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SOAP AND DETERGENT

Soap is now an essential everyday item and finds its importance in everyday life. Soaps and Detergents are chemical compound or mixture of compounds used as a cleansing agent. Soap is a sodium salt or potassium salt of many combinations of fatty acids having cleansing action in water whereas Detergent surfactants are much better solutions for the cleaning purpose as the hardness of water does not affect them.

SOAPS:

A soap is a water-soluble compound which is made via a process called saponification by the reaction between sodium hydroxide or potassium hydroxide with vegetable or animal oil (fats). Soaps are potassium or sodium salts of a carboxylic acid having a long aliphatic chain attached to it. They are surfactants (compounds that reduce the surface tension between a liquid and another substance) and therefore help in the emulsification of oils in water. Soaps are generally prepared via the saponification of fats and oils. The carboxylate end of the soap molecule is hydrophilic whereas the hydrocarbon tail is hydrophobic.

Characteristics of Soap:

1. **Hardness** – Harder soap which is a dense bar lasts longer.
2. **Cleansing** – The first reason the majority of people use soap is to get clean. A soap molecule consists of a chain of carbon atoms where one end of the chain attracts oil and the other attracts water. Soap should be balanced and not too much or too less of cleansing ingredient should be added.
3. **Conditioner** – Soap conditioners are referred to as emollients. Once you have washed your hands and what's left behind on your skin after you

rinse, depends on the type of soap a person uses. For instance, consider a person with dry skin, he/she should select a soap with moisturizing emollients that can prevent water evaporation.

4. **Lather** – Most people like soap which produces lather. The balance of bubbles and cleansing, soothing cream makes lather so satisfying.
5. **Fragrance** – It is an essential factor. Aromas evoke a unique combination of personal memory and enrich our daily life. Fragrances revitalize us, calm us, and most importantly mask our body odors.

Types of Soaps:

1. **Toilet Soaps:** Potassium soaps are softer than sodium soaps.
2. **Floating Soaps:** These can be prepared by beating soap bubbles.
3. **Transparent Soaps:** These contains soap dissolved in excess of alcohol and it is evaporated.
4. **Medicated Soaps:** These contain soaps by adding little amounts of Dettol, Savlon etc.
5. **Laundry Soaps** mainly contains Sodium rosinate, borax.

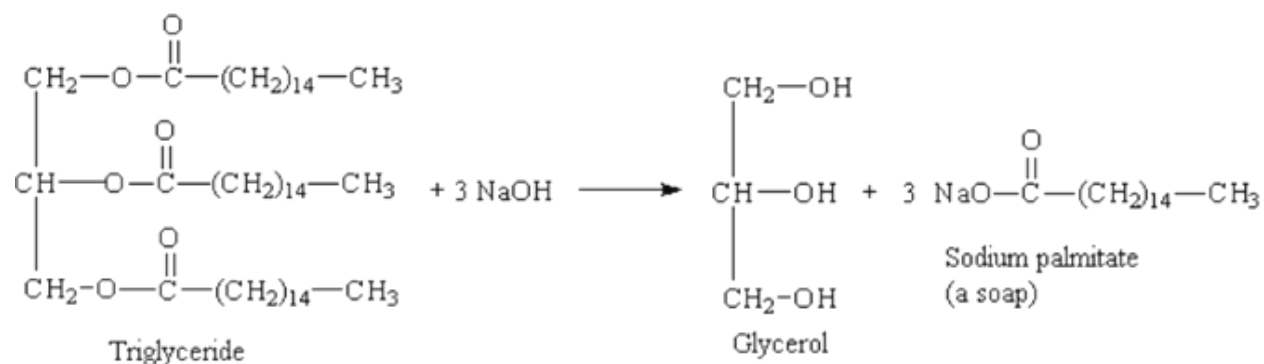
Soaps are prepared by the alkaline hydrolysis of fats and oils or the saponification process. The ingredients of soaps and detergents and their percentage (percent of total by weight) used can be listed as follows-

- Surfactants (30-70%)
- Plasticizers and binders (20-50%)
- Lather enhancers (0-5%)
- Fillers and binders (5-30%)
- Water (5-12%)
- Fragrance (0-3.0%)
- Opacifying agents (0-0.3%)
- Dyes and pigments (less than 1%)

MANUFACTURE OF SOAPS:

