

## INTRODUCTION

The word surfactant derived from the contraction of the terms surface-active-agent and covers a group of molecules which are able to modify the interfacial properties of the liquids (aqueous or nonaqueous) in which they are present. The peculiar properties of these molecules reside in their amphiphilic character which stems from the fact that each surfactant molecule has both a hydrophilic part and a hydrophobic (lipophilic) part. As a result, they concentrate at the interfaces separating immiscible phases, thereby decreasing the interfacial tension.

Surfactants have the property of micelle formation that may be as fundamental as their property of being adsorbed at interfaces. It's the property of forming colloidal sized clusters in solution. Micelle formation, or micellization, is an important phenomenon not only because a number of important interfacial phenomena, such as detergency and solubilization that depend on the existence of micelles in solution, but also because it affects other interfacial phenomena, such as surface or interfacial tension reduction, that don't directly involve micelles (*Hiemenz, P.C., et al, 1997*). Changes in temperature, concentration of surfactant, additives in the liquid phase and structural groups in the surfactant all may cause change in the size, shape, and aggregation number of the micelle, with a structure varying from spherical through rod- or disk like to lamellar in shape (*Winsor, P.A., 1968*). It is well known that the physico-chemical properties of surfactants vary markedly above and

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below a specific surfactant concentration that is called critical micelle concentration (CMC) (*Myers, D., 1988 and Krawczyk, M. A., et al, 1991*). CMC values are important in virtually all of petroleum industry surfactant applications, where a surfactant must usually be present at a concentration higher than the CMC because the greatest effect of the surfactant, whether in interfacial tension lowering (*Shramm, L.L., 1994*) or in promoting foam stability (*Rieger, M.M., et al, 1997*), is achieved when a significant concentration of micelles is present.

### **I.1. Classification of Surfactants**

Depending on the nature of the hydrophilic moiety of the molecule, major surfactants can be divided into anionic, cationic, amphoteric, and nonionic classes. Regarding the hydrophobic moiety of the molecule, it is a hydrocarbon chain in most common surfactants; however, in some more specialized surfactants, this hydrophobic part can be a nonhydrocarbon chain such as a polydimethylsiloxane or a perfluorocarbon.

#### **I.1.1. Ionic Surfactants**

##### **I.1.1.1. Anionic Surfactants**

By definition, the hydrophilic part of the molecule carries a negative charge.

##### **I.1.1.1.1. Carboxylic Acids and Salts**

This group of surfactants includes three classes; first, carboxylic acids which derived from oleochemistry,

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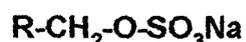
carboxylates salts can be produced by alkaline hydrolysis of animal and vegetable glycerides or from neutralization of fatty acids obtained by acidification of carboxylates, fatty acid salts show good water affinity. Ester carboxylic acids are the second class, they are monoesters of di- and tricarboxylic acids. These esters are produced by condensation reactions involving different types of molecule; either an alcohol with a polycarboxylic acid, or a hydroxyacid with a carboxylic acid, they show good foaming properties. The third class is ether carboxylic acids, they are formed by the reaction of sodium chloracetate with ethoxylated alcohols. Due to the addition of ethoxylated groups, they are more soluble in water and keeping the best properties of nonionic surfactants, where they do not exhibit any cloud point and show good wetting and foam stability.



#### **I.1.1.1.2. Sulfuric Acid Derivatives**

This group of surfactants contains two main types; the first one is alkyl sulfates, they are organic esters of sulfuric acid where the sulfur atom is bridged to carbon atom of the hydrocarbon chain via an oxygen atom. They are produced by sulfation of the corresponding fatty alcohols, the process is achieved by using either sulfuric acid, chlorosulfonic acid, amidosulfonic acid, or a gaseous sulfur trioxide/air mixture. They are generally good foamers, show excellent oil/water emulsifying and detergency properties. Alkyl ether sulfates are the second type, they are resulting from the sulfation of an ethoxylated

alcohol. Compared to alkyl sulfates, the alkyl ether sulfates show higher water solubility and, depending on the ethoxylation degree and they show foaming characteristics slightly lower than the corresponding alkyl sulfates.



