releasing a fatty acid and glycerol. The soap is then separated out by precipitating it with a saturated solution of sodium chloride (NaCl).

Industrially,soap is manufacturedfrom tallow (fat from animals) or vegetable oil by heating with sodium hydroxide till the saponification reaction is completedand sodium chloride is added to precipitate the soap. The water layer is drawn off the top of the mixture and the glycerol is recovered using vacuum distillation.Sand or pumice may be added to produce a scouring soap. Other treatments may result in laundry, cosmetic, liquid soaps.

Mechanism:

Base Catalysed Hydrolysis of an fatty acid/Ester:

In aqueous solution, esters are subject to hydrolysis to the corresponding carboxylic acid and alcohol components.

Reaction

Esters Carboxylic acid Alcohol - Mechanism of the base hydrolysis of esters

Step 1:

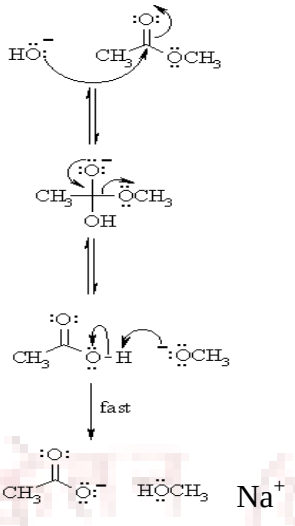
The nucleophiles i.e. the hydroxide attacks at the electrophilic C of the ester C=O, breaking the π bond and creating the tetrahedral intermediate compound . (Hybridization of C changes from sp^2 to sp^3)

Step 2:

The intermediate compound collapses, re-forming the C=O which results in the loss of the alkoxide ion RO^-(leaving group), leading to the formation of the carboxylic acid.

Step 3:

An acid / base reaction. A very fast reaction occurs where the equilibrium is attained by deprotonating the carboxylic acid by the base alkoxide, RO^- forming the alcohol and the carboxylate ion which combines with Na/K to form the soap.



The disadvantages of soaps are:

1.When soaps are used in hard water they combine with the calcium and magnesium ions present in hard water to form insoluble calcium and magnesium salts which generate curd like precipitates called scums which stick to the surface.

$$2CH_3(CH_2)_{16}COO^-Na^+(aq) + Mg^{2+}(aq) \rightarrow [CH_3(CH_2)_{16}COO]_2Mg(s) + 2Na^+(aq)$$

Sodium stearate — Magnesium ion — Insoluble magnesium stearate (scum) — Sodium ion

$$2CH_3(CH_2)_{16}COO^-Na^+(aq) + Ca^{2+}(aq) \rightarrow [CH_3(CH_2)_{16}COO]_2Ca(s) + 2Na^+(aq)$$

Sodium stearate — Calcium ion — Insoluble calcium stearate (scum) — Sodium ion

2.Soaps cannot be used in acidic solution because they precipitate the insoluble free fatty acids which adhere to the fabric and prevent the removal oil and grease.

$$R\text{-}COO\text{-}Na + H_2O \leftrightarrow R\text{-}COO^- + Na^+ + H_2O \leftrightarrow R\text{-}COOH + NaOH$$

The short- comings of the soap were overcome by synthesizing detergents which did not form precipitates in hard water and acids.Thus, their cleansing action is not affected.

$$2CH_3(CH_2)_{11}OSO_3^-Na^+(aq) + Ca^{2+}(aq) \longrightarrow$$
Sodium dodecyl sulphate — Calcium ion

$$[CH_3(CH_2)_{11}OSO_3^-]_2Ca^{2+}(aq) + 2Na^+(aq)$$
Soluble calcium dodecyl sulphate — Sodium ion

$$2CH_3(CH_2)_{11}OSO_3^-Na^+(aq) + Mg^{2+}(aq) \longrightarrow$$
Sodium dodecyl sulphate — Magnesium ion

$$[CH_3(CH_2)_{11}OSO_3^-]_2Mg^{2+}(aq) + 2Na^+(aq)$$
Soluble magnesium dodecyl sulphate — Sodium ion

