K.T.S.P. Mandal's

Hutatma Rajguru Mahavidyalaya, Rajgurunagar

Department of Chemistry

T.Y.B.Sc. Sem-V

Industrial chemistry paper CH-505

Associate Prof. Kolekar S.S.

As per new revised choicebased credit system syllabus w.e.f. June 2021

Soap And Detergents

Meaning of the Terms Related to Detergents, Classification of Surfactants, Raw materials used for Detergents

Cleaning action of Detergent, Cleaning action of soap , Comparsion of soap and detergent Advantages of Detergents

Meaning of the Terms Related to Detergents

1. Detergent and Surfactants

A detergent may be regarded as a chemical formulation, which essential consists of surfaceactive agents (or surfactants) and subsidiary constituents, such as fillers, builders, boosters etc. The detergent may be in the form of solid, liquid or powder. The most important advantages of the synthetic detergents is better wetting and cleaning action and no by hard consumption because of higher solubility of their Ca^{2+} and Mg^{2+} ions.

Surfactants are nothing but the surface active agents. These are the most important ingredient of synthetic products. When dissolved in water or dispersed in a liquid it cleans the surface by removing oil, in which dust particles are dispersed. The cleaning action of a surfactant depends upon its surface activity. It is a property which decrease the surface tension at the boundary surface between two phases. Thus, **those substances that lower the surface tension of water are called surfactants**. Surfactants are the organic compounds in which two dissimilar groups: water soluble and water insoluble are present within the molecule, e.g. sodium lauryl sulphate, sodium stearyl sulphate, sodium aryl sulphonates linear alkyl benzene sulphonate (LAS), amide sulphonates etc.

2. Emulsion and Emulsifying agents

Emulsion refers to any dispersion of one liquid in another. When two immiscible liquids (e. g. water and oil) are shaked together, the oily liquid is dispersed in fine droplet but the emulsion is not stable. The liquids separate into two layers because of coalescence of the fine droplets into bigger ones and then ultimately form a separate layer.

Emulsifying agents (emulsifiers) are the agents that lower the interfacial surface tension so that the emulsion is easily formed and also stabilise the emulsion by protecting the dispersed fine droplets of oil by forming a layer around them. The layer is formed by

solubilizing the non-polar part of the emulsifying agent in oil drop, while the polar group remains in water. Foaming is enhanced due to the lowering of water/air interfacial surface tension due to adsorption of emulsifying agent (surfactant) at the interface.

A. Wetting and Non-wetting

Wetting means the spreading of liquid on a surface with case and this is attributed a very small contact angle (zero or close to zero) between the liquid and the big surface, so that the liquid spreads over the solid surface easily. The wetting action generally, accomplished by the use of surfactant additives which lowers the interfacial surface tension.

In case of non-wetting the contact angle between the liquid and the solid surface greater than 90^{o} and hence the liquid tends to ball up and run off the solid surface.

Wetting agents consists of polar non polar type molecules (i.e with amphipathic structure). The polar porsion of the molecule may be one of the functional groups of organic chemistry containing oxygen (e.g. as in carboxylic acids, esters, ethers or alcohol), Sulphur (e. g. as in sulphonic acids, their esters or sulphates) or even phosphorus, nitrogen or halogens, the groups may or may not be ionic. The non-polar portion is hydrocarbon chain (aliphatic or aromatic).

4. Hydrophobic and Hydrophilic nature

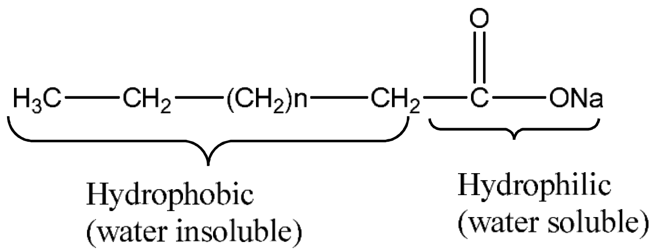
Hydrophobic means water hating or water disliking or water repelling substances which are insoluble in water and hence repel water. In hydrophobic sols, there is no affinity between the particles water. These sols are less stable as compared to the hydrophilic sols.

Hydrophilic means "water-loving' or 'water liking substances. In hydrophilic colloids, there is an interaction between the colloidal particles and water. Water combine with particles. The hydrophilic sols are more stable than the hydrophobic sols.

