Chapter 4: Soaps and detergents

I. Objectives:

In the end of this chapter the student will be able to:

- Understand the fundamental chemistry of Soaps and Detergents.
- Differentiate between Soaps and Detergents.
- Comprehend the mechanism of cleaning action.

II. Introduction:

Soaps and detergents are everyday cleaning agents essential for maintaining hygiene and cleanliness. They work by breaking down grease, dirt, and other impurities, making them easier to wash away with water. Soaps are made from natural ingredients such as animal fats or vegetable oils combined with an alkali through a process called saponification. Detergents, on the other hand, are synthetic surfactants produced from petrochemicals or renewable resources and are designed to perform effectively even in hard water.

These substances are used in various applications, from personal care to laundry and industrial cleaning. While soaps are biodegradable and environmentally friendly, detergents are formulated for specific cleaning needs, offering superior performance in a range of conditions. Together, they contribute significantly to public health and hygiene.

III. Soaps:

III.1. Definition:

Soap is a cleaning agent created through a chemical reaction called **saponification**, where fats or oils react with a strong alkali (typically sodium hydroxide for solid soaps or potassium hydroxide for liquid soaps) to produce salts of fatty acids. These salts have both hydrophilic (water-attracting) and hydrophobic (water-repelling) properties, allowing them to dissolve and remove oils, dirt, and grime when mixed with water.

III.2. Historical Background:

The origins of soap-making date back thousands of years. Evidence of soap-like substances has been found in ancient Babylonian records around 2800 BCE, where fats and ashes were mixed to create a rudimentary soap used for cleaning wool and textiles. Similarly, ancient Egyptians and Greeks developed early soap-making techniques, using animal fats and plant ash.

During the Middle Ages, soap-making became more sophisticated in Europe and the Middle East, with regions like Castile in Spain becoming famous for their high-quality olive oil-based soaps.

By the 18th and 19th centuries, soap production became industrialized, especially after chemists understood the saponification reaction more clearly. This allowed for large-scale soap production, and soap became increasingly accessible to the general public.

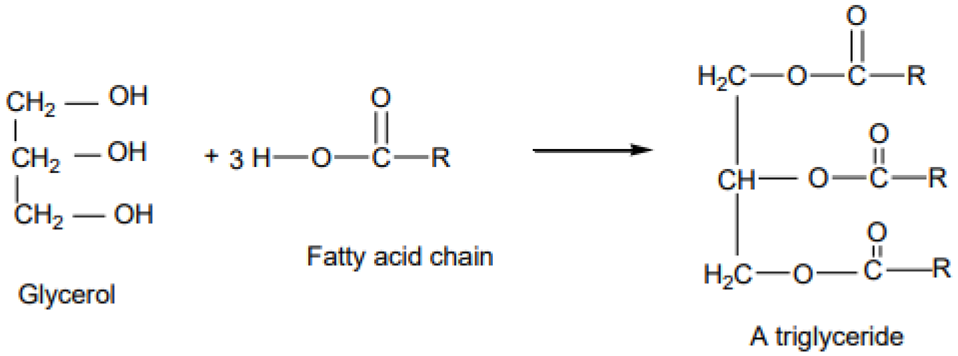
In modern times, advancements in chemistry and manufacturing processes have led to the creation of specialized soaps for various uses, such as antibacterial soaps, moisturizing bars, and eco-friendly options. Soap has evolved from a luxury item to an essential product for hygiene and health worldwide.

III.3. Chemistry of Soap:

Soap making involves the hydrolysis of a **triglyceride** (fat or oil) using an **alkaline** solution usually lye, chemical name **sodium hydroxide**. **Triglycerides** are typically **triesters** consisting of 3 long-chain aliphatic carboxylic acid chains appended to a single glycerol molecule (see Equation 1).

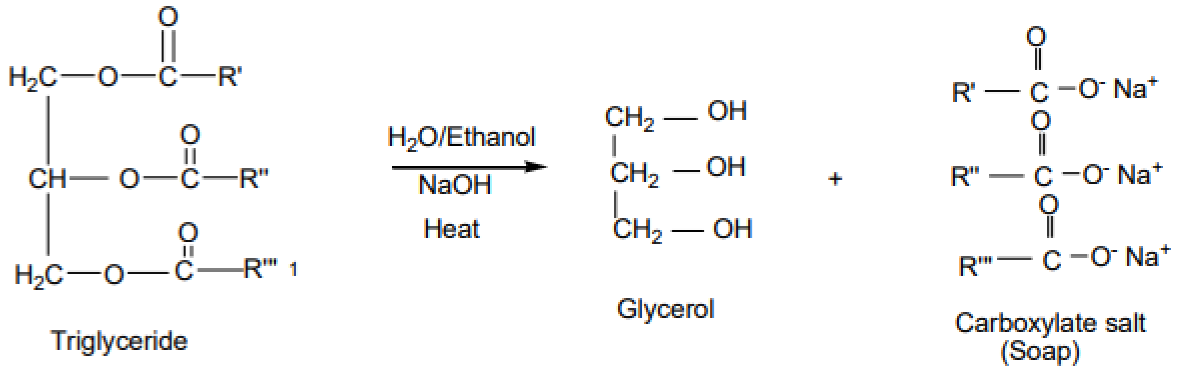
This process of making soap is known as **saponification**. The common procedure involves heating animal fat or vegetable oil in lye (sodium hydroxide), therefore **hydrolyzing** it into **carboxylate salts** (from the combination of carboxylic acid chains with the cations of the hydroxide compound) and glycerol.

