Introduction

1. INTRODUCTION

1.1 Synthetic surface active agents:

Surface active agents can be defined as those which affect the interfacial tension between two surfaces such as solid / liquid, liquid/liquid, or even liquid/gas. They include compounds with emulsifying, wetting, softening, penetrating and detersive properties. As can well be understood, not all surface active agents must fulfill all the above requirements. The chemical constitution of the surface active agents is an important factor in its behavior. For a compound to be a surface active agent, it is necessary that the molecule should contain two kinds of groups, one lipophilic or oil-soluble and the other hydrophilic or water-soluble. These groups enable the compound to locate itself at an oil-water interface, in such a manner that oil-soluble group is in the oil layer, while the water-soluble one remains in the aqueous phase. It is because these essential groups can occur in so many different forms, there exists a wide variety of surface active agents.

In general, however, the oil-soluble grouping is provided by a hydrocarbon chain of sufficient length to give the required oil solubility. The water-soluble grouping can be sulphate, sulphonate, carboxylate, hydroxyl and other polar groups.

2. CLASSIFICATION OF SURFACE ACTIVE AGENTS

Synthetic surface active agents fall into the following main groups:

2.1 Nonionic surfactants:

These surfactants do not ionize in solution. Commercially available nonionic surfactants are of two types:

1- Long-chain fatty acid esters derived from ethylene or propylene oxide, polyhydric alcohols such as glycols, glycerol, sorbitol or sucrose.

2- Eithers of long-chain fatty alcohols, alkylated phenols or mercaptans which were prepared by direct reaction with ethylene or propylene oxide.

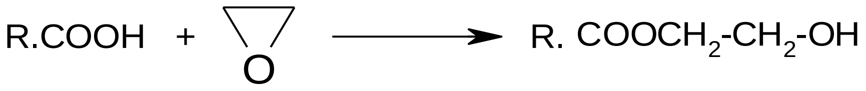
Ethylene and propylene oxide condensation is one of the principal processes which was employed to introduce hydrophilic functional group into the molecular structures of organic compounds. The ultimate objective of the process is the production of surface active agents having the desired hydrophile-lipophile balance for such commercial applications as detergency, emulsification, wetting, textile processing, etc. Ethylene or propylene oxide is characterized by their great reactivity, the three-membered ring is under great strain and can readily be opened, and is therefore easily added to compounds having active hydrogen atom contained in a functional group with which it is being condensed to form a hydroxyl ethyl or hydroxyl propyl derivatives. The active hydrogen of hydroxyl ethyl or hydroxyl propyl derivative is then available for reaction with an additional epoxide group and by repetition of this process, a poly oxyethylene or poly oxypropylene compound can be formed.

Most of the important nonionic surfactants are synthesized in an anhydrous environment in the presence of an alkaline catalyst.

Classification of nonionic surfactants:

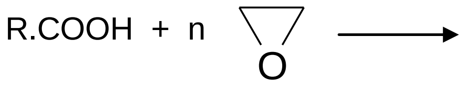
2.1.1 Carboxylic acid ethoxylated surfactant:

The addition of ethylene oxide to a carboxylic acid takes place to give monoglycol ester (1):



(1)

This results in the production of the monoglycol ester of the carboxylic acid. The ethoxylation will then be continued with the formation of poly ethylene glycol mono esters as (2)[1,2]:



$R. COO(CH_2-CH_2-O)_n+1H$ (2)

Formation of the diesters (3) will take place by the transesterification using alkaline catalysts.

$$2R\text{-}COO(CH_2\text{-}CH_2\text{-}O)_mH \longrightarrow R\text{-}COO(CH_2\text{-}CH_2O)_n\text{-}COR + HO\text{-}(CH_2\text{-}CH_2O)_n\text{-}H \quad (3)$$

The polyethylene glycols are produced and the product will consist of mono and diesters of polyethylene glycol and of free polyethylene glycol. A similar reaction takes place when one molecule of carboxylic acid is esterified with one molecule of poly ethylene glycol[3]. The ester structure of these surfactants makes them generally unsuitable for use in strong acid or alkali solutions because of its tendency to hydrolyze.