Functional groups which have tendency to bind water are hydrophilic in nature. For example, the-O-H groups in hydroxides and in polysuccharides (sugars), the -COOH and $–NH_2$ groups in proteins are hydrophilic. These substances are **water-soluble** as they contain the water solubilizing groups.

5. Amphipathic structures

If a molecule contains two dissimilar structural groups e.g. water soluble and water insoluble, such a molecule is known to have **amphipathic structure.** Common compounds of this class are soaps and detergents (i. e. surfactants).



(Na-Soap)

6. Micelles

Micelles are the aggregates of many small molecules or groups of atoms which arm held together by secondary valencies i. e. by cohesive or Vander Waal's forces or micelles are spherical with dimensions of the order of 2.5 to 5 nm, depending on the emulsifier used. Many organic colloids, emulsion soaps and detergents generally form such micelles micelles colloids. Soap in water is colloidal, the particles are composed of a number of small molecules of sodium or potassium salts of fatty acids. However, the same soap is dissolved in alcohol as single molecules. The micelles are usually less soluble than macro molecules. The soap micelles are split even by dilution or heating of the soap sol.

Classification of Surfactants

On the basis of their hydrophilic or solubilizing groups present in the molecule the surfactants are classified into four types anionic, non-ionic, cationic and ampholytic.

(A) Anionic surfactants

The hydrophilic group in anionic surfactant is polar and negatively charged in aqueous solutions or dispersions. These are best for water absorbing fibres such as cotton, wool and silk.

(i) Salphates and sulphated products e.g. fatty alcohol sulphates, ethylene oxide adduct Sulphates

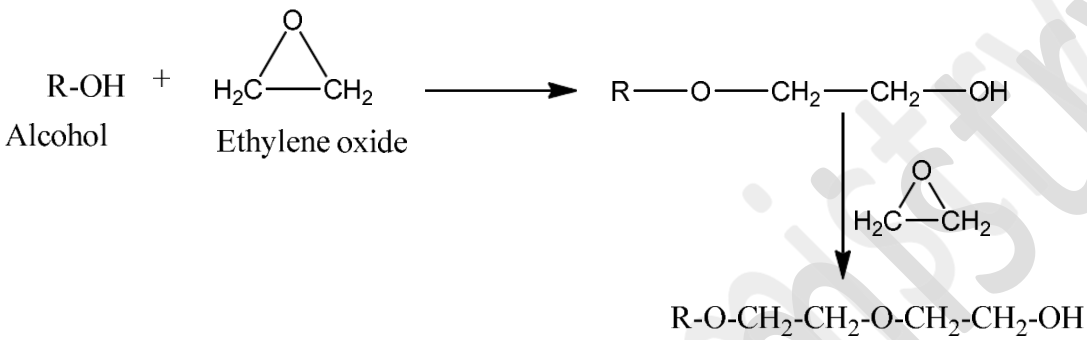
(ii) Sulphonates e.g. alkyl benzene sulphonates (ABS) linear alkyl benzene sulphonate (LAS), petroleum sulphonates, diallyl sulphonates, olefin sulphonates etc.

(iii)Carboxylates-e.g. soaps and amino carboxylates

(iv)Phosphate esters- e.g. Na or K-alkyl phosphates

(B) Non-lonic Surfactants

These surfactants bear no charge when dissolved or dispersed in aqueous medium. The hydrophilic tendency in a non-ionic surfactant is due to presence of oxygen molecule phenol, alcohol) which hydrates by hydrogen bonding with water molecules.



Hydroxyl groups and ether linkages are the strongest hydrophilic groups in non-ionic surfactants. Ethylene oxide condensates of fatty alcohols illustrate the molecular structure of non-ionic surfactants.

Non-ionic surfactants are more effective than anionic surfactants in removing soil at the lower temperatures necessarily for laundering synthetic fibres. They are also more effective for removing body oils. eg. **(i) Ethylene oxide adducts** e.g. polyoxy ethylene surfactants, ethoxylated alkyl phenols and aliphatic alcohols etc.

(ii) Polymeric non-Ionics.

(iii) Alkylol-amides and sorbitol compounds.

(iv) Carboxylic esters and amides.