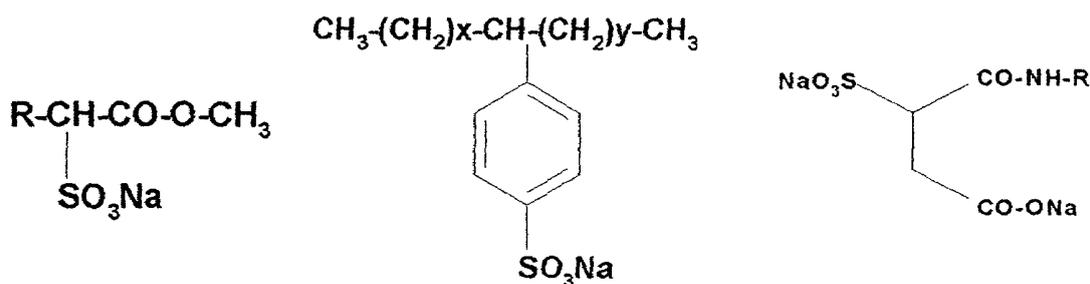
### I.1.1.1.3. Sulfonic Acids and Salts

There is an important difference between the above alkyl sulfates and the alkyl sulfonates. In the latter, the sulfur atom is directly linked to the carbon atom. The C-S bond makes sulfonates not prone to hydrolysis and they can be stored in a concentrated sulfonic acid form. The sulfonating agents are the same as those used in the sulfating reaction (chlorosulfonic acid, oleum, or gaseous sulfur trioxide); at variance, the sulfonation takes place on a hydrogen atom directly linked to a carbon atom. Sulfonic acids and salts are divided to five groups; the first is alkyl sulfonates, which includes primary and secondary paraffin sulfonates and  $\alpha$ -olefin sulfonates. paraffin sulfonates are generally formed by sulfoxidation of n-paraffins, they are very water soluble surfactants, good foamers, and good O/W emulsifiers.  $\alpha$ -Olefin sulfonates derive from  $\alpha$ -olefins that come from ethylene (Ziegler process) are preferred over those from petroleum cracking. The major sulfonation process uses sulfur trioxide as the reactant. The second type is alkyl aryl sulfonates, Linear chains are preferred over the branched ones due to their improved biodegradability, linear olefins or chlorinated straight chain paraffins with benzene in the presence of Friedel-Crafts-type

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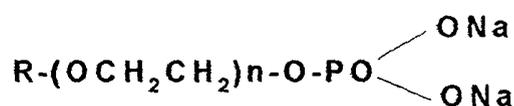
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catalysts ( $\text{AlCl}_3$  or HF) yields linear alkylbenzene (LAB). The sulfonation of LAB can be achieved using oleum, sulfuric acid, or gaseous sulfur trioxide. The sulfonate is obtained after neutralization of the sulfonic acid with an appropriate base. They exhibit good chemical and thermal stabilities, and used as emulsifiers, foaming, and dispersing agents. Sulfosuccinates are the third type, they generally result from the condensation of maleic anhydride with fatty alcohol, followed by sulfonation with sodium bisulfite ( $\text{NaHSO}_3$ ). When using equimolar ratios, monoesters are obtained, whereas with excess alcohol, diesters are obtained. Disodium salts of monoesters deliver good detergency and foam properties. The fourth type is sulfo fatty acid esters, the  $\alpha$ -sulfo fatty acid esters that have the sulfonate group linked to the carbon adjacent to the ester, and the  $\psi$ -sulfo fatty acid esters which have an internal sulfonate group statistically distributed along the carboxylate chain. Finally, fatty acid isethionates and taurides, where isethionates are prepared by the reaction of a fatty acid chloride with sodium isethionate, and show good wetting, foaming, and emulsifying properties. But, taurides or taurates are acylamino alkane sulfonates, they are prepared by the reaction of a fatty acid chloride with N-methyl taurine, they show good foaming and emulsifying properties.



#### I.1.1.1.4. Phosphoric Acid Esters and Salts

This class of surfactants includes alkyl phosphates and alkyl ether phosphates. These surfactants are produced by the reaction of fatty alcohols with two possible phosphating agents: orthophosphoric acid and phosphorus pentoxide. Resulting surfactants are mixtures containing mainly mono and dialkyl phosphoric acid esters; additionally, a small amount of unreacted phosphoric acid and unconverted alcohol. The sodium salts of alkyl phosphoric acid esters are readily water soluble and not affected by water hardness. When esterification is achieved with ethoxylated alcohols, it is possible to obtain a fine adjustment of the HLB and thereby vary the water solubility and wetting efficacy. Phosphate esters derived from straight alcohols remain stable at an extreme pH. Ethoxylated phosphate esters are only subjected to hydrolysis under acidic conditions. Phosphate esters show excellent heat stability. They impart antistatic and anticorrosion properties to the substrates on which they are adsorbed. Those with short alkyl chain exhibit hydrotropic properties.