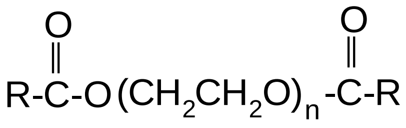
The principal carboxylic acids used in the manufacture of polyoxyethylene ester condensates are the fatty acids. Castor and hydrogenated caster oils fatty acids have main composition 85% ricinoleic and 12. hydroxystearic acids respectively [4]. The reaction of ricinoleic and/or 12-hydroxystearic with EO and /or PEG (Mol. Wt. 1000), afforded ricinoleic polyethylene glycol ester (4).

Polyethylene glycol ricinoleate (4)

And/or 12-hydroxystearic acid polyethylene glycol (5). The products are useful as defoamer in sugar solution and laundry detergent [5].

Polyethylene glycol 12-hydroxystearate (5)

Furthermore, fatty acids (linear or branched) based upon PEG diester, especially PEG-600 (6) used as emulsifiers in the pharmaceuticals, cosmetics, food industry and as wetting agents in the manufacture of fibers and paints, and also, as plasticizers in the plastic industry according to their type and purity degree[6,7].



$$R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O(CH_2CH_2O)_n\text{-}\overset{\overset{O}{\|}}{C}\text{-}R$$

(6)

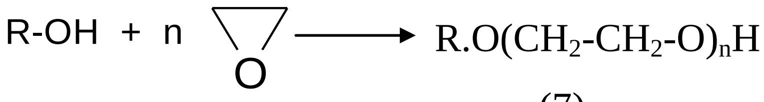
where R = linear or branched (C_{10}-C_{18}), n = 14 mole, EO (PEG Mol.wt. 616).

The foaming properties of the poly oxyethylene tall oils are quite low, which makes them adaptable to mechanical washing operation where strong agitation is encountered. They also exhibit good tolerance to metallic ions found in hard water. Carboxylic acid esters of aliphatic and cyclic polyglycols are widely used as bases for ethoxylation**[8,9]**. The variables such as the type of the fatty acid used, the degree of esterification, and degree of ethoxylation made the number of these compounds quite large. The sensitivity of the ester linkage to hydrolysis limited the use of these compounds in spite of their excellent surfactant properties. These products find more used in emulsification and specially in detergent applications**[10]**.

Another type of nonionic surfactants which is complex mixtures, was prepared by the reaction of glyceride, such as caster oil or soya bean oil, with ethylene oxide or alternatively by reaction of these glycerides with polyoxyethylene or / and polyoxypropylene. The products are principally used as de-emulsifiers and stabilizers for synthetic lattices**[11]**. Oxypropylated diol monoesters of palmitic and oleic acids were prepared by reacting oxypropylated diols with boric acid, esterifying the resultant borate with fatty acid, and selectively hydrolyzing the borate ester. Also their surface active properties were evaluated. An increase in molar mass of oxypropylated diol increased the surface tension. The presence of a double bond improved the wetting and emulsifying properties[12].

2.1.2 Fatty alcohols ethoxylated surfactant:

Ethylene oxide adds to alcohols to yield ether adducts (7):



(7)

The hydrogen of the hydroxyl group of the starting material is less active than that present on the terminal hydroxyl groups of the glycol ethers. Quantitative yields of monoglycol are not therefore obtained at first when reacting with ethylene oxide, but the higher polymer homologues start to form, while the free alcohol is still present[13]. Consequently, the addition rate is slower at the start then increases gradually and becomes constant when all has been converted to the monoglycol ether. The activity of hydrogen differs in primary, secondary and tertiary alcohols. The length of the hydrophobic part and its structure either straight or branched also has the same effect[14-15].