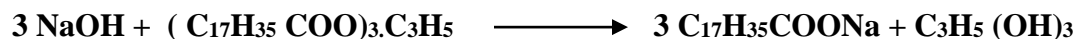
(I) Saponification:

Saponification is the *hydrolysis of an ester* with NaOH or KOH to give alcohol and sodium or potassium salt of the acid. Saponification is simply *the process of making soaps*. Soaps are just potassium or sodium salts of long-chain fatty acids. During saponification, ester reacts with an inorganic base to produce alcohol and soap. Generally, it occurs when triglycerides are reacted with potassium or sodium hydroxide to produce glycerol and fatty acid salt, called 'soap'. This process is called saponification.



Saponification Reaction:

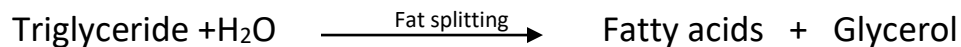
Triglycerides are generally animal fats and vegetable oils. When they are reacted with sodium hydroxide, a hard form of soap is created. This is where potassium comes and creates a softer version of the soap. The equation can be written as:



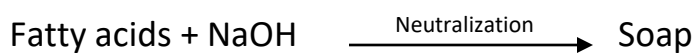
Method:

- The saponification of triglycerides with an alkali is a bimolecular nucleophilic substitution (SN₂).
- The rate of the reaction depends on the increase of the reaction temperature and on the high mixing during the processing.
- In the saponification of triglycerides with an 'alkali', the two reactants are immiscible.
- The formation of soap as a product affects the emulsification of the two immiscible reactants, which causes an increase in the reaction rate.

- The fatty acids are sent to a flash tank, where the water is separated or flashed off.



- The resulting crude mixtures of fatty acids may be used, but a separation into more useful components is made.
- The hot fatty acids are cooling down to room temperature into two parallel condensers prior to neutralization with 50% caustic soda in a high-speed mixer neutralizer.
- The fatty acids are converted into sodium salts, which form the soap.



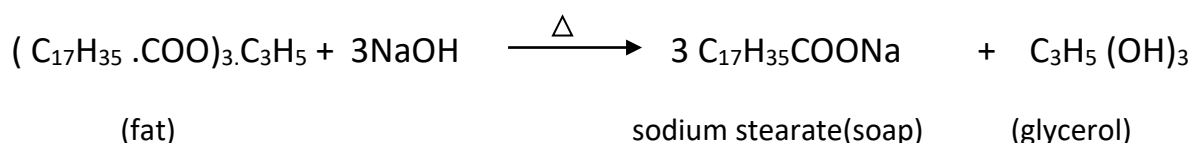
Uses of Saponification:

- **Wet chemical fire extinguishers:** To extinguish cooking oils and fats, we use a saponification reaction. This is because cooking oils and fats have a flashpoint which is above 37 degrees which render regular fire extinguishers useless.
- **Creating hard and soft soaps:** By using different types of alkali in the process the type of reaction product can be altered between hard and soft.
 - Using KOH: We can obtain soft soaps
 - Using NaOH: We can obtain hard soaps

(II) Kettle Process:

The kettle process is the old process. This process is carried in a steel tank or kettle from which it gets the name. The following steps are involved:

(i)Boiling: The fat and sodium hydroxide(NaOH) solution are fed into the kettle and boiled with steam entering from a perforated coil at the bottom. The boiling is continued till saponification is nearly 80% complete.



(ii) Salting out: Common salt is then added and boiling resumed till soap has separated by common ion effect. The soap being lighter floats to the surface as a curdy mass. The lower layer containing glycerol and salt is drawn off, leaving soap plus unreacted fat in the kettle.

(iii) Addition of Fresh Lye: The soap from step (2) contains 20% fat which escaped esterification earlier. It is boiled with more of NaOH solution. More soap is formed. The lower layer is drawn off. The soap layer left in the kettle is boiled with water to wash away excess of lye (NaOH).

(iv) Finishing: The soap in the kettle while still molten, is pumped into the crutcher by means of swing pipe. The crutcher is a steam jacketed tank fitted with a blade-stirrer. Here the soap is mixed with colour and perfumes, till it becomes a homogeneous mass. The crutched soap is poured into frames and on solidification cut into cakes. For making toilet soap, the neat crutched soap is shredded, dried and stamped into cakes.