Equation 1: Reaction between glycerol and fatty acids to form a triglyceride

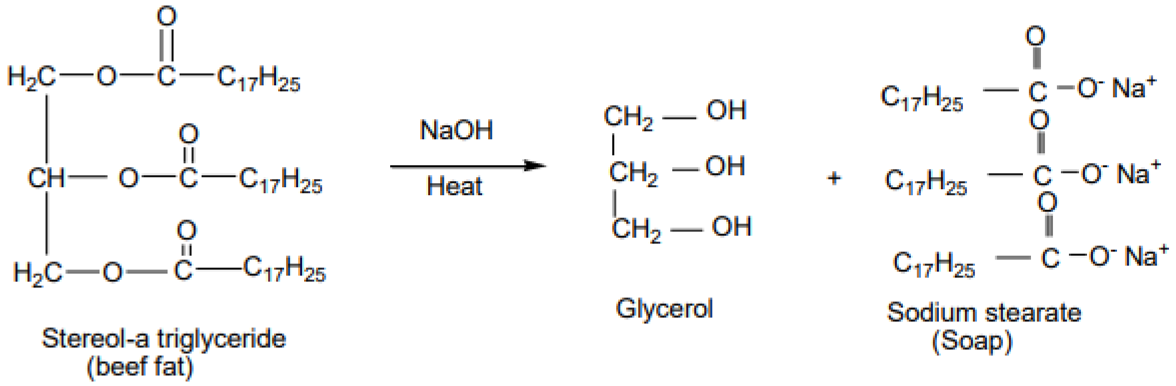


Equation 2 shows the general reaction between triglycerides and sodium hydroxide, while **Equation 3** shows an example of a specific reaction between beef fat and sodium hydroxide to form soap.

Equation 2: General model showing the hydrolysis of triglycerides with sodium hydroxide.

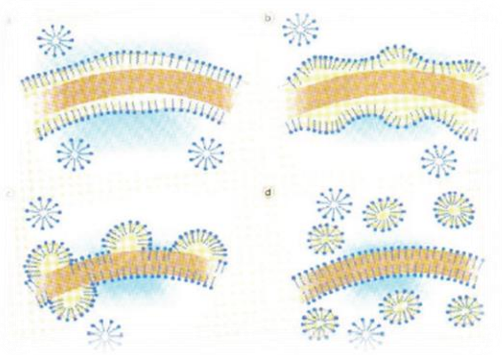
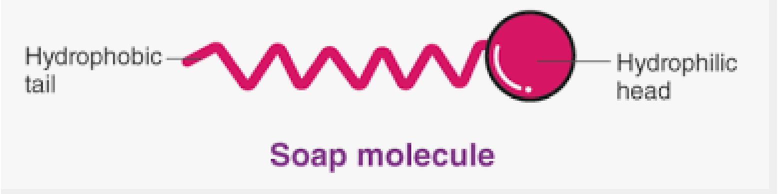
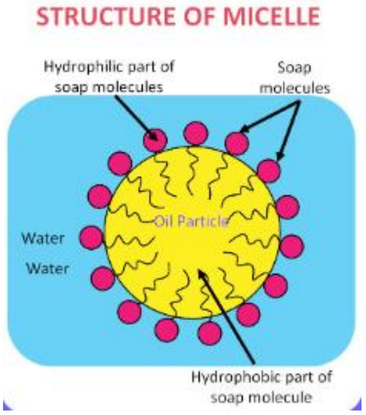


Equation 3: A specific model of hydrolysis of beef fat with sodium hydroxide.



III.4. Physical and chemical properties:

pH	- Soaps are mildly alkaline, typically with a pH of 9 to 10. - This alkalinity helps in breaking down oils and grease during cleaning.
Solubility	- Soaps dissolve in water, forming a colloidal solution. - Solubility decreases in hard water due to the formation of insoluble salts with calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions.
Color	- Pure soap is typically white or slightly off-white. - Additives such as dyes can give soaps various colors.
Odor	- Neutral in pure form. Fragrances are often added for a pleasant scent.
State and Form	- Solid Soaps: Commonly made with sodium salts (e.g., bar soaps). - Liquid Soaps: Typically, potassium salts (e.g., handwash or body wash).
Lather Formation	- Soaps produce a foam or lather when mixed with water, aiding in cleansing.

