Soaps and Detergents

1

Soap

- Soap is a cleansing agent made from heating fats and oils with alkali like sodium or Potassium hydroxide.
- Oils and fats for soap are esters of fatty acids which react with alkalis such as sodium hydroxide to form glycerol and the sodium salt of the fatty acid.
- The fatty acids required for soap making can come from animal fats, grease, fish oils, and vegetable oils.

2

Fatty acids used to make soap

- Fatty acids are straight-chain monocarboxylic acids.
- The most common fatty acids range in size from 10-20 carbons and most often have an even number of carbon atoms including the carboxyl group carbon.
- The carbon-carbon bonds in saturated fatty acids are all single bonds, while unsaturated fatty acids have one or more carbon-carbon double bonds in their chains.
- One example of a saturated fatty acid is palmitic acid, $CH_3\text{-}(CH_2)_{14}\text{-}CO_2H$.

3

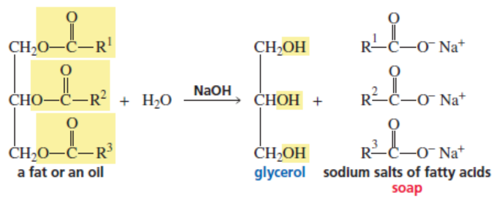
Fatty acids in Nature: Triglyceride

- Sodium palmitate $CH_3(CH_2)_{14}COO^- Na^+$ is the salt of palmitic acid $CH_3(CH_2)_{14}COOH$, a fatty acid with a 16 carbon chain.
- Fatty acids are seldom found as free molecules in nature but are most often a part of a larger molecule called a triglyceride.
- Triglycerides consist of a three-membered carbon chain (glycerol backbone) with a fatty acid bonded to each of the three carbon atoms in the glycerol backbone.

4

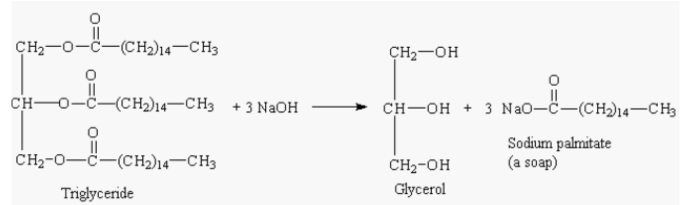
Synthesis of soap from Triglyceride

- The bond between the fatty acid and the glycerol backbone is referred to as an ester linkage.
- In the saponification process the ester linkage is broken to form glycerol and soap.



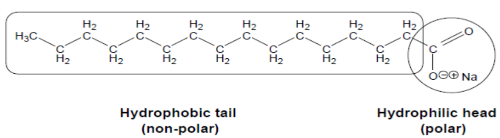
Synthesis of soap from Triglyceride

- For example, in the case of palmitic acid, the equation is as shown below:



Structure of soap

- Notice the particular structure of the soap molecule: it has a long nonpolar tail (the hydrocarbon chain of the fatty acid) and a highly polar end (the ionic group COO-). The non polar or hydrophobic tail can dissolve the grease and dirt whereas the polar or hydrophylic end is attracted to water molecules.



Structure of soap

- A large hydrocarbon portion of the molecule allows the soap to accomplish its special cleaning function.
- The inorganic ionic end of the salt remains soluble in the aqueous solution while the long hydrocarbon portion becomes embedded in the grease or dirt that you are trying to remove.

Soap action

- In the process of washing with soap, a particle of grease is surrounded by soap molecules.
- The hydrophobic ends attach to the grease particle, thus leaving the hydrophilic (COO-) end exposed to the water.
- This allows the grease particle to freely move around in the water and, therefore, be washed away.

9

More about soaps: Unsaturation

- The fats and oils used in making soap consist mainly of seven different fatty acids.
- If all of the carbon bonds in the fatty acid chain are single bonds, we have a saturated fatty acid.
- If any of the carbon bonds are double bonds, we have an unsaturated fatty acid.
- Unsaturated fats can be converted to saturated fats by adding hydrogen atoms at the locations of the double bonds.
- The amount of unsaturated fatty acids in the soap can affect the firmness of the soap.

10

More about soaps

- Potassium soaps are more soluble than sodium soaps and readily produce lather.
- Therefore, potassium soaps are used to make liquid soap and shaving cream.
- Soaps from highly saturated, solid fats, such as tallow, lard, or shortening, are hard.
- Saponification of an unsaturated oil, such as olive oil, gives a soft soap.

11

Soap Making

- Soap is produced industrially in four basic steps.
- **Step 1 - Saponification**
- A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and heated. The soap produced is the salt of a long chain carboxylic acid.

12

Soap Making

- **Step 2 - Glycerine removal**
- Glycerine is more valuable than soap, so most of it is removed.
- Some is left in the soap to help make it soft and smooth.
- Soap is not very soluble in salt water, whereas glycerine is, so salt is added to the wet soap causing it to separate out into soap and glycerine in salt water.

13

Soap Making

- **Step 3 - Soap purification**
- Any remaining sodium hydroxide is neutralised with a weak acid such as citric acid and two thirds of the remaining water removed.
- **Step 4 - Finishing**
- Additives such as preservatives, colour and perfume are added and mixed in with the soap and it is shaped into bars for sale.

14

More on Glycerine removal

- The glycerine is extracted from the soap with lye - a brine solution that is added to the soap at the saponification stage.
- Wet soap is soluble in weak brine, but separates out as the electrolyte concentration increases. Glycerine, on the other hand, is highly soluble in brine.
- Wet soap thus has quite a low electrolyte concentration and is about 30% water (which makes it easily pumpable at 70^{o}C).
- To remove the glycerine, more electrolyte is added, causing the the wet soap to separate into two layers: crude soap and a brine/glycerine mixture known as spent lye, neutral lye or sweet waters.