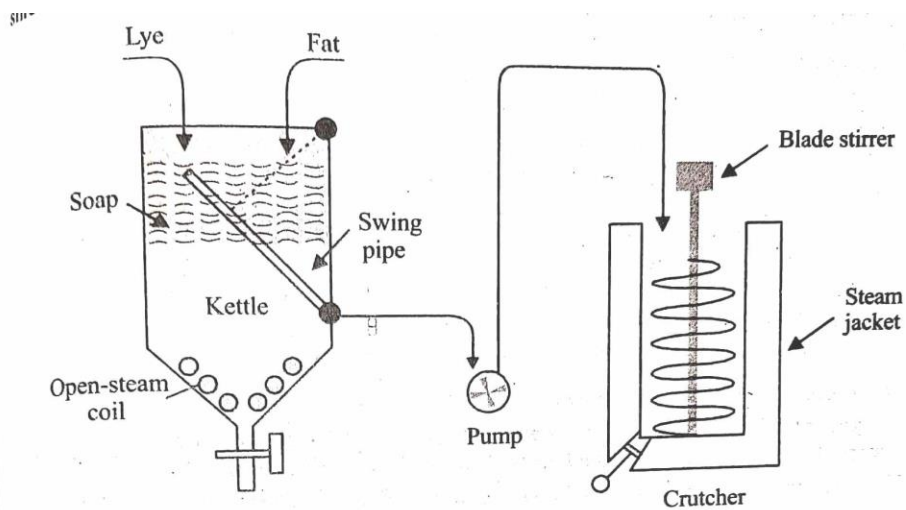


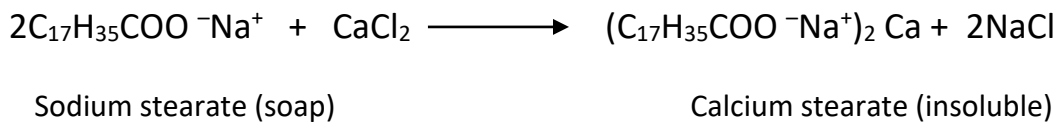
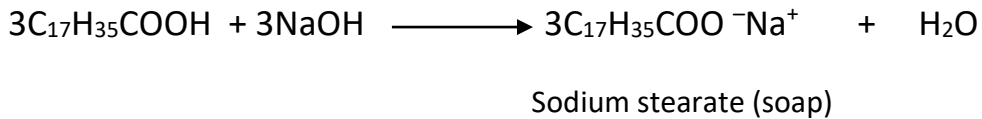
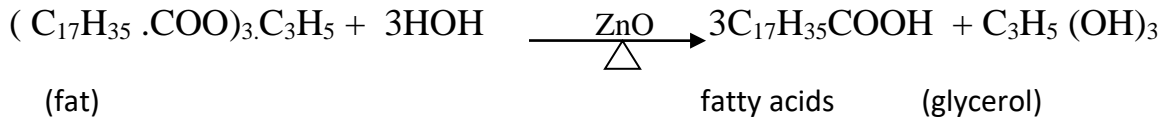
Fig : Manufacture of soap by Kettle Process

(III) Hydrolyser Process:

This is the modern continuous process for soap manufacture. It is more economical than the kettle process and gives better quality product. The following steps are involved here:

- (a) Hydrolysis of fat with water in the presence of zinc oxide at high temperature and pressure.

- (b) Distillation of fatty acids under vacuum.
- (c) Neutralization of the condensed fatty acids with alkali.
- (d) Process of cleansing.



The flow sheet of the Hydrolyser Process is shown in fig. The fat mixed with zinc oxide catalyst and water are heated to 230-250⁰C under 40-45 atm. pressure in the Hydrolyser. The fatty acids mixed with water are discharged at the top into a steam flash-tank. The water vaporizes, cooling the fatty acids which are then vacuum –distilled in the vacuum still. The vapours of fatty acids are passed through water condenser. The condensed fatty acids are finally neutralized in the mixture and we obtain plain soap. It is then mixed with colour and perfumes as explained in the kettle process. Soap are not effective cleaning agents with water containing dissolved impurities of calcium, magnesium and iron salt. These impurities are generally present in hard water. In such cases, insoluble stearates are formed which hinder the process of cleansing.