	- The amount of lather depends on the soap composition and water quality. 
Melting Point	The melting point of soaps, even when the fatty acid salt is unique and purified, remains quite ill-defined, varying between 200 °C and 250 °C. Sodium soaps (hard soaps) generally have higher melting points than potassium soaps (soft soaps).
Density	Less dense than water, which is why many bar soaps can float.
Amphiphilic Nature	Soap molecules have two distinct parts: Hydrophobic Tail: Long hydrocarbon chain repels water and interacts with oils/grease. Hydrophilic Head: Carboxylate group (-COO⁻) interacts with water.  This dual nature allows soap to act as a surfactant, emulsifying oils and dirt.
Micelle Formation	In water, soap molecules aggregate into spherical structures called micelles. The hydrophobic tails trap grease and oil inside the micelle, while the hydrophilic heads remain in contact with water, facilitating the removal of dirt. 

Emulsification	Soaps enable the mixing of oil and water by stabilizing oil droplets in water, forming an emulsion.

III.5. Soap manufacture:

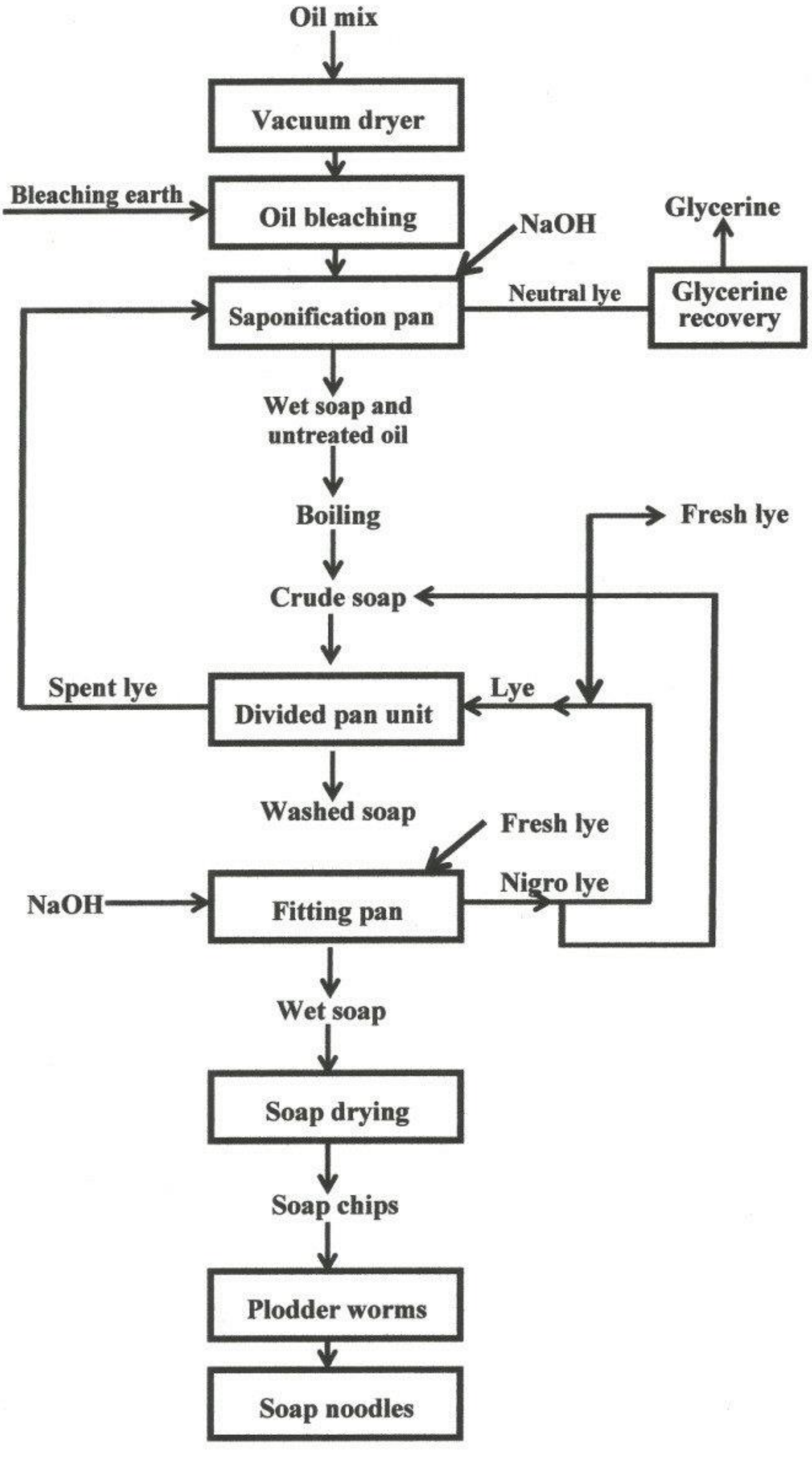
Two different ways are used to obtain soap. One is to hydrolyse the oil or fat by alkali, this is called as **saponifrcation (Batch process)** and other is **neutralization (Continous process)** to neutralize the directly the fatty acid by alkali.