15

Soap Purification

- The water levels in soap must be reduced down to about 12%.
- This is done by heating the soap to about 125^{o}C under pressure (to prevent the water from boiling off while the soap is still in the pipes) and then spraying it into an evacuated chamber at 40 mm Hg

16

Laboratory Soap making procedure using Vegetable oil

1. Place 20g of vegetable oil (roughly 22-23 mL) in a 250 mL beaker and add 20 mL of ethanol. The ethanol and the oil will separate in two layers. Swirl the beaker well.
2. Add 25 mL of 5M NaOH solution. Mix well.
3. Heat gently on a hot plate. Stir with a glass rod until the solution turns into a paste. As soon as the consistency begins to turn pasty stir carefully to avoid foaming. The paste is made up of glycerol and soap (this step takes about thirty minutes).
4. When all the paste has formed, let the beaker cool on your bench top.

17

Laboratory Soap making procedure

5. After the paste is cold add 100 mL of saturated NaCl. Stir thoroughly, breaking the pieces of paste against the walls of the beaker. This is called the “salting out step” where the Na^+ and Cl^- ions bind to water molecules and help separate them from the soap.
6. *Optional:* add 3 or 4 drops of a scented essential oil (for example lavender or jasmine)
7. Use suction filtration to separate the soap from the rest. Wash the soap with 25 mL of ice water through the suction filter. Continue filtering for about ten minutes to help dry the soap.

18

Disadvantages of Soap

- Although soaps are excellent cleansers in soft water, they are ineffective in hard-water conditions.
- Hard water contains aqueous salts of magnesium, calcium, and iron.
- When soap is used in hard water, the insoluble calcium salts of the fatty acids and other precipitates are deposited as curds.
- This precipitate is commonly referred to as bathtub ring or scale.

19

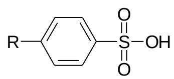
Disadvantages of Soap

- Soon after World War II the soap industry began to develop detergents as a way to deal with the dual problems of
- 1) competing with the food and feed industries for a limited supply of natural fats and oils, and
- 2) poor cleaning performance in areas with hard waters

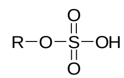
20

Detergents

- "Detergent" comes from the Latin *detergere* which means "to wipe off."
- detergents are salts of sulfonic acids though some have been made from alkyl sulphonates.
- The latter ones do not have a benzene ring.



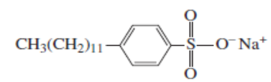
Benzene Sulphonic Acid



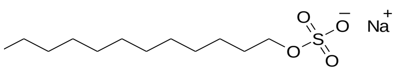
Alkyl Sulphate

Detergents

- Because the polar head of a detergent is negatively charged, it is called an *anionic surfactant.*
- This is the type of detergent used for cleaning.
- Typical structures of detergents are shown below:



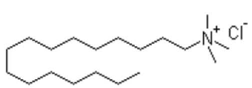
an anionic surfactant
a detergent



Sodium lauryl sulphate
(Sodium dodecyl sulphate)

Detergents

- *Cationic surfactants are used* widely as fabric softeners and hair conditioners.
- Contemporary fabric softeners are based on quaternary ammonium salts with one or two long alkyl chains



trimethylhexadecyl
ammonium chloride
(cationic)

THE DETERGENT MANUFACTURING PROCESS: Solids

Step 1 - Slurry making

- The solid and liquid raw ingredients (**Table 1**) 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.

Ingredients of a typical detergent

Ingredient	Function
Sodium tripolyphosphate (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).

25

THE DETERGENT MANUFACTURING PROCESS: Solids

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 2**.

26

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.

27

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 neutralizing fatty acids (rather than fats themselves) with either caustic soda (NaOH) or potassium hydroxide.

28

Liquid detergent manufacture

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 has been covered above.

Step 3 - Enzyme addition

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

Biodegradability of Detergents

- After the initial introduction of detergents into the marketplace, it was discovered that straight-chain alkyl groups are biodegradable, whereas branched-chain alkyl groups are not.
- To prevent non-biodegradable detergents from polluting rivers and lakes, detergents should have straight-chain alkyl groups

Advantages of phosphate builders

- The builder in detergents serves to tie up polyvalent cations such as calcium and magnesium ions, which otherwise interfere the surfactant.
- The builder is particularly necessary in hard waters . Without builders, manufacturers would have to add more surfactants, which are relatively more expensive.

Advantages of phosphate builders

- Phosphates (compounds with phosphorus, oxygen and sometimes hydrogen) are excellent builders, and are often used as either sodium tripolyphosphate (dry detergents) or sodium/potassium phosphates (liquid detergents).
- These phosphates are capable of tying up calcium, magnesium, iron and manganese ions, thereby improving overall washing performance.
- Phosphates also help peptize and suspend certain types of particulate matter, and aid in killing germs.

Problem with phosphate builders

- Often times phosphates are used as builders which causes rather serious environmental problems.
- Detergents containing phosphates end up in wastewater where they cause excessive growth of algae and other aquatic plants.
- When those die, bacteria in the dead matter consume oxygen and less oxygen is available for fish and other aquatic life.

33

Current solution of algae build-up caused by phosphate builders

- The *Phosphorus Concentration Regulations* set out the allowable levels of concentrations of phosphorus, by percentage, in any laundry detergent, and prescribes the approved methods of determining those concentrations.
- The Regulations limit the concentration of phosphorus in laundry detergents to 5% by weight expressed as phosphorus pentoxide or 2.2% by weight expressed as elemental phosphorus.

34