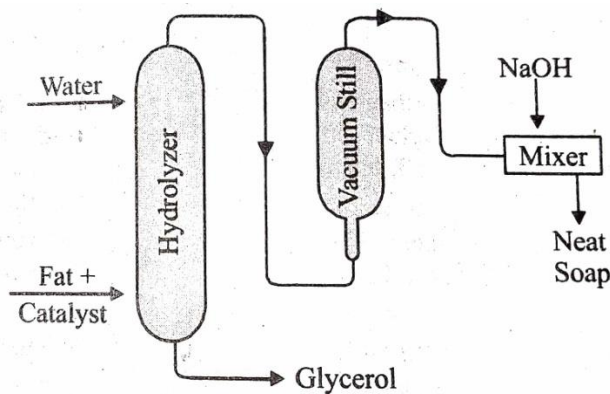
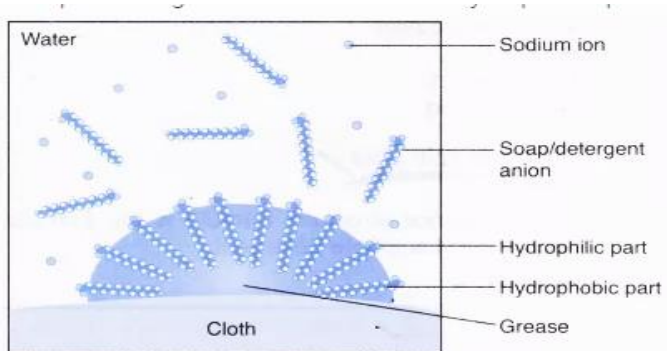


Fig.: Soap Manufacture by Hydrolyser Process

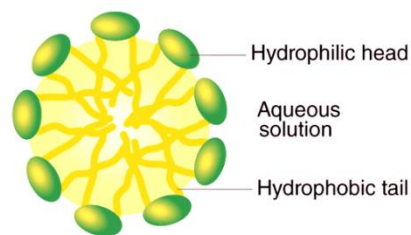
Cleansing Action of Soap:

Most of the dirt is oily in nature and oil does not dissolve in water. The molecule of soap constitutes sodium or potassium salts of long-chain carboxylic acids. In the case of soaps, the carbon chain dissolves in oil and the ionic end dissolves in water. Thus the soap molecules form structures called micelles. In micelles, one end is towards the oil droplet and the other end which are the ionic faces outside. Therefore, it forms an emulsion in water and helps in dissolving the dirt when we wash our clothes.

A Soap or detergent anion consists of a hydrophobic end and hydrophilic end. The first one is the hydrophilic end which dissolves water and is attracted to it whereas the second one is the hydrophobic end that is dissolved in hydrocarbons and is water repulsive in nature. If on the surface of the water, soap is present then the hydrophobic tail which is not soluble in water will align along the water surface. Soap reduces the surface tension of water.



(a)



(b)

Fig :(a) Emulsified grease globule(Micelle formation)

(b) Micelle in water

Difference between Soap and Detergent

The key differences between soaps and detergents are tabulated below.

Difference Between Soap and Detergent	
Soaps	Detergents
Consist of a '-COONa' group attached to a fatty acid having a long alkyl chain.	Consist of a '-SO ₃ Na' group attached to a long alkyl chain.
They are not effective in hard water and saline water	They do not lose their effectiveness in hard water and saline water.
Soaps are completely biodegradable	Detergents containing a branched hydrocarbon chain are non-biodegradable
They have a tendency to form sum in a hard water environment.	These compounds do not form scum.
They are derived from natural sources such as vegetable oils and animal fats.	Detergents are synthetic derivatives.
Soaps are environment-friendly products since they are biodegradable.	These compounds can form a thick foam that causes the death of aquatic life.
Examples : sodium palmitate and sodium stearate.	Examples : deoxycholic acid and sodium lauryl sulfate.

Synthetic Detergents

Detergents are amphipathic molecules that contain both polar and hydrophobic groups. The charged hydrophilic group is also called the head and the long lipophilic hydrocarbon group is called the tail. Detergents are also known as surfactants as they have the ability to decrease the surface tension of water.