(C) Cationic Surfactants

They include amine salts, and quaternary ammonium compounds. The amino group or quaternary nitrogen bears a positive charge when dissolved in aqueous medium. The acts as wetting agents rather than detergents. They are more expensive. They are also used as softners for textiles and paper. They can also be used as antibacterial algicidal agents. e.g.

(i) Amines containing oxygen amine oxides, poly oxyethylene, alkylamines $(\overset{+}{-N}(CH_3)_3, C_2H_5\overset{+}{N})$

(ii) Amines not containing oxygen (aliphatic mono di and polyamines and resin derived amines.

(iii) Amines having amide linkage and quaternary ammonium salts.

(D) Ampholytic Surfactants

These surfactants contain both cationic and anionic groups (i.e. both acidic and basic hydrophilic group). They can behave as anionic or cationic according to whether the solution is in the basic or acidic pH range.

They are used in cosmetics, shampoos, water emulsion paints and a corrosion inhibitors, emulsifying and wetting agents.eg-

(i) (N-fatty-β-amino propionic ester.

(ii)Sodium lauroyl-sarcosinate is used in tooth paste composition.

These surfactants are relatively expensive because of the raw materials involved and processing costs.

Raw materials used for Detergents

The important raw materials used for the manufacture of detergents are:

(A) Straight chain alkyl benzenes

(B) Fatty acids and alcohols

(C) Builders

These raw materials are obtained as follows:

(A) Straight Chain alkyl benzenes: Detergents are made primarily from phenyl substituted n-alkanes containing 11 to 14 carbon atoms. The straight chain paraffins or olefins needed are produced from petroleum as follows -

(I) From Petroleum fraction

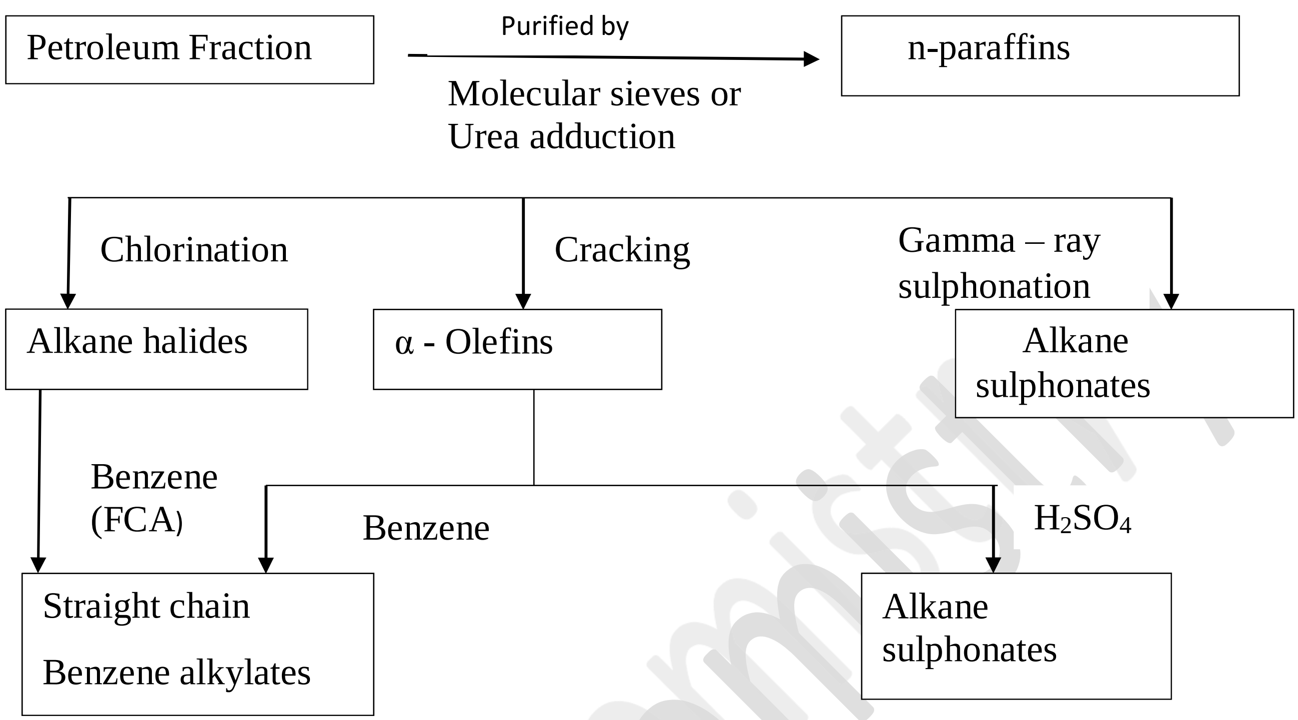


Fig. 3.2 (a) Simple paths to detergent compounds.