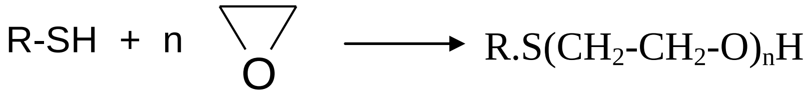
The nonionic surfactants derived from alcohols have excellent surfactant properties and chemical stability[16,17]. The principal alcohols used in preparing these surfactants include the naturally derived fatty and rosin alcohols, synthetic lipophilic alcohols, and hydrophilic polyhydric alcohols. The lipophilic alcohols derived from natural fats and oils were among the first materials used in preparing nonionic polyoxyethylene surfactants, and they continue to represent the largest segment of aliphatic polyether class. These alcohols are prepared from fatty esters by sodium reduction or by catalytic hydrogenation.

The fatty alcohols used in producing aliphatic polyoxyethylene ether are lauryl, oleyl, cetyl, tallow and hydroabietyl. The aliphatic polyoxyethylene ethers exhibit excellent stability to acids and bases hydrolysis, but alkylethers are often preferred to other surfactants when using in raw wool scouring, dye leveling, liquid dish washing detergents, and also as emulsifier for a variety of materials including silicones and polyethylene[18].

Another hydrophobic base including linear propylene oxide polymers were described. The polyoxypropylene ethoxylates are to be used in conjunction with other surfactants when high efficiency of wetting or detergency properties are required[19].

2.1.3 Mercaptan ethoxylated surfactant:

Alkyl mercaptans condense with ethylene oxide to form polyoxyethylene thioethers (8).



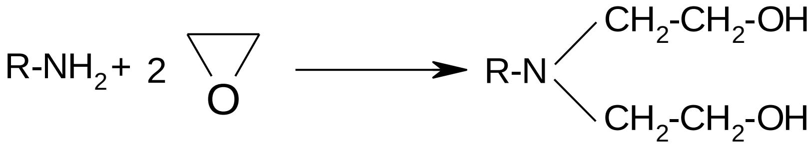
(8)

The reaction of the mercaptan with one molecule ethylene oxide, gives the monoglycol ether, then further ethoxylation, gives a mixture showing a poison distribution of the polymer homologues.

Mercaptan adducts are unstable in the presence of chlorine, bleaching agents, and stronger acids, but are stable in neutral and in warm, strong alkaline solution[20,21]. Their use is limited because of their smell. The alkyl mercaptans usually employed for condensation with ethylene oxide are of the C_{10} to C_{18} branched chain types made from olefinic polymers. The mercaptan adducts are used as emulsifiers, detergent santitizers and dairy cleaners.

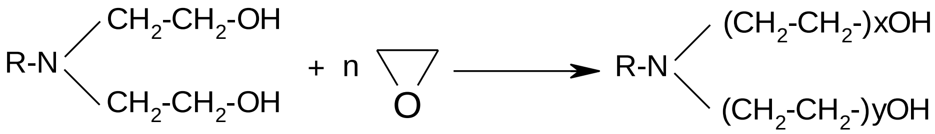
2.1.4 Amine ethoxylated surfactant:

The condensation of higher alkyl amines with ethylene oxide produces a nitrogen-based polyoxyethylene surfactants (9).



(9)

The degree of substitution depends, amongst other conditions, on the choice of the catalyst and the temperature[22,23]. A polymer homologue (10) will be formed if two ethylene oxide units alkyl amine adducts are reacted with additional ethylene oxide as follows:



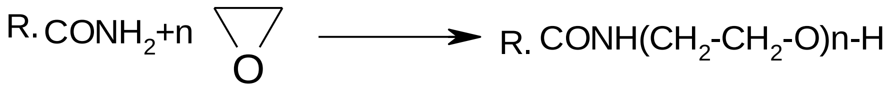
(where $x + y = n+2$) (10)