III.5.1. Batch Soap Manufacturing Process:

In a batch process, soap is produced in distinct quantities, one "batch" at a time. This traditional method is still widely used, particularly for small-scale or specialty soap production.

- **Steps in the Batch Process:**

1. **Preparation of Raw Materials**: Fatty acids or triglycerides (such as animal fats or vegetable oils) and an alkali (commonly sodium hydroxide) are weighed and prepared.
2. **Saponification:** The raw materials are mixed in a large kettle or reactor and heated. The alkali reacts with the fats to produce soap and glycerin.
3. **Separation:** Once saponification is complete, the soap mixture is allowed to settle. Glycerin, being denser, separates at the bottom and is removed.
4. **Purification and Finishing:** The soap is washed to remove excess alkali and impurities. It is then dried, milled, and shaped into bars or other forms.


Oil mix
Vacuum dryer
Bleaching earth
Oil bleaching
NaOH
Glycerine
Saponification pan
Neutral lye
Glycerine recovery
Wet soap and untreated oil
Boiling
Fresh lye
Crude soap
Spent lye
Divided pan unit
Lye
Washed soap
Fresh lye
Nigro lye
NaOH
Fitting pan
Wet soap
Soap drying
Soap chips
Plodder worms
Soap noodles

Types of batch soap manufacturing process:

1- Cold Process :

- The cold process is a traditional soapmaking technique that requires minimal heating, making it ideal for artisanal and small-scale production. This method involves mixing oils or fats with a lye solution to trigger the saponification reaction, which creates soap and glycerin.
- This process is carried atcomparatively low temperature 3l3-318 K (40-45°C), coconut oil and tallow are used.
- The process is carried out in a cylindrical flat bottomed **crutcher.**
- The oil or oil mixture or fat is taken in the crutcher and heated to 313-3l8 K when a homogeneous liquid is formed.
- Calculated alkali is now slowly added to the pan with continuous stirring.
- Saponification starts and the reaction being exothermic does not require further heating.
- At this stage thick mass form and into that fillers, colours and perfumes are added with continuous stirring.
- This thick mass is now poured in cooling frames which is kept for 24 hrs to become hard material.
- Now it is ready for cutting into slabs and for packing.
- In this method also glycerine remains in soap and is lost

2- Semi boiled process :

- The principle used in this method as that used in cold process. The difference in the two methods is the temperature at which the process is carried out.
- Semi boiled carried out at about 353 K i.e. at 80°C.
- The oil or fat is taken in a big size pan which is kept in a furnace. The material is heated to about 353K when it becomes a homogeneous liquid to this calculated quantity of alkali is added with continuous stirring.
- Boiling is continued for few hours and fillers, colours, perfume are added at the end.The hot mass poured into frames and allowed to cool. This is then cut into bars, and packed.
- In this method also glycerine remains in soap and is lost.
- Good quality laundry and toilet soaps are manufactured by this or by fee next hot or full boiled process.

3- Boiled Process :

The boiled process (also known as the hot process) is a traditional and industrial soapmaking method that involves boiling fats or oils with an alkali in large kettles or reactors. This process is designed for efficient saponification and allows for the separation of impurities, resulting in high-quality soap.

a. Saponification: Fats or oils are mixed with an alkali solution (such as sodium hydroxide) in a large kettle and heated to boiling. This initiates the saponification reaction, where the fats are converted into soap and glycerin while the mixture is continuously stirred to ensure uniformity.

b. Graining and Washing: Once saponification is complete, salt is added to the boiling mixture to separate the soap from glycerin and other impurities. The soap rises to the surface, while the glycerin and impurities settle at the bottom and are removed. The soap is then washed with water or a dilute salt solution to remove excess alkali and ensure a pure product.

c. Finishing: The soap is boiled again to remove any remaining moisture and concentrated further. Additives such as fragrances, colors, or moisturizers are incorporated into the refined soap. Finally, the soap is poured into molds, allowed to cool and solidify, and then cut or shaped into bars for packaging and distribution.