#### I.1.1.1.5. Acylamino Acids and Salts

This class of surfactants includes three groups; acyl glutamates which formed by the acylation of a natural amino acid, the acyl glutamates contain an amide function which can be hydrolyzed under extreme pH conditions. The second type is

acyl peptides, they are formed from hydrolyzed proteins. An acylation reaction occurs on the amine terminal functions and, possibly, on some side groups and thus leaves the carboxyl groups free, which must be neutralized. These surfactants are sensitive to hydrolysis, because of the presence of amide functions. Acyl sarcosides are the third type, they are the condensation products of fatty acids with N-methylglycine (sarcosine). The properties of sarcosinates are similar to those of isethionates.

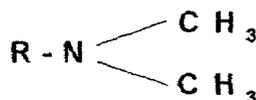
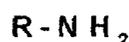


### I.1.1.2. Cationic Surfactants

Cationic surfactants differ from anionic and nonionic ones by the fact that they carry a positive charge on the hydrophilic part.

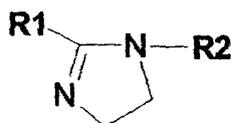
#### I.1.1.2.1. Alkyl Amines

This class of surfactant includes primary, secondary, and tertiary alkyl amines, especially their salts. The salts of tertiary amines obtained by neutralization of the amines with inorganic or organic acids have enough solubility to be fully considered as effective cationic surfactants. Organic salts are generally more water soluble than inorganic ones but are prone to the conversion into amides. Salts of fatty amines can deliver a germicidal activity; their fungicidal efficacy is enhanced when the amine is neutralized with salicylic or o-chlorobenzoic acid.



### I.1.1.2.2. Alkylimidazolines

Imidazolines are formed by reacting a fatty acid with a substituted ethylene diamine, heating the resulting amido-ethylamine yields the imidazoline, which is a five membered substituted ring. The imidazoline ring break down and open upon hydrolysis. Therefore, it is presumed that in aqueous solutions, the active molecule is no longer the imidazoline ring but it is the corresponding amido- amine.



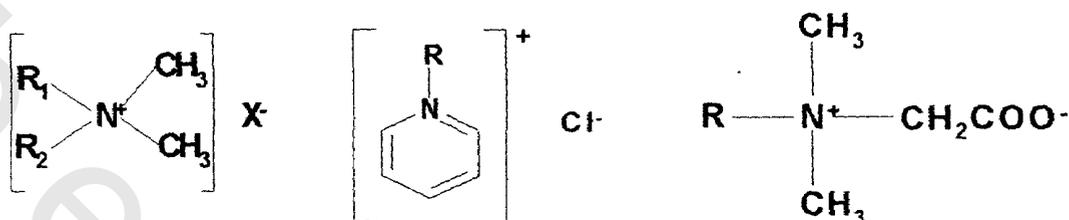
### I.1.1.2.3. Quaternary Ammonium Salts

This class of surfactants contains a positively charged nitrogen atom linked to four alkyl or aryl substituents. At variance with other amines, the positive charge is permanent, regardless of pH. It includes three groups; the first is tetraalkyl (-aryl) ammonium salts. They are prepared by the reaction of the respective tertiary amines with a quateranizing agent (methyl chloride, benzyl chloride, dimethyl sulfate, and rarely, long chain alkyl halides), they can adsorb on various substrates and impart various useful conditioning effects (softening, antistatic, corrosion inhibition). The second group is heterocyclic ammonium salts. They are derived from heterocyclic aliphatic or aromatic compounds in which a nitrogen atom constitutive of the cycle is quaternized. Alkyl betaines are the third group, which are N-trialkyl derivatives of amino acids. The positive charge is always carried by a quaternized nitrogen, whereas the anionic site can be a

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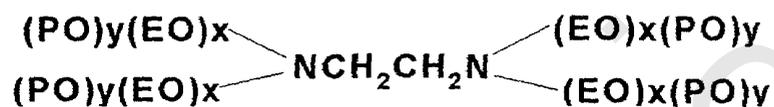
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carboxylate (betaine), a sulfate (sulfobetaine or sultaine), or a phosphate (phosphobetaine or phostaine). Betaines are good foaming, wetting, and emulsifying surfactants.