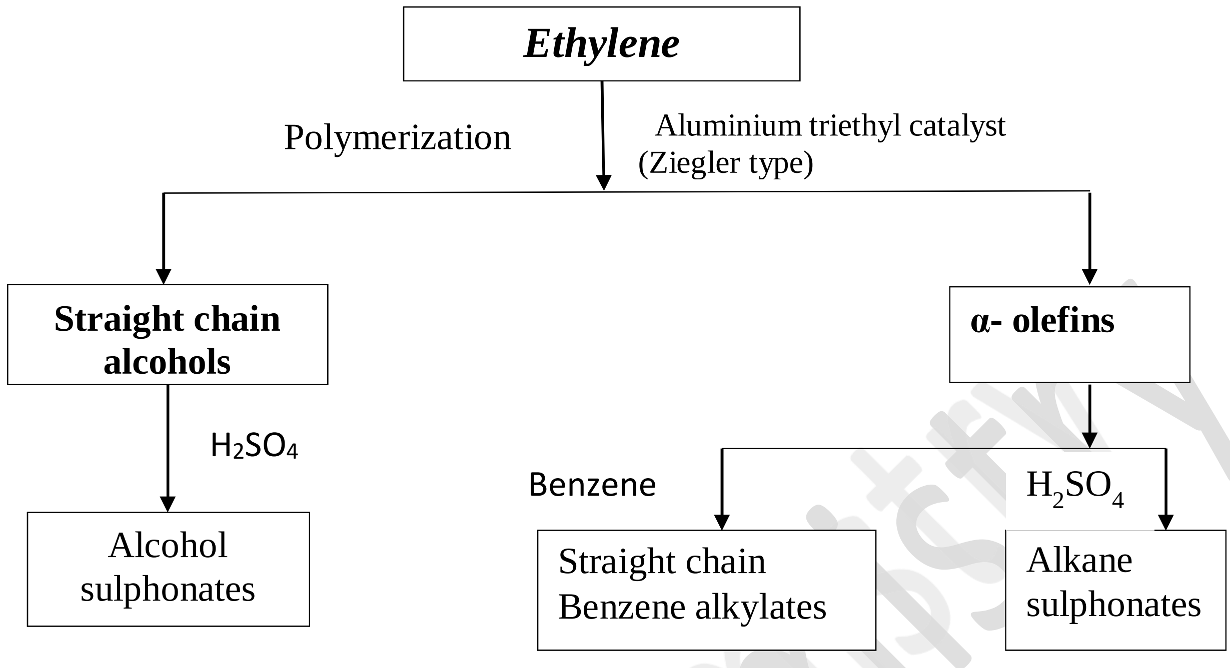
Separation of Paraffins:

Paraffins or n-alkanes are separated from kerosene by adsorption using molecular sieves. Branched chain and cyclic alkanes have large cross sectional diameters than do the linear molecules, thus making sieve separation possible. The separated paraffins are converted to benzene alkylates or cracked to olefins (see Fig. 3.2 (a)).

Polymerization of ethylene: Linear olefins are prepared by dehydrogenation of paraffins by polymerization of ethylene to a-olefins using an aluminium triethyl catalyst (Ziegler type). by cracking paraffin wax or by dehydrogenation of alkyl halides. (see Fig. 3.2 (b))

α -olefins or alkane halides can be used to alkylate benzene through the Friedel Craft reaction employing HF or AlF_3 as a catalyst.

II) From Ethylene :



Fig(b) : Simple paths to detergent compounds

(b) Fatty acid and alcohol

Fatty acids and fatty alcohols are mainly consumed in the manufacture of soaps and detergents. Saturated fatty acids (eg stearic acid) and unsaturated fatty acids (eg. olelic acid) have been used in many industries as free acids or their salts.