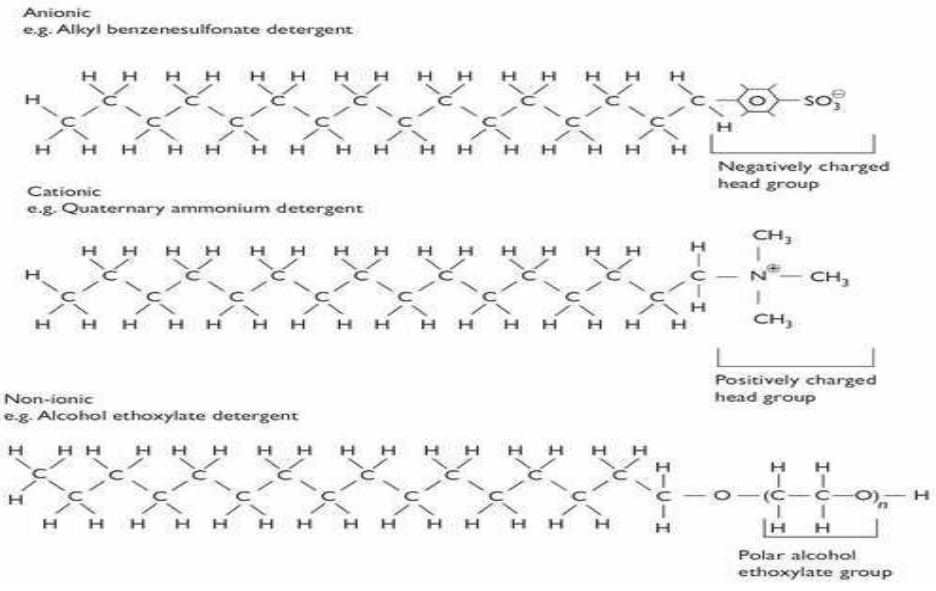
$$CH_3(CH_2)_{11}OSO_3^-Na^+(aq) + H^+(aq) \longrightarrow$$
Sodium dodecyl sulphate — Hydrogen ion

$$CH_3(CH_2)_{11}OSO_3^-H^+(aq) + Na^+(aq)$$
Soluble dodecyl sulphonic acid — Sodium ion

Synthetic detergents:.

The modern era saw the emergence of synthetic detergents to replace soaps as cleansing agents. Synthetic detergents are called the soap less soap and are unlike soap as they can be used satisfactorily even in hard water since they do not form curd like precipitate and also work in acidic solutions. "Detergent" (Latin-" detergere" means "away from", and "to wipe") is a sodium salt of long chain benzene sulphonic acid or a sodium salt of long chain alkyl hydrogen sulphate. However it is similar to soap as it consists a large non-ionic hydrocarbon chain that is oil soluble and an ionic endwhich may be a sulphonate (SO_3^- Na^+) or a sulphate (SO_4^- Na^+) group that is water-soluble.

Detergents are classified into three broad groupings, depending on the electrical charge of the surfactants.



1. Anionic detergents

Anionic detergents consist of a long hydrocarbon tail and a negatively charged head group. The 3 types of anionic detergents are:alkyl sulphonates, alkylbenzene sulfonates and alkyl phosphates where heads are benzenesulfonate or phosphate ions respectively.

Alkyl Sulphonates: The alkylanion is lipophilic and the sulfonate is hydrophilic-

$CH_3(CH_2)_nO(SO_2)O^-Na^+$ Commonly used in shampoos and cosmetics for example: sodium lauryl sulphate or sodium dodecyl sulphate (SDS), and sodium stearyl sulphate.

Alkylbenzene sulfonates: The alkylbenzene anion is lipophilic and the sulfonate is hydrophilic- $CH_3(CH_2)_n(C_6H_6)O(SO_2)O^-Na^+$ T**his is the most commonly used detergent in day today life, for example: linear alkyl benzene sulphonates (LAS) such as sodium dodecyl benzene sulphonate**

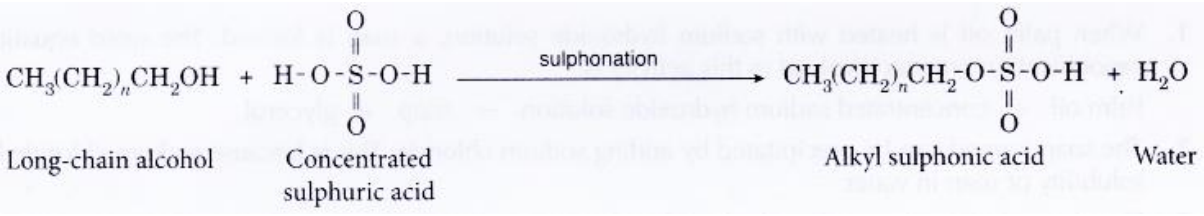
Synthesis

Long- chain hydrocarbon obtained from petroleum fractions is converted into an organic acid which is then neutralised with sodium hydroxide solution to produce a neutral salt called a detergent.