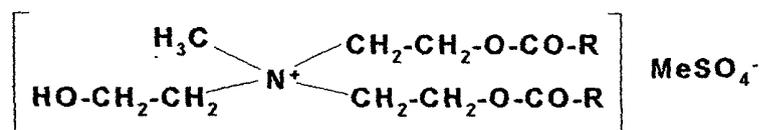
#### 1.1.1.2.4. Ethoxylated Alkyl Amines

Ethoxylated amines are formed by ethoxylation of primary or secondary fatty amines. With primary amines, the ethoxylation takes place initially on both hydrogens directly linked to the nitrogen and is pursued, afterward on the terminal hydroxyl groups. The ethoxylation degree mainly governs the hydrophilic character of the fatty amine. Tetrafunctional products are obtained by successive reactions of ethylene diamine with ethylene oxide and propylene oxide; four block copolymer chains are obtained.



#### 1.1.1.2.5. Esterified Quaternaries

Esterified quaternaries (esterquats) are produced by the esterification of the hydroxyl groups of secondary or tertiary amino alcohols with selected fatty acids. The resulting esteramine is further quaternized by adequate quaternizing agents. They are also nonsensitizing agents in the dermatological sense and are readily biodegradable.



### I.1.1.3. Amphoteric Surfactants

These surfactants can carry a positive charge on a cationic site and a negative charge on an anionic site. The charge of the molecule must change with pH, showing a zwitterionic form at an intermediate pH. This class is divided to two types; acyl ethylenediamines and derivatives is the first type, they are made by the reaction of an alkylimidazoline with chloroacetic acid or with acrylic acid. These surfactants show amphoteric properties and zwitterionic form appears around neutral pH. The second type is N-alkyl amino acids or imino diacids; they can be produced by the reaction of chloroacetic acid or acrylic acid with an alkyl amine. Alkylation of the primary amine leads to the secondary or tertiary amine which is more easily protonated than the original primary amine. The sodium salts of alkylamino acids are readily soluble in acidic and alkaline solutions. These surfactants are used as foaming agents in fire-fighting foam production appliances.



### I.1.2. Nonionic Surfactants

By definition, the surfactant molecule does not carry any charge. These surfactants include the following types:

### **I.1.2.1. Alcohols**

Fatty alcohols are not generally considered to be true surfactants, despite their surface and interfacial activities, because these molecules exhibit very weak solubility in water. Alcohols are the precursors of other surfactants such as ethoxylated alcohols, which have been so far the most widely used nonionics. Fatty alcohols are synthesized by two major processes; Ziegler process which uses ethylene and trialkyl aluminum as major reactants and yields even numbered alcohols with some branching and secondary alcohols. The oxo-process is based on a hydroformylation reaction and uses an olefin, hydrogen, and carbon monoxide as raw materials and the transition metal hydrocarbonyl  $[HM(CO)_n]$  as the catalyst; cobalt is the most commonly used metal. The resulting aldehydes are further converted to corresponding alcohols with hydrogenation catalysts.

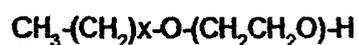
### **I.1.2.2. Ethers**

This group of surfactants includes four types; alkoxyated alcohols which covering ethoxylated or propoxylated alcohols. Ethoxylated alcohols are produced from the reaction of fatty alcohols with ethylene oxide. Propoxylated alcohols are obtained with propylene oxide. Due to the low hydrophilicity of propylene glycol, this group does not increase water solubility of the molecule. Therefore, the same surfactant molecule generally combines ethylene oxide units to compensate for the hydrophobicity of polypropylene glycol chains. The second type is EO/PO block polymers, which is a polymeric surfactant, consists of the combination of the

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assembly of polypropylene glycol chains and polyethylene glycol chains. A major property of EO/PO nonionics is their low foaming profile. The third type is alkylpolyglucosides, they are produced by the alkylation of short chain glucosides resulting from the acidic alcoholysis of polysaccharides such as starch. They are good emulsifiers, and provide good wetting and foam profile. Finally, Ethoxylated Oils and Fats is the fourth type, they are the ethoxylated derivatives of lanolin and castor oil. Ethoxylated products of lanolin and castor oil are good and excellent emulsifiers, respectively.



### I.1.2.3. Alkanolamides

This class of surfactants divided to alkanolamides, which are N-acyl derivatives of monoethanolamine and diethanolamine, they are good foamers, and ethoxylated alkanolamides, which are produced by the reaction of an alkanolamide with ethylene oxide leads to an ethoxylated amide, they have benefits of thickening, and foam stabilization.



### I.1.2.4. Esters

This class of surfactants contains many types; first, ethoxylated fatty acids which comprise monoesters and diesters that result from the reaction of fatty acids with either ethylene oxide or polyethylene glycol, they show foam quality poorer than other nonionics. They are chemically unstable, and readily hydrolyzed under acidic or alkaline conditions. The second type is glycol esters, glycerol esters, and ethoxylated