III.5.2. Continuous Soap Manufacturing Process:

The continuous soap manufacturing process is an efficient and modern method for producing soap and glycerin from fats and oils. This method has largely replaced traditional batch processes due to its ability to produce large quantities of soap with consistent quality and reduced production times. Here’s an overview of the key stages involved in continuous soap manufacturing:

1. Raw Material Preparation

The process begins with the preparation of raw materials, which typically include vegetable oils or animal fats and a caustic soda solution (sodium hydroxide). These ingredients are carefully measured and mixed in precise proportions.

2. Saponification Reactor

The prepared oil blend and lye are continuously fed into a **saponification reactor**. This reactor operates at high temperatures (approximately 130–140°C) and under pressure, allowing the saponification reaction to occur rapidly. The reactor is designed to ensure thorough mixing and efficient contact between the reactants.

3. Continuous Mixing

Inside the reactor, the fats and alkali react to form soap and glycerin. The design often includes a static vessel with a special internal geometry that promotes optimal mixing and reaction rates. This setup allows for a continuous flow of materials, where newly introduced reactants mix with already formed soap.

4. Cooling and Separation

After the saponification reaction, the soap/lye mixture is cooled down to a temperature suitable for separation. This is typically done using a cooling system that prepares the mixture for static separation in a **static separator**. Here, the lighter soap phase rises above the denser lye phase, allowing for easy separation.

5. Washing

The separated soap is then washed to remove residual lye and impurities. This washing process often involves a rotary disc contactor where a washing solution (a mixture of caustic soda, brine, and water) is introduced to further purify the soap.

6. Neutralization

After washing, the soap may contain excess sodium hydroxide that needs to be neutralized. This is done by mixing it with a neutralizing agent, such as fatty acids from coconut oil, ensuring that the final product is safe for consumer use.

7. Drying

Once neutralized, the soap undergoes drying to reduce moisture content to acceptable levels (typically around 12% for toilet soaps). This is often accomplished using vacuum drying techniques that also help in cooling the soap.

8. Final Processing

The finished soap can then be cut into bars or other desired shapes, packaged, and prepared for distribution.

III.5.3. Comparaison between Batch and Continuous Soap manufacturing process:

Table 1: Comparison between Batch and Continuous Soap manufacturing process

	Batch process	**Continuous process**
Temperature, deg. C	150-175	230-250
Pressure, mPa (g)	5.2 - 10	4.1- 4.9 40 – 45 atm
Catalyst	Alkyl aryl Solfonic acid, Oxides of calicium, zinc and magnesium i,e. CaO, ZnO, MgO	Same catalyst or opitional
Acid used	sulfuric acid	/
Time, h	12-48	2-3
Operation equipment	batch	Continuous
Hydrolysis	85-98%	97 – 99%
Glycerol obtained	5 – 15%	10 – 25%
Advantages	Law temperature, adaptable to small scale	Small floor space, uniform product quality, high yield of acids, high glycerine concentration, automatic control.
Disadvantages	Catalyst handling, ling reaction time, need more than one stage for good yield.	High temperature and pressure, high cost and greater operating skill

III.6. Types of Soap:

Soap is classified based on its ingredients, preparation methods, and purposes. Here are the main types of soap:

III.6.1. Based on Composition

a. Hard Soap: Made with sodium salts of fatty acids.

b. Soft Soap: Made with potassium salts of fatty acids.

c. Transparent Soap: Produced by adding solvents like glycerin or alcohol during manufacturing. Clear in appearance and mild on the skin.

d. Superfatted Soap: Contains extra fats or oils for moisturizing. Ideal for sensitive or dry skin.

e. Medicated Soap: Enriched with antibacterial or therapeutic agents.

Examples: Soaps for acne, fungal infections, or antiseptic purposes.

f. Glycerin Soap: High glycerin content, making it moisturizing and mild. Often translucent and gentle on the skin.

III.6.2. Based on Usage

a. Toilet Soap: Made for personal hygiene and skin care. Refined and scented for everyday use.

b. Laundry Soap: Designed to clean fabrics. Stronger cleansing agents and sometimes contains additives for stain removal.

c. Kitchen Soap: Designed to remove grease and food residues.

Example: Dishwashing soaps.

d. Industrial Soap: Used in heavy industries for cleaning machinery, tools, or hands. Often abrasive or degreasing.

III.6.3. Based on Form

a. Bar Soap: Traditional and compact form.

Example: Solid bath soaps or detergent bars.

b. Liquid Soap: Made with potassium salts or surfactants.

Examples: Handwash, body wash, and shampoos.

c. Powdered Soap: Used for laundry or heavy cleaning. Dissolves in water to form a cleaning solution.