Detergents are the potassium or sodium salts of a long alkyl chain ending with a sulfonate group. They are soluble in hard water. This solubility is attributed to the fact that the sulfonate group does not attach itself to the ions present in hard water. Commonly, anionic detergents such as alkylbenzenesulfonates are used for domestic purposes. Detergent surfactants are much better solutions for the cleaning purpose as the hardness of water does not affect them. Today detergent is a better liquid form solution used for cleaning purposes. The surfactants used in detergents are made up of petrochemical solutions.

Properties of Detergents:

1. Detergent the concentration at which micelles formation starts is called as critical micelle concentration (CMC). The temperature at which the detergent solution is around or above its critical micelle concentration separates into two phases is called the cloud point.
2. Detergents can align at aqueous/non-aqueous interfaces.
3. Resulting in reduced surface tension.
4. Increased miscibility.
5. Stabilization of emulsions

Factor affecting of Detergent:

Detergent is dependent on the following factors:

- (a) Detergent concentration
- (b) Ionic strength
- (c) Length of the alkyl chain
- (d) pH- value

(e) Presence of organic additives

(f) Purity

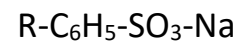
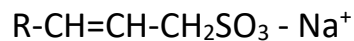
(g) Temperature.

Chemical classifications of detergents:

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

(i) Anionic detergents:

Typical anionic detergents are alkylbenzene sulfonates. The alkylbenzene portion of these anions is lipophilic and the sulfonate is hydrophilic. Two different varieties have been popularized, those with branched alkyl groups and those with linear alkyl groups. They are poorly biodegradable. Example: Methyl ester sulfonates (MES), Alkylbenzenesulfonates,



Alkylsulfonates (R = C₈₋₁₂) (anionic surfactants) , Alkylbenzenesulfonates

(ii) Cationic detergents:

Cationic detergents are similar to the anionic ones, with a hydrophilic component, but, instead of the anionic sulfonate group, the cationic surfactants have quaternary ammonium as the polar end. The ammonium sulfate center is positively charged.



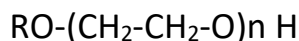
Dialkyl dimethylammonium chlorides (cationic surfactants)

(iii) Non-ionic and zwitter ionic detergents:

Non-ionic detergents are characterized by their uncharged, hydrophilic head groups. Typical non-ionic detergents are based on polyoxyethylene or a glycoside. Common examples of the former include Tween, Triton, and the Brij series. These materials are also known as ethoxylates and their metabolites, nonylphenol.

Glycosides have a sugar as their uncharged hydrophilic head group. Examples include octyl thioglucoside and maltosides.

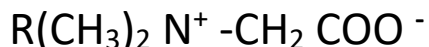
Example-



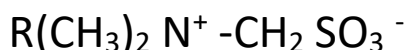
Alkyl poly(ethylene glycol)ethers (non-ionic surfactants)

(iv) Zwitter ionic detergents(Amphoteric):

Amphoteric Surfactants includes both acidic and basic groups in the same molecule. These compounds have the characteristics of both anionic detergents and cationic fabric softeners. They work best at neutral pH, and are found in shampoos, skin cleaners and carpet shampoo. They are very stable in strong acidic conditions and have found favor for use with hydrofluoric acid. These surfactants are rarely employed in laundry detergents due to their high costs. Example: Alkylbetaines Betain, Alkylsulfobetaines.



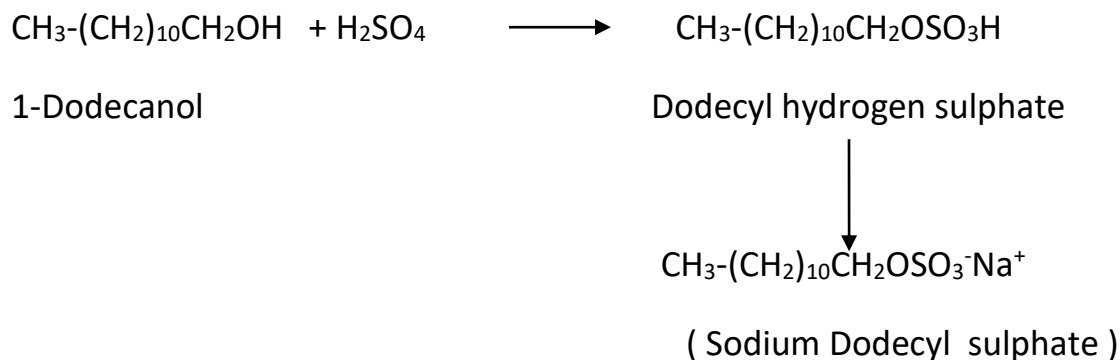
R = C₁₂₋₁₈ Alkylbetaines Betain (amphoteric surfactants)