Example -

i) Magnesium stearates in face powders.

ii) Calcium or aluminium soaps (insoluble) employed as water repellents in water proofing textiles and walls.

iii) Triethanolamine oleate is dry cleaning and cosmetics.

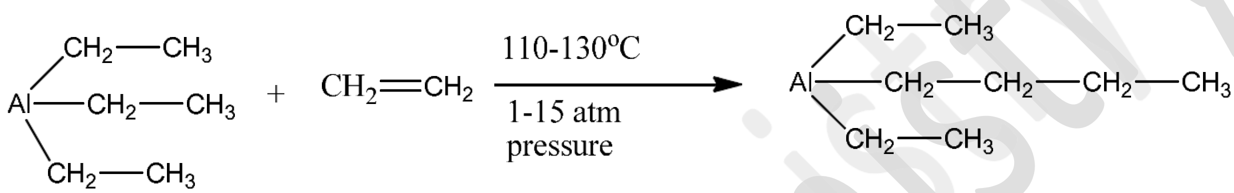
iv) Resin soap consumed as a sizing for paper.

Manufacture of fatty acids

Basic raw materials such as oils and fats have been used for long time for manufacture of fatty acids. Fatty acids are drawn off from the distillate receiver for sale of further conversion to fatty acid salts (Ca, Mg, Zn etc.) Fatty acids are purified by using the methods like-planning and pressing, fractional distillation and solvent crystallization.

Manufacture of fatty alcohols: They are prepared by two important methods- Ziegler Nata catalytic process and methyl ester hydrogenation process, starting from α-olefins.

The continuous by hydrolysis of fats fishes fatty acids which may be hydrogenated fatty alcohols e.g. Gaseous ethylene is converted to higher, linear aluminium trialkyls by the action of aluminium triethyl catalyst (Ziegler-Nata catalyst)



Aluminium triethyl
(Ziegler -Natta catalyst)

(c) Builders: Since detergents are highly concentrated and hence never be used in pure form. Several other substances like sodium sulphate, sodium carbonate, sodium silicate and phosphate are added before the detergents are marketed. These substances are called as **detergent builders** because they increase the cleaning and washing action of surfactants present in detergents and thus make the detergent more effective.

Washing action of Soap

Soap is represented by a general formula, $R\text{-}CO\overset{\ominus}{O}\,\overset{\oplus}{Na}$. The soap molecule has two parts, a polar group (-COO$^-$ Na$^+$) and a non-polar group (R-hydrocarbon part). The polar group is called the **head** and the non-polar group is called the **tail.** Thus, **the soap molecule bass polar head and a non-polar hydrocarbon tail.** The polar head is hydrophilic (water loving) in nature and the non-polar tail is hydrophobic (water repelling) in nature. (Fig. 3.3)

General representation of Soap molecule:

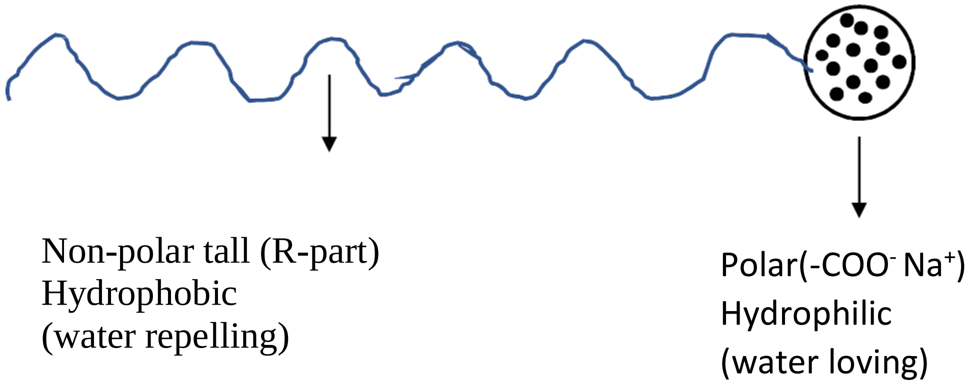


Fig. 3.3: General Seap Molecule

Both soap and detergent are functionally similar. In studying how soap works, it is useful to consider a general rule of nature "like dissolves like." The non-polar hydrophobic tails of soap are lipophilic (oil loving) and so will embed into the grease and oils that help dirt and stains adhere to surfaces. The polar hydrophilic heads, however remain surrounded by the water molecules to which they are attached.