The most distinguishing chemical characteristics of the polyoxyethylene alkyl amines are their cationic properties and their ability to form salts with acids in a similar manner to the alkyl amines themselves. As the number of moles of the condensed ethylene oxide is increased, the cationic activity of these compounds diminishes and they become more like nonionic compounds in their behavior towards anionics. The cationic properties of the polyoxyethylene alkyl amines result in their preferential adsorption on negatively charged surface, such as cellulosic and certain synthetic textile fibers[24]. The alkyl amines which are widely used in the preparation of polyoxyethylene condensates are the primary fatty amines and dehydroabietyl amine derived from rosin. The nature of the alkyl amine has an influence on the physical and functional properties of the polyoxyethylene derivatives. Branched chain alkyl groups have been found to give properties different from the straight chain alkyls, also differences in properties between derivatives of saturated and unsaturated alkyl groups occurred [25,26].

A series of fatty amines (undecyl, tridecyl, pentadecyl and heptadecyl amines) was prepared from the corresponding commercial fatty acids. The alkali-catalyzed reaction of propylene oxide with these fatty amines was carried out to obtain nonionic surfactants containing an approximate range of 4-8 propylene oxide moles per molecule. The surface active properties of these products were evaluated. They generally showed good properties. A saturated fatty amines mixture was treated in the same manner, giving a product with useful surface active properties[27].

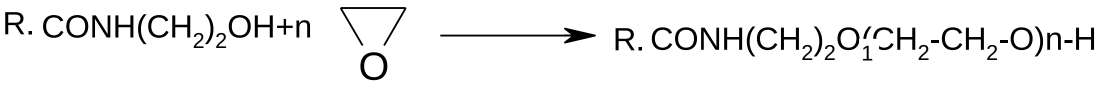
2.1.5 Amide ethoxylated surfactant:

The amide adducts (11) are obtained by the addition of ethylene oxide to acid amides as follows:

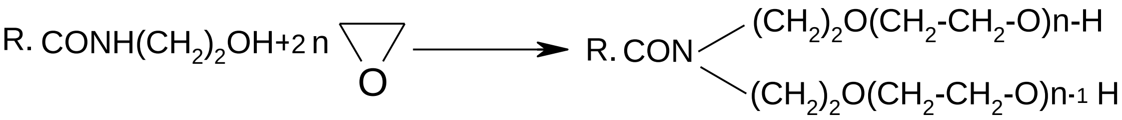


(11)

Ethylene oxide can be condensed with each of the two hydrogens in a higher alkyl amide to form N, N-disubstituted polyoxyethylene acid amides[1]. These products are similar to the polyoxyethylene esters in their physical properties but are generally more resistant to hydrolysis. They are used principally as emulsifiers and are frequently combined with other nonionic surfactants or with anionic to obtain the desired performance in certain applications. The alkylolamide types of product are basically amides of an alkylol amine and a fatty acid, certain members of this class exhibit detergency, and others do not. To convert the non-detergent materials into detergents, they can be condensed with ethylene or propylene oxide[28-29]:



(12)



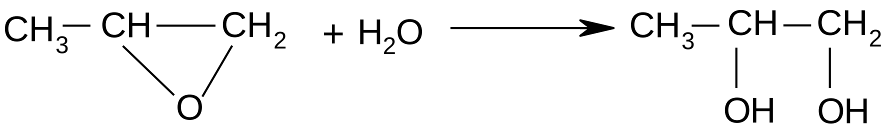
(13)

Again, the last reaction product is shown to have the ethylene oxide equally divided between the two possible directions, but there is no absolute reason for this. The ethylene oxide is divided at random in the two directions, may be added to one H at NH_2 to form (12), or added to two H of NH_2 to form (13).

2.1.6 Condensation products of ethylene and propylene oxides:

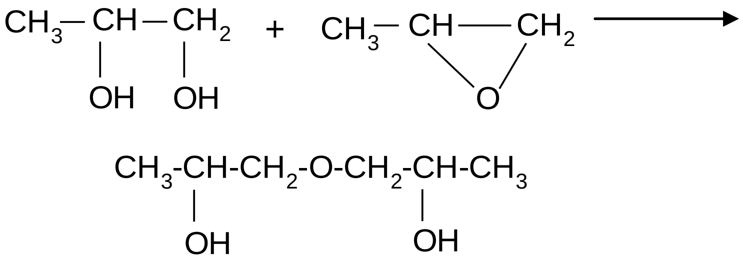
Recently, certain nonionic manufacturers have found that a combination of propylene oxide with ethylene oxide gives enhanced detergency. The product is first condensed with one molecule of propylene oxide, and the required amount of ethylene oxide is then added.