Sodium alkyl sulphate:

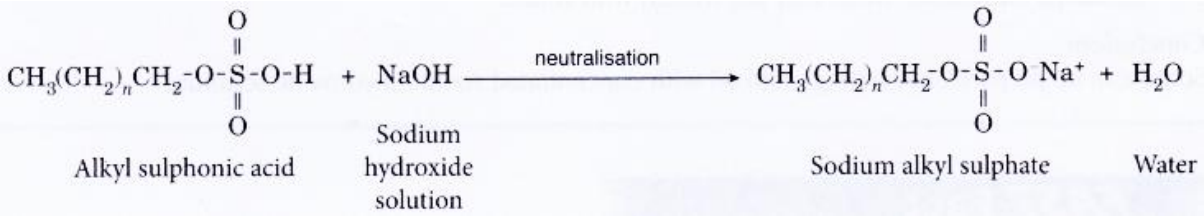
Step 1: Formation of an organic acid

A long-chain alcohol reacts with concentrated sulphuric acid to form alkyl sulphonic acid.



Step 2: Neutralisation

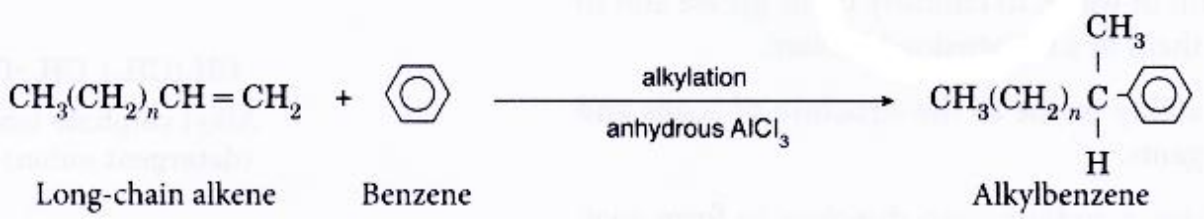
The resulting acid is then converted to a sodium salt by a reaction with sodium hydroxide.



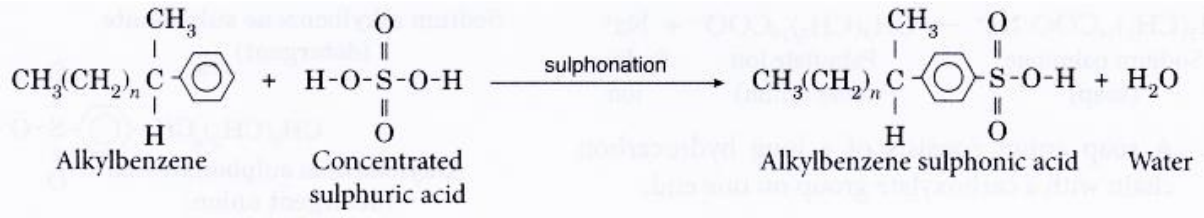
Sodium alkylbenzene sulphonate:

Step 1: Formation of an organic acid

A long-chain alkene reacts with benzene to form alkylbenzene.

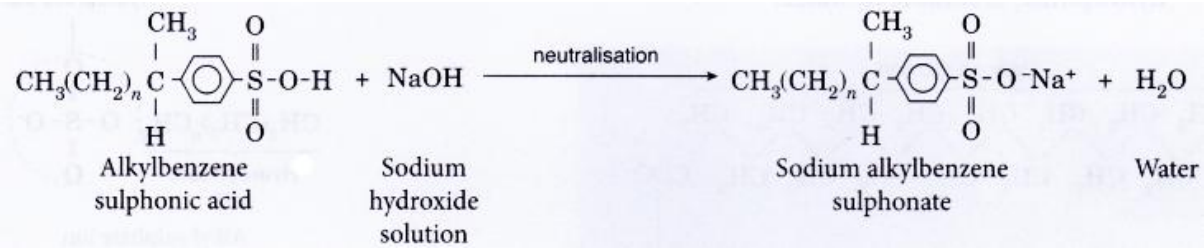


The alkylbenzene formed is then reacted with concentrated sulphuric acid to form alkylbenzene sulphonic acid.