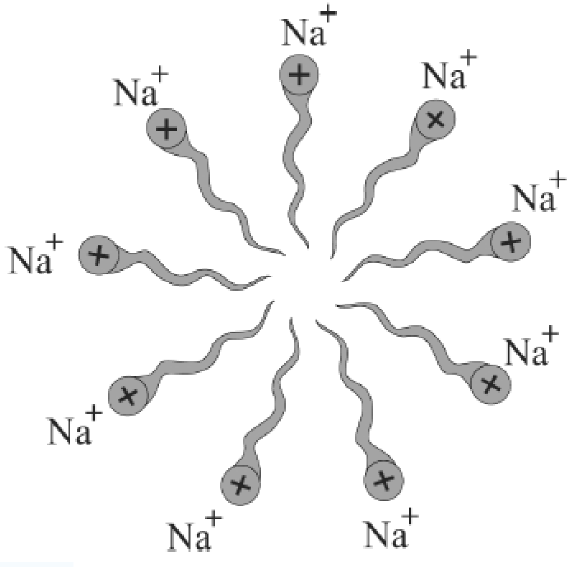
d. Foaming Soap: Pre-lathered when dispensed, used for handwashing.

III.7. Cleansing action of soap:

The molecules of soaps are smaller than the colloidal particles. These molecules associate and get the colloidal particle size range. This associate form is known as micelles. Soap dissociates in ions when dissolve in water being electrolyte in nature.

$$\underset{\textbf{Soap}}{C_{17}H_{35}COONa} \longrightarrow C_{17}H_{35}COO^- + Na^+$$

The long chain of hydrocarbon, which is hydrophobic is nature (insoluble in water) directed towards the centre while the head (hydrophylic water soluble part) is on the surface in control of water.



The initial concentration at which micellization begins is called critical micellization concentration (CMC). The formation of micelles starts above a definite temp, that is called kraft temperature (TK).

The cleansing action of soap is due to micelles. The micelles are absorbed by grease/dirt in cloth. Because both are non-polar. The polar head is directed towards water the rubbing by hands or mechanical stirring break the grease particles in to smaller droplets and form emulsion with water. As a result, the cloth gets free from dirt and grease. The droplets and washed away with water.

IV. Detergents:

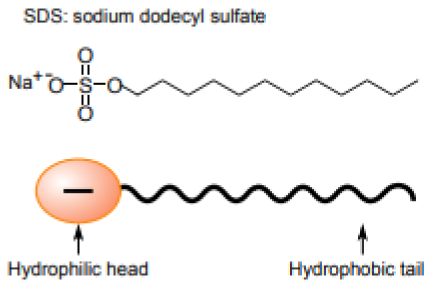
IV.1. definition:

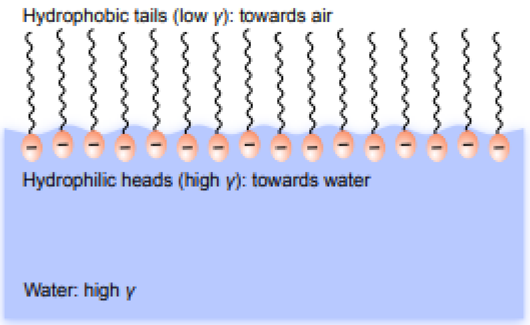
Detergents are chemicals that are effective surface and coming instead of soap in many of the uses and areas, in the home and even the factory are preferred in some uses because of its specification is better than soap in hand uses this. The chemical composition is different for the installation of soap, but the same mechanism by the soap, not adversely affected by hard minerals in the water.

The functional chemical components inside detergents are the **surfactants**, which remove oil from dishes and dirt from clothes. The term **surfactant** is short for surface active agent that "activates" the surface by reducing the surface / interfacial tension.

IV.2. Basic mechanism of surfactants:

A **surfactant** or **surface-active** agent is a compound that reduces the surface tension between two surfaces. Surfactant compounds are **amphiphilic** molecules, meaning they have two parts with different polarities: one **lipophilic (Hydrophobic)** and **non-polar** (which attracts oily substances: **e.g**. long hydrocarbon chains), and the other **hydrophilic** and polar (which is miscible in water: **e.g**. small polar or charged group, like -OH, -COOH, -CN, $-SO_3^-$, $-OSO_3^-$, etc.). This allows them to solubilize two immiscible phases; they interact with the non-polar part (that is, lipophilic and therefore hydrophobic) through their hydrophobic part, while interacting with the polar phase through their hydrophilic part.





IV.3. Classification of Surfactants

Synthetic surfactants are distinguished, which are further divided into two groups: ionic and non-ionic surfactants; and natural surfactants. There are various possible classifications of surfactants; they can be classified based on:

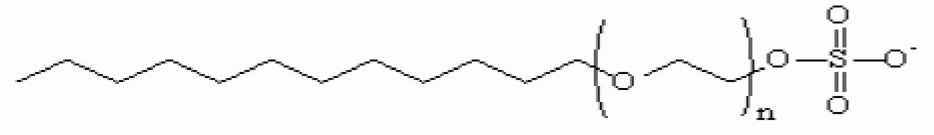
- The nature of their polar head (non-ionic; anionic; cationic; or amphoteric)
- The length of the lipophilic part, which allows surfactants to be classified as wetting agents (C_8-C_{10}); detergents (C_{12}-C_{16}); emulsifiers or softeners (C_{18}-C_{22}).
- Their origin: natural or synthetic.