In this field, a new and interesting series of materials known as the pluronics are prepared. Propylene oxide reacted with water to form propylene glycol (14).



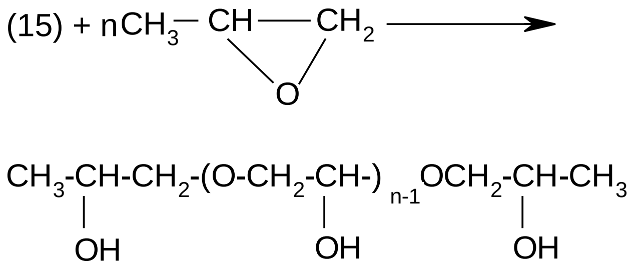
(14)

This propylene glycol reacted with a further molecule of propylene oxide yielding dipropylene glycol (15).



(15)

Further addition of propylene oxide, give rise to polypropylene glycol (16).



$$CH_3\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_2\text{-}(O\text{-}CH_2\text{-}\underset{\displaystyle OH}{CH}\text{-})_{n-1}OCH_2\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_3$$

(16)

Although initially soluble in water, this polypropylene glycol becomes insoluble when the molecular weight reaches approximately 1000. This product having two terminal –OH groups is thus eminently suitable as the starting hydrophobe for condensation with ethylene oxide. This leads to the series of pluronic detergents whose general formula is (17):

$$HO\text{-}(C_2H_4O)_a\text{-}(C_3H_6O)_b\text{-}(C_2H_4O)_a\text{-}OH$$

(17)

By varying the amounts of propylene and ethylene oxides, the hydrophobe / hydrophile balance can be adjusted to any particular requirement. It is of interest to record the results of research done in Germany, where both the hydrophobic portion of the molecule and the number of ethylene oxide units were varied then the last product was sulphonated, in an attempt to establish the best possible structure for a particular process. For this work it appeared that all of the following had roughly the same detergency.

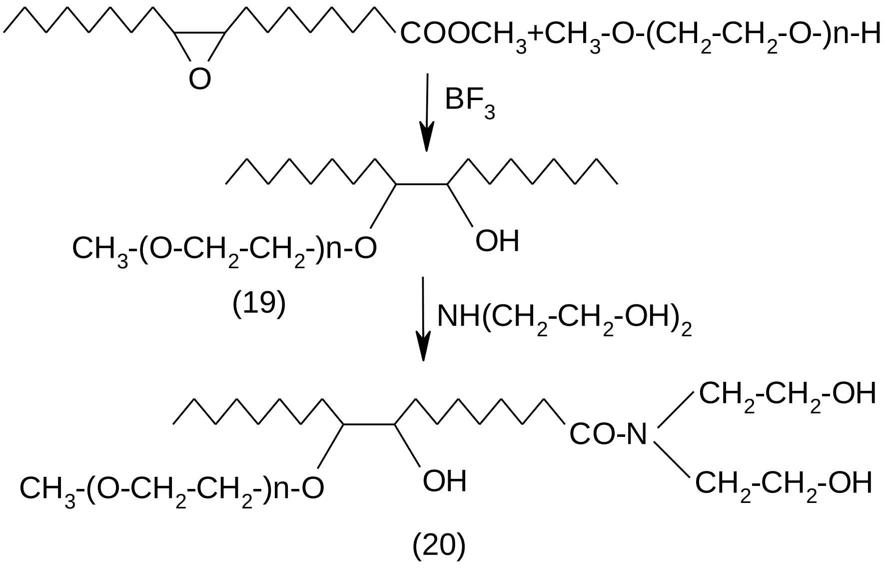
Alkyl-beta-naphthol with 6-7 carbons in the side chain and 4 molecules of ethylene oxide, sulphated and neutralized. Dialkyl phenol with 12-14 carbons in the side chain and 7-molecules of ethylene oxide. It will be seen that sulphation of a nonionic detergent of this type can result in a saving of ethylene oxide. It is, however, questionable whether sulphation of an already first-class detergent will improve the detergency further.