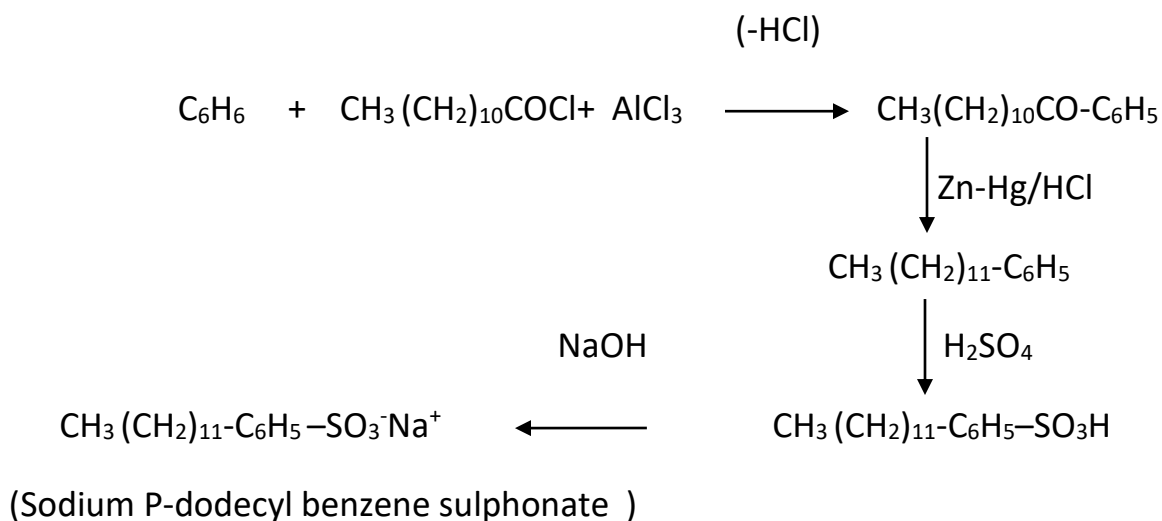
R= C₁₂₋₁₈ Alkylsulfobetaines

Synthesis of Detergent: Synthetic detergents are either salts of alkyl sulphonate or alkyl benzene sulphonate as given below.

(i)Sodium alkyl sulphates: These detergents consist of sodium alkyl sulphates obtained from long chain alcohols. The alcohol was treated with concentrated sulphuric acid to form a sulphate ester which was neutralized with sodium hydroxide to obtain a detergent known as sodium dodecyl sulphate (SDS) .It is mainly used in shampoo and cosmetics.



(ii) Alkyl benzene sulphonates: The most commonly used detergents these they are linear alkylbenzenesulphonates such as sodium dodecylbenzenesulphonates. They are ionic detergents and are obtained by conversion of benzene into alkyl benzene followed by sulphonation and treatment with alkali as show below:



Advantages of Synthetic Detergents Over Soaps :

Synthetic detergents are widely used these days as cleaning agents. Synthetic detergents have the following advantages over soaps:

(i) Synthetic detergents can be used even in hard water whereas some of the soap gets wasted if water is hard.

(ii) Synthetic detergents can be used even in acidic medium as they are the salts of strong acids and are not decomposed in acidic medium.

(iii) Synthetic detergents have a stronger cleaning action than soaps.

(iv) Synthetic detergents are more soluble in water than soaps.

(v) Synthetic detergents are prepared from the hydrocarbons obtained from petroleum. This saves vegetable oils which are otherwise used in preparation of soap.

Critical Micelle Concentration (CMC)

Surfactants are organic substances, which significantly decrease the surface tension of water at relatively low concentrations, at least partially water soluble. Because surfactants are absorbed mainly on the surface of the solution, creating a thin monolayer, they are called surface active substances. When dissolved them, after they reach a certain value of concentration, molecules or ions of surfactants begin to associate and to organize themselves into more complex units, also called **micelles**. The characteristic concentration value, where the association process begins, is called the critical micelle concentration (CMC). The CMC is one of the most useful physicochemical characteristics of many biologically active substances and drugs.