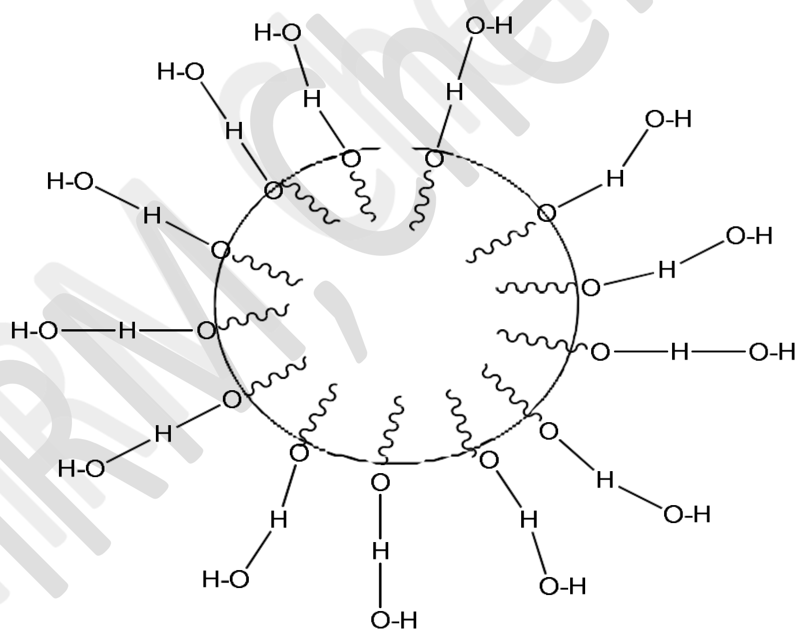


Fig. 3.4. A Soap Micelle

As more and more soap molecules embed into a greasy stain, they eventually surround and isolate little particles of grease and form structures called **micelles that are lifted** into solution. In a micelle (Fig. 3.4) the **tails** of the soap molecules are oriented towards and into the grease while the **heads** face outward into the water, resulting in an **emulsion** of soap grease particles suspended in the water

With agitation, the **micelles** an dispersed into the water and **removed** from the previously dirty surface. In essence soap molecules partially dissolve the greasy stain to form the emulsion that is kept suspended in water until it can he rinsed away.

The removal of dirt (ie. mixture of oily material and solid particles) adhered to the surface, by soap solution proceeds according to the general equation

$$\text{Surface-Dirt} + \text{Soap} \longrightarrow \text{Surface-Soap} + \text{Dirt-Soap}$$

The dirt itself is emulsified by the soap and carried away by moving water.

Soap do not work well in hard water containing calcium and magnesium ion because the calcium and magnesium salts of soap are insoluble, they tend to bind to the calcium and magnesium ions, eventually precipitating out of solution. In doing so, soaps actually dirt the surfaces they were designed to clean.

Thus, soaps have been largely replaced in modern cleaning solutions by synthetic detergents, that have a sulphonate ($R\text{-}S0_3^-$) group instead of the carboxylate head ($R\text{-}COO^-$) Sulphonate detergents tend not to precipitate with calcium or magnesium ions and are generally more soluble in water.

Cleaning action of Detergent

The cleaning action of detergent consists of

a) Thoroughly wetting the dirt and the surface of the article being washed.
b) Removing the dirt from the surface and
c) Maintaining the dirt in a stable solution or suspension

The cleaning action of an anionic detergent is shown in Fig. 3.5.