2.1.7 Alkylolamides:

Another group of synthetic detergents which falls into the nonionic category is the fatty acid alkylolamides. They were first prepared by reacting fatty acids with alkylol amines[30-31] (18):

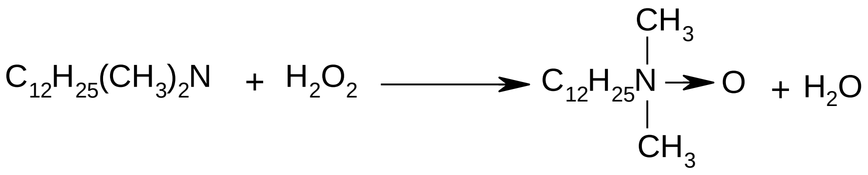
$$RCOOH + H_2N\ C_2H_4OH \longrightarrow RCONHC_2H_4OH + H_2O \qquad (18)$$

The reaction outlined above is between a fatty acid and a monoethanol amine. This has neither detergent properties nor soluble to any great extent in water. The uses of this type of compounds will be dealt with below. However, if certain fatty acids are reacted with a dialkylol amine as above, and if the amide formed is then reacted with a further molecule of the dialkylol amine, the resultant product becomes water soluble and has detergent properties. The materials commonly used for this condensation are lauric acid, myristic acid, coconut fatty acids, palm kernel fatty acids, and occasionally the fatty acids of vegetable oils with higher molecular weights. The alkylolamines used are generally monoethanol amine and diethanolamine, but the isopropanol amines are also employed. The alkylol amides are rarely used by themselves as detergents, but as additives to other detergent materials, for example, with dodecyl benzene sulphonates. They act as foam boosters and increase the detergency synergistically, and in liquid products they increase viscosity without increasing the cloud point. They also have the valuable property of acting as skin protecting agents, whereas detergents in general tend to defat the skin, the emoliient effect of these alkylol amides helps to overcome this tendency. Monoethanolamides, especially those derived by reacting a fatty acid methyl ester with monoethanol amides, are further condensed with ethylene oxide. Depending on the type of fatty acid methyl ester and the number of molecules of ethylene oxide, nonionic surfactants with excellent detergency power may be obtained[32], prepared alkylol amides from methyl 9,10-epoxy stearate by reacting with a polyoxyethylene alcohol in presence of BF_3 as dehydrating agent to produce methyl ester of the hydroxyl alkoxypolyoxy ether, (19) substituted carboxylic acid followed ammolysis using diethanol amine to give (20).



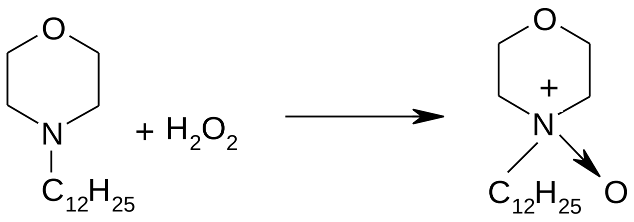
2.1.8 Fatty amine oxide:

A further type of nonionic detergent is the group known as fatty amine oxide (21, 22). These again offer many different possibilities, but basically they are prepared by treating tertiary amines with hydrogen peroxide. For our purposes, these amines which contain at least one long-chain group, usually from a fat source are detergents. Two typical reactions are shown.



$$C_{12}H_{25}(CH_3)_2N + H_2O_2 \longrightarrow C_{12}H_{25}\overset{CH_3}{\underset{CH_3}{N}} \rightarrow O + H_2O$$

(21)



(22)

Again, these two representative types include the dodecyl grouping. These amine oxides are in themselves good detergents[33,34], but their main use is as foam boosters, viscosity increase, and skin protecting agents in liquid detergents. They are sticky materials and are not suggested for incorporation into powdered materials.