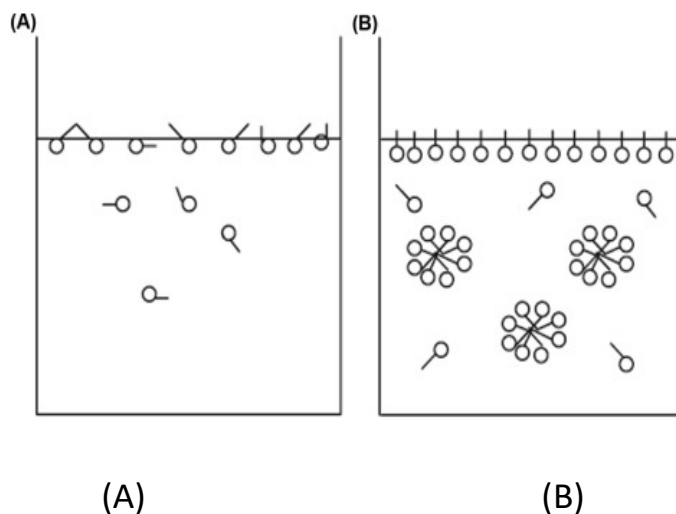


Fig.: Description of distribution of surfactant molecule **(A)** below CMC and **(B)** above CMC

Based on the charge and the nature of the ion which generates surface activity. We can divide the ionic surfactants into following classes:

1. *Anion-active (anionic) surfactants* - e.g. sodium or potassium salts of higher fatty acids (soaps), salts like sodium dodecyl sulfate, sodium tetradecyl sulfate etc.
2. *Cation-active (cationic) surfactants* - e.g. quaternary ammonium salts – hexadecylpyridinium bromide, carb ethopendecinium bromide (Septonex) etc.
3. *Ampholytic surfactants* – e.g. long-alkyl amino acids, with pH dependent charges.

Ionic surfactants are generally well soluble in water and at concentrations below the corresponding CMC. The variation of the CMC with chemical and physical parameters provides a good insights into the nature of the surfactant self-association. There are quite abrupt changes in the concentration dependence of a larger number of physico-chemical properties at a particular concentration.

The physical methods for CMC determination includes conductivity, solubility, viscosity, light scattering, measuring the surface tension by Wiebelmy slide method or by the method of maximum bubble pressure , measurement of

ion activity and by dye incorporation method, Gel filtration spectrophotometrically and counterion magnetic resonance.

The CMCs of the various homolog's of surfactants with a linear alkyl chain follow the equation:

$$\text{Log CMC} = A - Bn$$

Where, n is the alkyl chain and A and B are constants

Figure : shows a linear relationship between log CMC and the no. of carbon chain length.

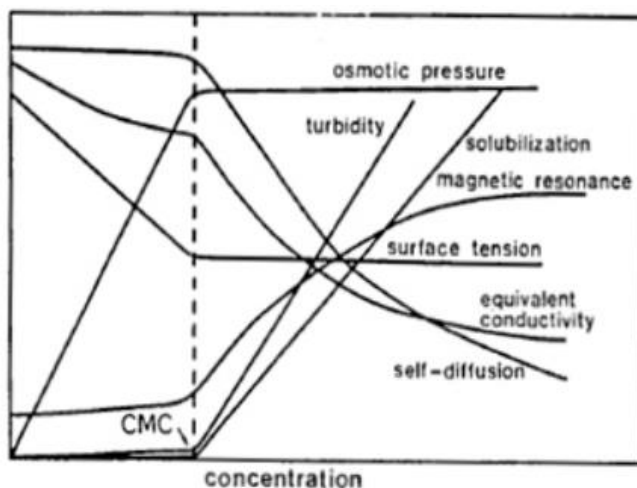


Figure : Schematic representation of the concentration dependence of some physical properties of solutions of a micelle-forming surfactant.

For a given alkyl chain, CMCs increase in the order nonionic (Polyoxyethylene glycol monoethers) < Zwitterionic < ionic (Cationic or anionic).

