Introduction

SYNTHETIC SURFACE ACTIVE AGENTS

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Surfactant is a short hand of surface active agent, they are substance with molecular structure consisting of two parts, one is hydrophobic (oil-soluble) and the other hydrophilic (water-soluble). Hydrophilic part may be

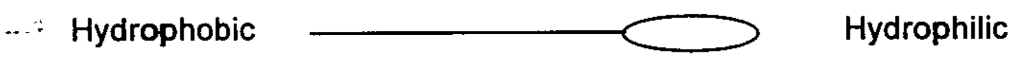
a- Anionic has negative charge like (sulfate, sulfonate, carboxylate, hydroxyl).

b- Cationic has positive charge like (tetra alkyl ammonium chloride).

c- Amphoteric has both positive and negative charges like betaine.

d- Uncharged likes nonionic (poly glycol ether groups) and hydrophobic part (is a hydrocarbon chain linear or branched) has sufficient length to give the required oil solubility.

The representation examples are:



The position of the hydrophilic part can be arranged at any placed of hydrophobic chain:

These compounds have a special property in solvents due to the variation of the structure and due to a conflict between hydrophilic and hydrophobic parts. Hydrophobic part is distributed in the oil layer, while the hydrophilic part arranged at the phase borders, an orientating alignment of surfactants molecules occur, this result in change of system properties such as:

a) Lowering of interfacial tension between water and adjacent phase.

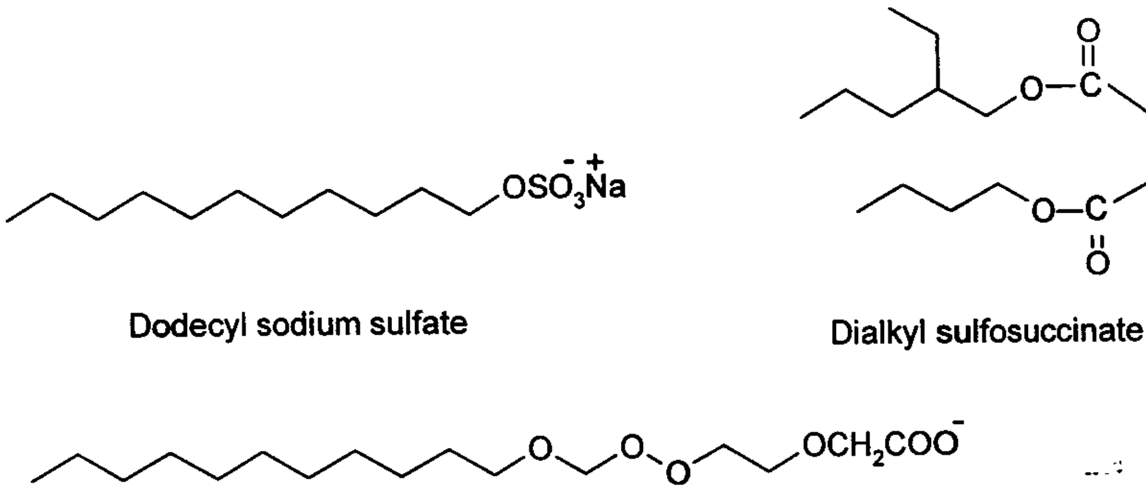
b) Change of wetting properties.

c) Formation of electrical double layer at the interfaces.

Surface active agents fall into the following main groups.

a- Anionic surfactants.

Anionic surfactant molecule is consisting of a linear or branched chain with the polar negative group (carboxylate, sulfate, sulfonate and phosphate) carry the surface character, sulfonate and sulfates are especially important anions, the most common counter-ions (cations) used are sodium and potassium (e.g. Fig 1).

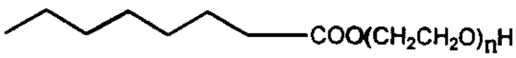


Alkyl ether carbonate

Fig. 1

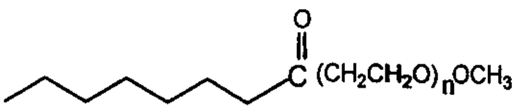
b- Nonionic Surfactants.