2.2 Anionic surfactants :

These are capable of undergoing ionization in solution to give oil-soluble anion and a metallic cation, the anion being the active part of the molecule.

Anionic surfactants include:

1- Carboxylic acid soaps RCOONa.
2- Alkyl sulphates: primary, $ROSO_3Na$ and secondary $R\text{-}CH\text{-}(OSO_3Na)CH_3$.
3- Alkyl sulphonates RSO_3Na.
4- Alkyl aryl sulphonates e.g.: isododecyl benzene sulphonate

They are surface active substances in which one hydrophobic hydrocarbon group is connected with one or two hydrophilic groups dissociate in aqueous medium into negative charge (anion) and positive charge (cation) the anion is the carrier of the surface active properties as: Akylbenzene sulfonate ($R\text{-}C_6H_4.\ SO_3\ Na$, $R= C_{3-10}$), Sodium salt of α sulfonated fatty acid methyl ester [$R\text{-}CH\ (SO_3Na).COOCH_3, R=C_{12-16}$] this by far the largest class of detergents[35]. In practice and for the purposes of this study which does not claim to deal with the very specialized or proprietary types of detergents, we can safely say that, the anionic detergents fall into the main groupings as the following:

Synthesis of anionic surfactants:

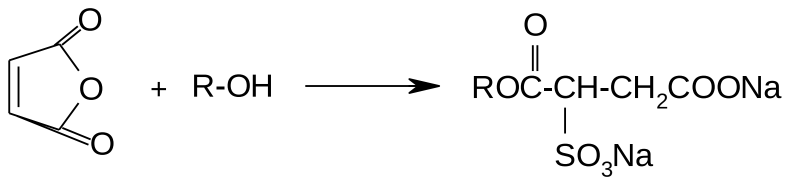
2.2.1 Fatty alcohol sulfates.

The normal C_{8-18} alkyl sulfates were found to posses surface-active properties similar to those of fatty soaps and they were the first synthetic detergents produced commercially. They are prepared by sulfation of either alcohols or olefins. The product is neutralized and may then be separated from the excess sodium sulfate or the latter is left in. Certain special sulfating methods used:

1- Sulfation with the sulfur trioxide in dioxan complex[36].
2- Sulfation with the sulfur trioxide pyridine complex with may be made from pyridine and chlorosulfonic acid in an inert solvent.
3- Sulfation with sodium or potassium chlorosulfonate[37].
4- Sulfation with sulfuric acid and urea or other lower acid amide or with the complex addition of chlorosulfonic acid and urea or other lower acid amide[38].
5- Sulfation with the complex addition of sulfur trioxide and sodium nitrite.
6- A number of other sulfating methods have been described e.g. sulfating in the presence of acetic acid or acetyl chloride, heating fatty alcohol's with ammonium hydrogen sulfate between (100-150)^{O}C.[39]

Anionic surfactants prepared from sulfates of ethoxylated hydrophobes have found broad acceptance because of their ability to impart excellent foam stability to formulations, especially in the presence of greasy soil. In addition, they are relatively low in cost as compared with other competitive materials.[40]

Disodium of 4-alkyl-3-sulfonatosuccinates (23) were synthesized by using maleic anhydride with an fatty alcohol, then added an aqueous sodium sulfite or bisulfite solution and the mixture was neutralized by sodium hydroxide to yield anionic surfactants. The properties of these products were evaluated.[41-43]



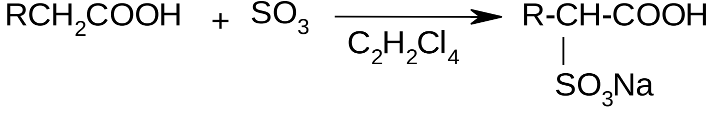
(23)