Determining Critical Micelle Concentration (Surface Tension Method):

Surfactant monomers assemble to form a closed aggregate (micelle) in which the hydrophobic tails are shielded from water while the hydrophilic heads face water. The critical aggregation concentration is called the critical micelle concentration

(CMC) when micelles form in an aqueous medium. The CMC is a property of the surfactant. It indicates the point at which monolayer absorption completes and the surface active properties are at an optimum.

The typical CMC values at room temperature are 10^{-3} to 10^{-2} M for anionic surfactants, 10^{-3} to 10^{-1} M for amphoteric and cationic surfactants and 10^{-5} to 10^{-4} M for non-ionic surfactants.

The following factors contribute CMC decrease :

- (a) An increase in the number of carbon atoms in the hydrophobic tails
- (b) The existence of polyoxypropylene group
- (c) Fluorocarbon structure
- (d) An increased degree of binding of the counterions
- (e) The addition of electrolyte to ionic surfactants
- (f) The existence of polar organic compounds (such as alcohols and amides)
- (g) The addition of xylose and fructose

The following factors contribute to CMC increase:

- (a) Branch hydrophobic structure .
- (b) Double bonds between carbon atoms.
- (c) Polar groups (O or OH) in hydrophobic tail.
- (d) Strongly ionised polar groups (sulphates and quaternaries).
- (e) Hydrophilic groups placed in the surfactant molecule centre.
- (f) Increase in the number of hydrophilic head.
- (g) Trifluoromethyl groups.
- (h) An increase in the effective size of hydrophilic head.

(i) An increase in the pH of weak acids (such as soap).

(j) A decrease in pH from isoelectric region and increase in pH from isoelectric region for amphoteric surfactants (low CMC at the isoelectric region and high CMC outside the isoelectric region).

(k) addition of urea, formamide, and guanidinium salts, dioxane, ethylene glycol and water soluble esters.

The CMC decreases with temperature to a minimum and then increases with further increase in temperature. The minimum appears to be around 25°C for ionic surfactants and 50°C for non-ionic surfactants.

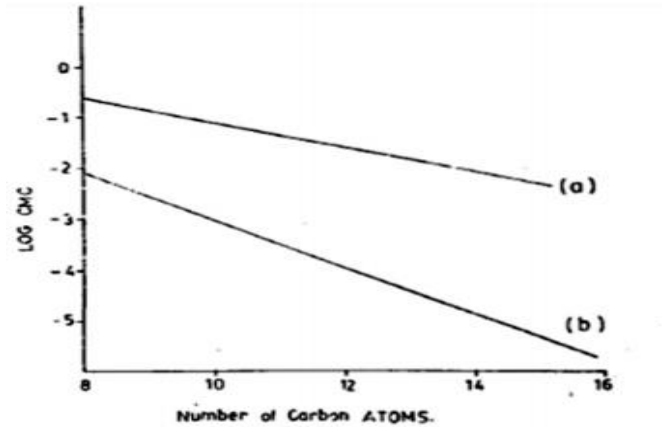
Several empirical correlations are available for the estimation of CMC values. For straight and saturated single tail ionic surfactants, the CMC can be calculated from-

$$\text{Log CMC} = A - Bn \quad \text{eqn.(i)}$$

Where, n is the number of carbon atoms in the hydrophobic tail, and A and B are temperature dependent constants for a given type of surfactant. The value of B is around 0.3 is equivalent to $\log_{10}2$) for the ionic surfactants because the CMC of the ionic surfactants is halved for each carbon atom added to the hydrophobic tail. B value is about 0.5(= 0.5 log 10) for the non-ionic and amphoteric surfactants because the CMC will decrease by a factor of 10 for each of the two methylene groups added to the hydrophobic tail. The values of A and B for some surfactants can be found.

The effect of electrolyte concentration on the CMC of ionic surfactant is given.

$$\log\text{CMC} = a - b \log C \quad \text{eqn.(ii)}$$



where a and b are constants for a given ionic hydrophilic head at a certain temperature and C is the total counter ion concentration in equivalent per litre. The effect of electrolyte concentration on the CMC of non-ionic and amphoteric surfactants is given).

$$\text{Log CMC} = x - y C_e \quad \text{eqn. (iii)}$$

Where $C_e < 1$ where x and y are constants for a given surfactant, electrolyte and temperature, and C_e is the concentration of electrolyte in moles per liter.