The term nonionic surfactants refer chiefly to polyoxyethylene and polyoxypropylene derivatives are uncharged molecule and the hydrophilic properties are provided by hydration of hydroxyl, ether, amine or amide groups (e.g. Fig 2).

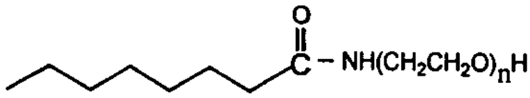


Fatty acid ethoxylate

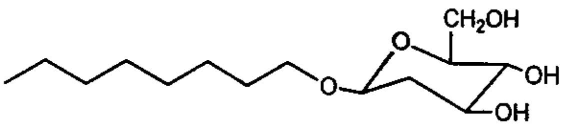
Fatty alcohol ethoxylate



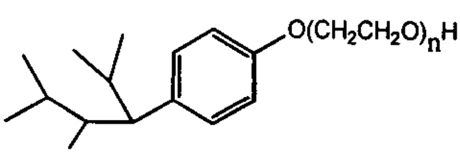
Fatty acid methyl ester ethoxylated



Fatty acid amide ethoxylated



Alkylglucoside

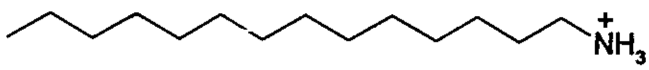


Alkylphenol ethoxylate

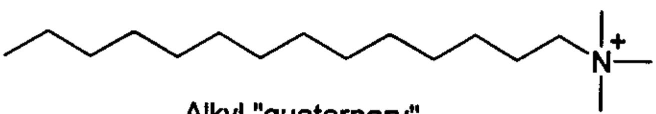
Fig. 2

c- Cationic Surfactants:

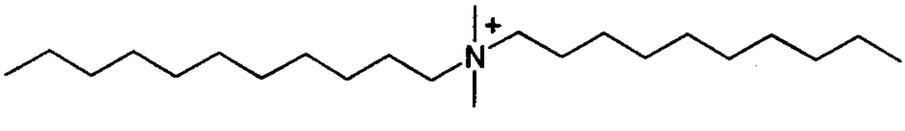
Most cationic surfactants have in their hydrophilic groups nitrogen atom carrying the positive charge which is the carrier surface character of this type (e.g. Fig 3).



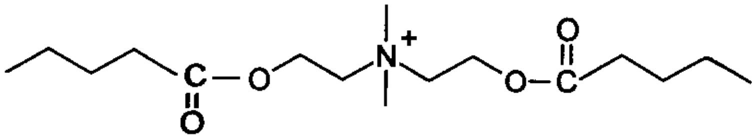
Fatty amine salt



Alkyl "quaternary"



Dialkyl quaternary

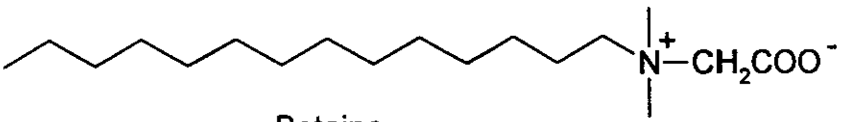


Ester quaternary

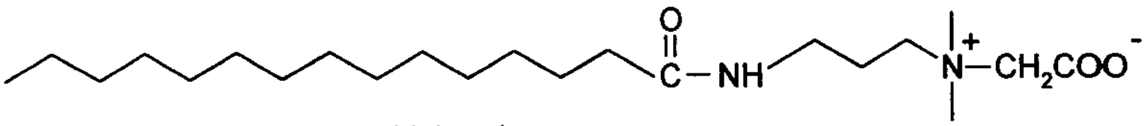
Fig. 3

d- Amphoteric Surfactants.

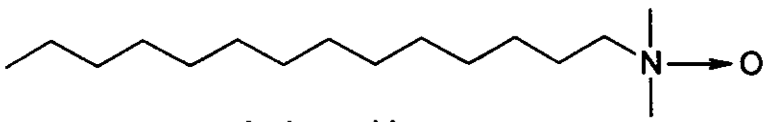
Amphoteric surfactants are characterized by a molecular structure containing two different hydrophilic groups, one with anionic and the other with cationic character. Most amphoteric surfactants are able to behave in acidic medium like cationic and in alkaline medium like anionic surfactant (e.g. Fig 4).