IV.3.1. Ionic surfactants:

Ionic surfactants are ionized in aqueous solution; being very hydrophilic, they are further divided into three sub-groups: anionic, cationic, and amphoteric surfactants.

a)- Anionic Surfactants:

The hydrophilic part carries a negative charge. They are primarily used as detergents, wetting agents, and foaming agents.



Sodium laureth sulfate

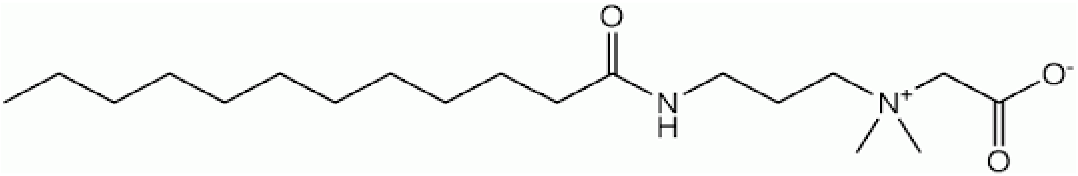
b)- Cationic Surfactants:

Cationic surfactants have a hydrophilic part that carries a positive charge. They are primarily used as antiseptics, conditioning agents, and keratin-binding agents (they adhere strongly to the surface of the skin, hair, and fur).

Fatty amine salt

c)- Amphoteric Surfactants:

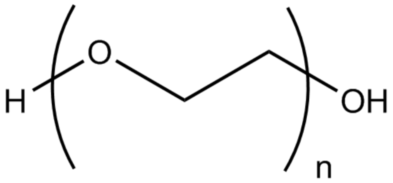
Amphoteric surfactants have a hydrophilic part that carries both a negative and a positive charge. The nature of the charge varies depending on the pH; they are cationic in acidic environments and anionic in alkaline environments. They possess both anionic and cationic properties, but to a lesser degree. Amphoteric surfactants are compatible (they can mix) with all types of surfactants when the pH of the medium is between 5 and 8.



Cocamidopropyl betaine

IV.3.2. Non-ionic surfactants :

Non-ionic surfactants are not ionizable; their lipophilic part consists of a fatty chain that can vary in length, and their hydrophilic part is also variable. As a result, this group includes substances that are very lipophilic as well as those that are very hydrophilic, along with all intermediates. Non-ionic surfactants are primarily used as emulsifiers, wetting agents, and solubilizers. They are not sensitive to changes in pH and are compatible with all types of surfactants.



Polyoxyethylene Glycol

IV.3.3. Natural Surfactants:

There are many examples of this type of surfactant, such as:

- **Cholesterol**: Of animal origin, used in cosmetics, it is part of the composition of liposomes.
- **Lecithin**: Of plant origin (glycerophospholipid); used in cosmetics as an emulsifying agent, it is also part of the composition of liposomes.
- **Saponins**: Of plant origin, used in cosmetics as foaming agents instead of synthetic surfactants.
- **Proteins**: Can come from various origins, primarily used as dispersion stabilizers.

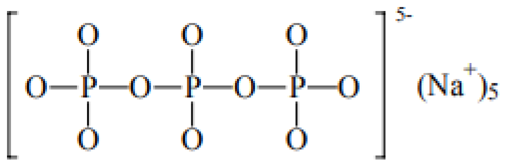
IV.4. The detergent manufacturing process:

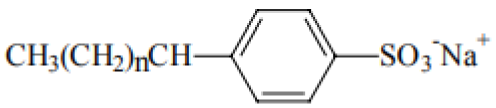
Detergents use a synthetic surfactant in place of the metal fatty acid salts used in soaps. They are made both in powder and liquid form, and sold as laundry powders, hard surface cleansers, dish washing liquids, fabric conditioners etc. Most detergents have soap in their mixture of ingredients, but it usually functions more as a foam depressant than as a surfactant.

IV.4.1. Detergent powder manufacture:

Step 1: Slurry making

The solid and liquid raw ingredients (**Table 2**) are dropped into a large tank known as a slurry mixer. As the ingredients are added the mixture heats up as a result of two exothermic reactions: the hydration of sodium tripolyphosphate and the reaction between caustic soda and linear alkylbenzenesulphonic acid. The mixture is then further heated to 85 °C and stirred until it forms a homogeneous slurry.