Step 2: Neutralisation

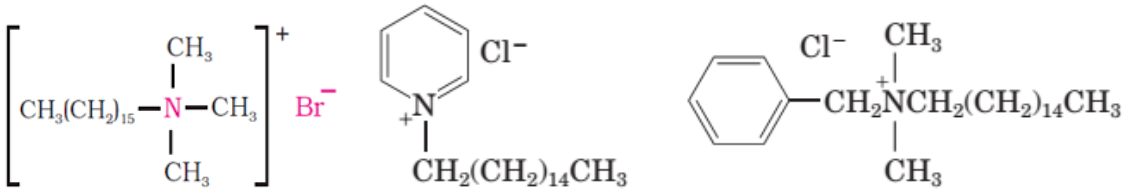
The alkylbenzene sulphonic acid is then converted to a sodium salt by a reaction with sodium hydroxide.



Detergents generally contain a number of additives. to enhance its cleaning efficiency.

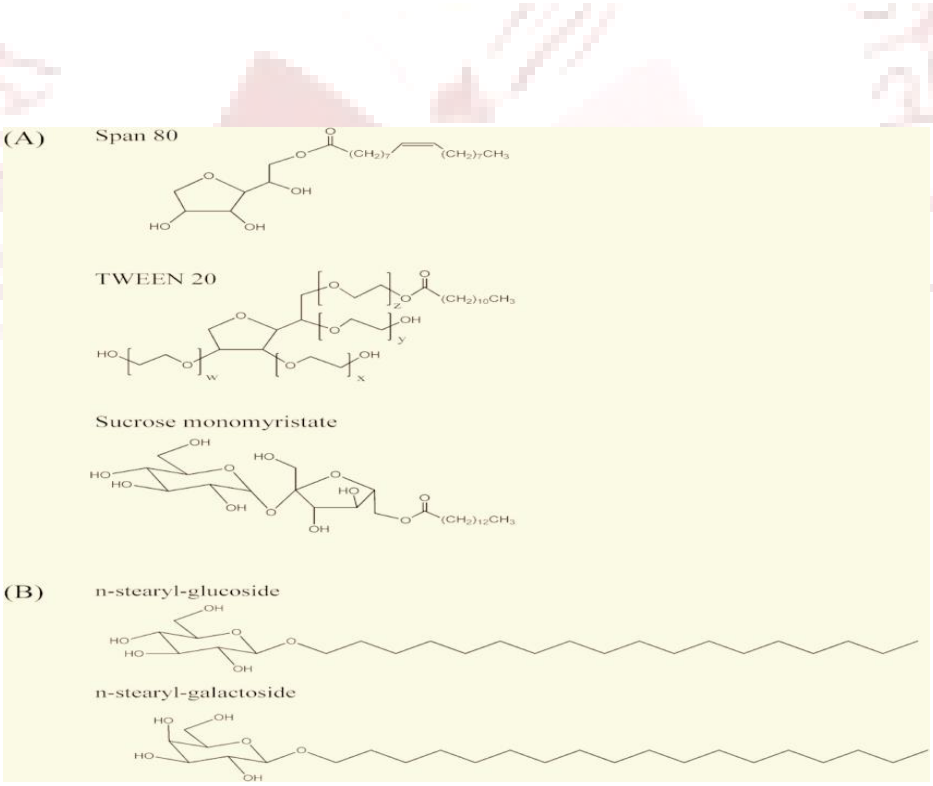
2.Cationic detergents

These detergents consist of a long hydrocarbon tail- hydrophilic component ,with a positively charged head, which is usually a quaternary ammonium group (alkyl ammonium group)- $CH_3(CH_2)_nN^+(CH_3)_3Cl^-$. They are called invert-soaps as their cleansing action is due to the positive ion which is the opposite to that of soap. They possess germicidal properties and are used in hospitals. The negative ion is often a halide (e.g. Br^- or Cl^-). Examples:



3.**Non-ionic and zwitter ionic detergents**

These are characterised by the presence of hydrophilic groups rather than charged heads. Zwitterionic detergents possess a net zero charge arising from the presence of equal numbers of +1 and −1 charged chemical groups- $CH_3(CH_2)_n\ O(CH_2CH_2O)_n(CH_2)_2OH$ (n= 5 to 50) They consist of a long hydrocarbon tail, and a polar alcohol ethoxylate poly-oxy-ethylene or a glycosides. They are used as detergents and as flocculating agents in applications such as dishwashing liquids, paints, adhesives, pesticides and cosmetics, as improved contact between polar and non-polar substances is required.Examples of the former include Tween,Span, Triton, Brij,octylthioglucoside and maltosides.



The Chemistry of the Cleansing action of Soap and Detergent:

All soaps and detergents contain a surfactant1 as their active ingredient. This is an ionic species consisting of a long, linear, non-polar 'tail' with a cationic or anionic 'head' and a counter ion. The tail is water insoluble and the head is water soluble - a difference in solubility

1.Makes the surfactant molecule a wetting agent and the tails migrate to align themselves with the solid:water interface, lowering the surface tension at that point so that it penetrates the fabric better.

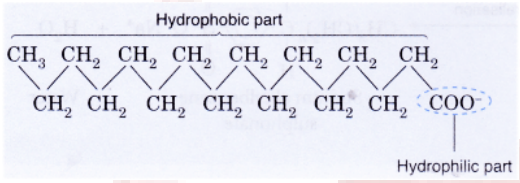
2.It allows the oily dirt particles to form an emulsion with the water: the tails of many surfactant molecules surround an oily dirt particle, forming a micelle with a drop of oil in the centre and the ionic heads of the surfactant molecules pointing outwards and hence keeping the micelle in the polar solution.

3.Repulsion between the droplets causes the droplets to be suspended in water, forming an emulsion. Thus, the droplets do not coagulate or redeposit on the cloth.

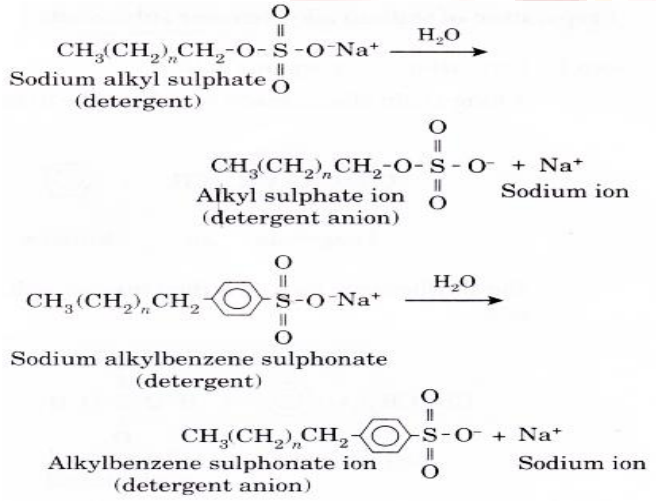
4.Rinsing washes away the droplets.

$R\text{-}COO\text{-}Na + H_2O \leftrightarrow R\text{-}COO^- + Na^+$

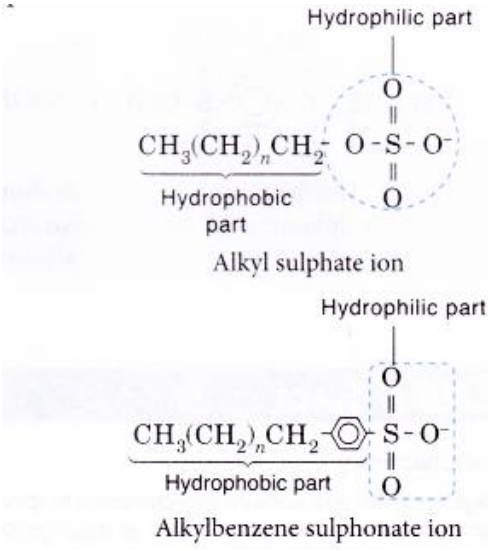
Ionization of soap



A soap anion consists of a long hydrocarbon chain with a carboxylate group on one end