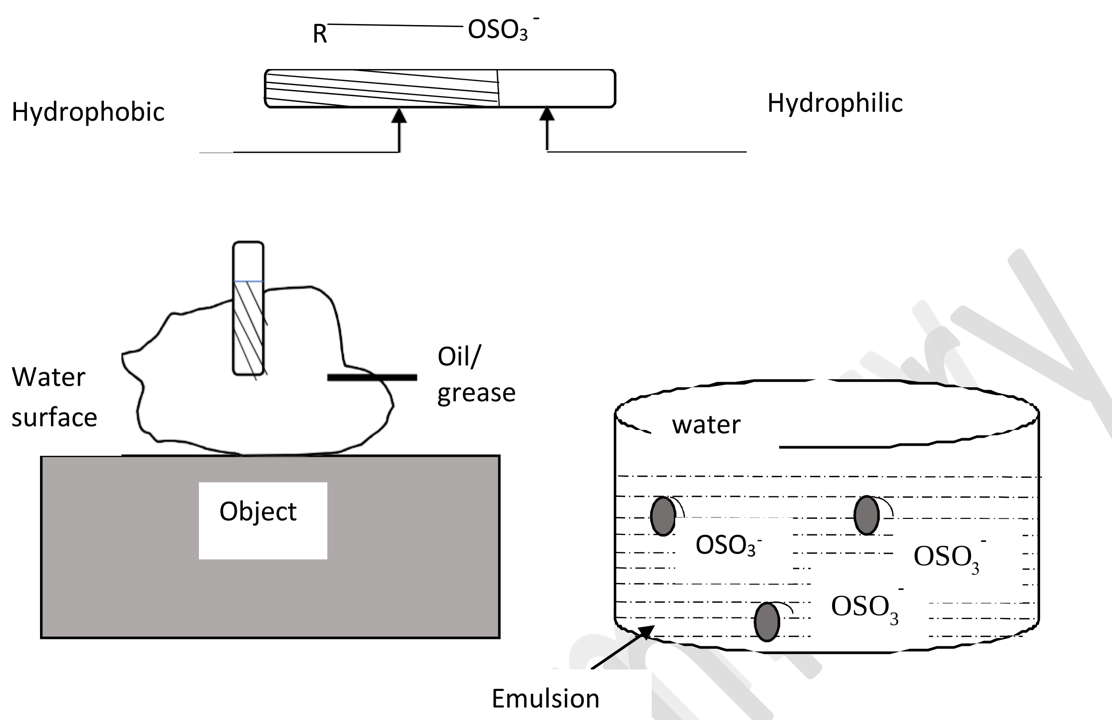


Fig. 3.5: Cleaning action of an anionic detergent

1. When washing is done with detergent (R-O-SO_3^- Na^+), it increases the wetting ability of the water so that it can easily penetrate the fabric and get to the location of the soil.
2. The soil is removed by the process of wetting, emulsifying dispersing or solubilizing the soil by the cleaning agent.
3. Detergent molecule can aggregate in water into spherical clusters called **micelles.**
4. The hydrocarbon part (R) of the molecules gather together on the inside of the micelle and the polar groups (-OSO_3) are on the outside.
5. Oil soluble, water insoluble compounds such as dyes are often dissolved into the centre of the micelle attracted by the hydrocarbon groups. This process is known as Solubilization.

In this way during soil removal, hydrophobic (water hating) ends of the molecules are attracted to a soil particle and then the soil particle is surrounded by the hydrophobic ends. At the same time hydrophilic ends are pulling the soil particles away from the fabric and then washed away. This action enables a soap or detergent to remove soil, suspend it and keep it away from redeposition on clothes.

Comparison between Soaps and Detergents

Soaps	Detergents
1. Its cleaning action is reduced in hard waters. Further soap gets washed in hard water.	1. It can be used in hard water and in textile processing industry.
2. It cannot be used in acidic solutions, due to formation of sticky precipitate which get adhered to textile agent.	2. It can be used in acidic solution and also for washing delicate fibres like knitted wool and silk.
3. It is poor foaming agent.	3. It is excellent foaming agent.
4. It is less active and requires more concentration.	4. It is more active and requires low concentration.
5. Soap making involves the use of oil and fats which have potential food values and costly.	5. They require surfactants, obtained from petroleum products which are cheap.
6. It has no germicidal and bactericidal properties.	6. It has germicidal and bactericidal properties.

Advantages of Detergents

1. It can be used in hard water and in textile processing industry.
2. Since detergents are made from the petroleum products, the oils and fats could be saved and this is a need of today because of the increasing population.
3. It can be used for washing delicate fibres like knitted wool and silk.
4. It is more active than soap in comparatively low concentration.
5. It is excellent foaming agent.
6. It has germicidal and bactericidal properties.

References: According to the new revised syllabus of Savitribai Phule Pune University from June 2021, Text book of Industrial chemistry for T.Y. B.Sc. course (CH- 505), Sem-V Manali Publication, Nirali Publication and google images