Betaine



Amidobetaine

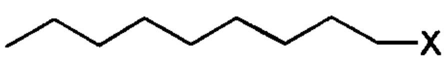


Amino oxide

Fig. 4

A- Anionic Surfactants.

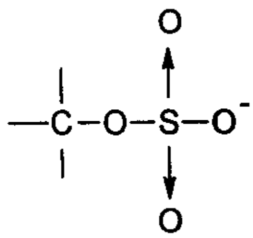
They are surface-active substances in which e.g. one hydrophobic hydrocarbon group is connected with one or two hydrophilic groups. In aqueous solution, dissociation occurs into a negatively charged ion (anion) and positively charged ion (cation). The anion is the carrier of the surface-active properties. The sulfated and sulfonated materials represent the largest group of surface-active agents, exclusive of soap. Chemically, these products are divided into two categories:



Where X = COO^-, OSO_3^-, SO_3^-

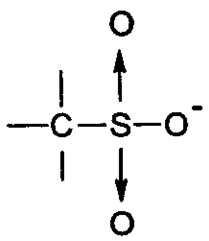
1- Sulfates.

Compounds in which sulfur is attached to the carbon chain through an oxygen:



2- Sulfonates:

Compounds in which the sulfur is attached directly to the carbon chain. A large number of sulfated and sulfonated surface-active agents are commercially available:



1.1- Sulfated oils.

The sulfation of fatty materials to yield surface-active compounds was discovered by Fermy almost 150 years ago, when he treated olive oil with sulfuric acid.[1] Historically, it is the earliest reported example of a non-soap organic surfactant. This so-called "sulfuric acid oil" was used as a mordant and was found to be superior to untreated olive oil which was also used for this purpose. Castor oil and rapeseed oils were ethoxylated and sulfates.[2,3] The resultant product were used in dying with alizarin red, laundering, dishwashing and detergents.[4]

1.2- Sulfated monoglycerides.

Colgate-Palmolive Co. [5-7] produced sulfated fatty monoglycerides in the United States in the early 1940. Sulfated monoglycerides were produced by the reaction of three relatively inexpensive raw materials; fat (coconut oil), glycerol and sulfuric acid (eq. 1).

$$\begin{array}{l} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \xrightarrow[2)\,NaOH]{1)\,H_2SO_4} \begin{array}{l} CH_2OSO_3^- \, Na^+ \\ | \\ CHOCOR \\ | \\ CH_2OSO_3^- \, Na^+ \end{array} + 3H_2O \quad \text{.........(Eq. 1)}$$

Coconut oil monoglycerides were used for many years by **Colgate-Palmolive Co.** in a number of major products, including a synthetic detergent bar (**Vel**), light-duty detergents, shampoos (Halo) and toothpaste. The surface active properties of pure monoglycerides sulfates were reported by **Biswas** and **Mukherji** [8,9] who found that the C_{14} homologues have the best foaming power and exhibit the greatest surface tension-lowering effect.

1.3- Fatty alcohol sulfates.

The fatty alcohols are normally derived from fatty acids by catalytic reduction under pressure. [10] Various glycerides and simple esters have been reduced to fatty alcohols with either sodium-alcohol, lithium aluminum hydride (LAH) [11], catalytic hydrogenolysis or by sodium borohydride ($NaBH_4$) in a mixture of t-butanol and methanol [12], sulfuric acid, chlorosulfonic acid, amidosulfonic acid also gaseous sulfur trioxide may be utilized in the production of primary fatty alcohol sulfates (eq. 2-5).

$$ROH + H_2SO_4 \longrightarrow ROSO_3H + H_2O \quad \text{...(Eq. 2)}$$

$$ROH + ClSO_3H \longrightarrow ROSO_3H + H_2O \quad \text{...(Eq. 3)}$$

$$ROH + NH_2SO_3H \longrightarrow ROSO_3^- \overset{+}{N}H_4 \quad \text{...............(Eq. 4)}$$

$$ROH + SO_3 \longrightarrow ROSO_3H \quad \text{...............(Eq. 5)}$$

The chain length and degree of branching of fatty alcohols mainly determine the properties of the fatty sulfates like foam intensive, surface activity and solubility. The later was decreased with increasing carbon chain