Step 2 : Spray drying

The slurry is deaerated in a vacuum chamber and then separated by an atomiser into finely divided droplets. These are sprayed into a column of air at 425 °C, where they dry instantaneously. The resultant powder is known as 'base powder', and its exact treatment from this point on depends on the product being made.

Step 3: Post dosing

Other ingredients are now added, and the air blown through the mixture in a fluidiser to mix them into a homogeneous powder. Typical ingredients are listed in **Table 3**.

Table 2: The ingredients of detergent base powder

Solids	
Ingredient	**Function**
Sodium tripolyphsophate (STP)	Water softener, pH buffer (to reduce alkalinity)
Sodium sulphate	Bulking and free-flowing agent
Soap noodles	Causes rapid foam collapse during rinsing.
Zeolite	Water softener (absorbs Ca^{2+} and Mg^{2+}) in contries where STP is not used; granulating agent for concentrated detergents
Sodium carboxymethyl cellulose	Increases the negative charge on cellulosic fibres such as cotton and rayon, causing them to repel dirt particles (which are positively charged)
Liquids	
Ingredient	**Function**
Linear alkylbenzene sulphonic acid (LAS)	Surfactant - the main active ingredient
Caustic soda solution	Neutralises the LAS
Coconut diethanolamide or a fatty alcohol ethoxylate	Nonionic detergent and foam former
Fluorescer	Absorbs UV light and emits blue light, causing ageing cotton to appear white rather than yellow
Water	Dissolves the various ingredients, causing them to mix better

Table 3: Typical post dosing ingredients

Ingredient	Function
Soda ash (anhydrous Na_2CO_3)	Keeps the pH at 9.0-9.5. This ensures optimum detergent function. Also forms insoluble carbonates with Ca and Mg, so acts as a water softener.
Bleach (usually sodium perborate - $NaBO_3$)	Bleaches stains without damaging colour-fast dyes. Sodium perborate breaks down at high temperatures to release H_2O_2, which functions this way.
Bleach activator (e.g. tetraacetylethylenediamine)	Catalyses sodium perborate breakdown at low temperatures.
Enzymes (e.g. alkaline protease)	Alkaline protease breaks down proteins in the alkaline conditions created by soda ash, helping to remove stains.
Colour and perfume	Create a more asthetically pleasing product.

IV.4.2. Liquid detergent manufacture:

Step 1: Soap premix manufacture

Liquid detergent contains soap as well as synthetic surfactants. This is usually made first as a premix, then other ingredients are blended into it. This step simply consists of neutralising fatty acids (rather than fats themselves) with either caustic soda (NaOH) or potassium hydroxide.

Step 2: Ingredient mixing

All ingredients except enzymes are added and mixed at high temperature. The ingredients used in liquid detergent manufacture are typically sodium tripolyphosphate, caustic soda, sulphonic acid, perfume and water. The functions of these ingredients have been covered above.

Step 3: Enzyme addition:

The mixture is cooled and milled, and the enzymes added in powder form.

IV.5. Advantages and Disadvantages of Synthetic Detergents:

The synthetic detergents are better than soaps in certain respects. Synthetic detergents can be used for washing of clothes even if the water is hard. Calcium and magnesium ions present in hard water make corresponding salts with detergent molecules. The calcium and magnesium salts of detergent molecules are soluble in water (unlike that formed by soap molecules).

However, detergent containing branched alkyl benzene sulphonate is not completely biodegradable. Soap is completely biodegradable. Therefore, excessive use of synthetic detergents is a cause of worry. The problem has been partly solved by using linear alkyl benzene sulphonate, which has better Chemistry in Everyday Life bio-degradability then the branched alkyl benzene sulphonates.

V. Environnemental implications :

Soap is designed to be used once and then flushed away, resulting in relatively low environmental impacts compared to other chemical processes. The main concerns are the safe transport and containment of raw materials and minimizing losses during manufacturing. The primary components of soap are oils, caustic substances, and perfumes are immiscible in water and can cause issues if spilled, although oils solidify at room temperature.

Transport is handled by trained carriers, and robust safety measures are in place, including bunded storage tanks to contain spills. Process areas within the plant are also bunded, with trade waste directed to an interception tank that monitors acidity and alkalinity. Spills can be isolated and neutralized before disposal.

Preventive measures are emphasized to identify potential problems early, allowing for reprocessing of off-spec products and minimizing waste. Continuous monitoring of key properties during manufacturing helps ensure product quality and reduce losses.

In recent years, there has been a shift towards biodegradable detergents, moving away from environmentally harmful options. The biodegradable detergents used in New Zealand meet Australian standards, with ingredients like sulphonic acid derived from linear alkylbenzene and non-ionic detergents made from ethoxylated long-chain alcohols. Sodium lauryl ether sulfates used in shampoos are also highly biodegradable. Phosphates in New Zealand detergent products are independently monitored and deemed not hazardous to the environment.