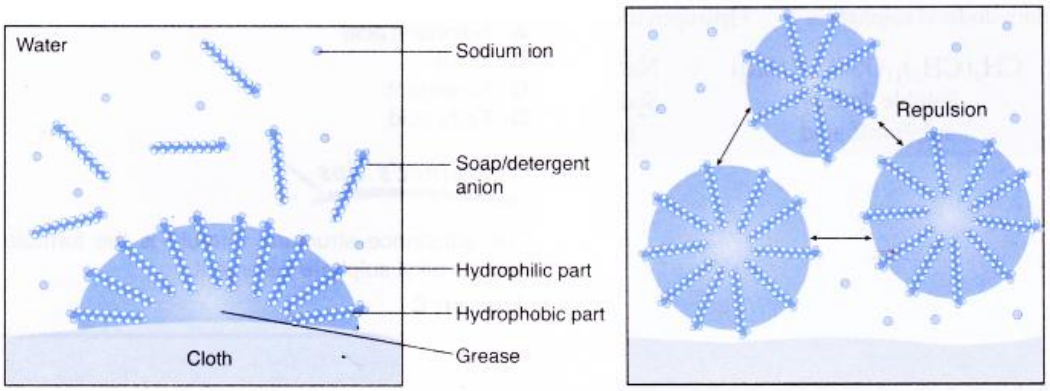


Ionization of detergents



Anion of a detergent consists of a hydrophobic part and a hydrophilic part

In aqueous solution, water molecules being polar in nature, surround the ions and not the hydrocarbon part of the molecule. When a soap or detergent is dissolved in water, the molecules associate together as clusters called **micelles**.



Environmental Concerns

The increase of phosphatesin water discharge, allows the algae to bloomand consumethe oxygen in the waters, killing fish and plants.Allowing a detergent to sit on any surface (such as skin or clothes) over time can cause an imbalance in pH and moisture content on the surface, damaging the fabric and injuring the skin.Soaps and detergents are 100% biodegradable, the micro-organisms present in the sewage completely oxidize it to CO_2 therefore it does not cause any water pollution.

References:

1. Willcox, Michael (2000). "Soap". In Hilda Butler (ed.). *Poucher's Perfumes, Cosmetics and Soaps* (10th ed.). Dordrecht: Kluwer Academic Publishers. p. 453. ISBN 978-0-7514-0479-1. Archived from the original on 2016-08-20. The earliest recorded evidence of the production of soap-like materials dates back to around 2800 BCE in ancient Babylon.
2. Helmenstine, Anne Marie, Ph.D. "How Saponification Makes Soap." ThoughtCo, Aug. 27, 2020, thoughtco.com/how-saponification-makes-soap-606153.
3. The Preparation of Sodium Alkyl SulfonatesR. M. Reed and H. V. Tartar
4. **Cite this:** *J. Am. Chem. Soc.* 1935, 57, 3, 570–571https://doi.org/10.1021/ja01306a055
5. David, K.A. (2000).The science of soaps and detergentsRetrieved on April 27, 2007 andSeptember 21, 2012 from the WorldWideWeb.http://www.scribd.com/doc/61766809/Soap-and-Detergent.[3]
6. Detergents. Retrieved on September 21,2012 from the World Wide Web.http://en.wikipedia.org/wiki/D
7. "synthesis of soap and detergent Ciara Maye A. Morales, John Ian V. Nacino, Dean Xavier C. New,Jason A. Ong, Mark Kenneth F. Ong and Leah Kristine C. Reyes Group 7 2B Medical Technology Organic Chemistry Laborator"

   https://www.scribd.com/doc/117421914/Synthesis-of-Soap-Detergent
8. Cold- Process Synthesis and Properties of Soaps Prepared from Different Triacylglycerol Sources Article in Nigerian Journal of Basic and Applied Sciences · January 2010 https://www.researchgate.net/publication/215484504
9. The Protein Man's Blog | A Discussion of Protein Research Detergents: Ionic, Non-Ionic, and Zwitterionic. What's the Difference? Posted by The Protein Man on Feb 8, 2017
10. UNIT-II: Fats and Oils. Dr. Sumanta Mondal _ Lecture Notes _Pharmaceutical
11. Organic Chemistry-II (BP 301T)_B.Pharm-III Sem https://www.researchgate.net/publication/326835500