R= C_8, C_{12} and C_{18}

The simultaneous sulfonation and alkylation of aromatic compounds using olefin sulfonic acid (s) have produced a new family of anionic surfactants. The resulting alkyl aryl sulfonic acids differ from existing products by having the sulfonate group asttached to the alkyl chain rather than the aromatic ring. Aromatic compounds that lend themselves to the new process include benzene, alkyl benzene, phenol, alkyl phenol, alkoxylated phenol, alkoxylated alky phenol, naphthalene and alkyl naphthalene. Any type of olefin that can be sulfonated used as the starting material, which is easily prepared. Alkyl benzene sulfonates of different alkyl chains C_{12} to C_{14} are studied, the surface and thermodynamic properties of these surfactants as well as their efficiency as collectors are also studied.

2.2.2 Fatty acid and ester:

A series of alpha-sulfo fatty acid (24) has been prepared by treating the fatty acid in tetra chloroethylene solution with sulfur trioxide as.



$$\mathrm{RCH_2COOH} + \mathrm{SO_3} \xrightarrow[\mathrm{C_2H_2Cl_4}]{\mathrm{NaOH}} \begin{array}{l}\mathrm{R{-}CH{-}COOH}\\ \quad\ |\\ \quad\mathrm{SO_3Na}\end{array}$$

(24)

This process is interesting since it converts fatty acid to lime resistant products of good detergency. These products differ from the sulfated glycerides in having much greater solubility, foaming and wetting power, where the α-sulfopalmitic acid was found to be the best detergent[44].

Butyl oleate sodium sulfate as a mild anionic surfactant was synthesized from rice bran oil (comprising of oleic and linoleic acid), butanol, and fuming sulfuric acid by esterfaication, sulfonation and neutralization[45].

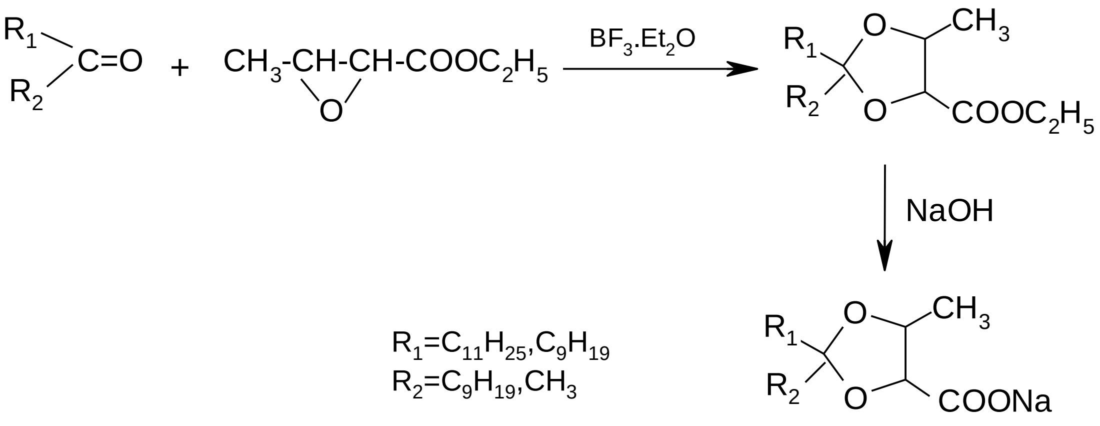
Vegetable oils are sulfated or sulfonated to give anionic surfactants. The product is controlled to allow the deviation of the acid number after the reaction and the separation to fall into a set limit, thus triethylene glycol lauryl ether was treated with SO_3 and separated with the deviation of acid number 0-1[46].

Novel sulfonated ester is (sodium sulfonated ester) types of surfactants were easily prepared by acid-catalyzed esterification of 1-o-alkyl glycerols with bromocarboxylic acids. These surfactants have a good solubility in water.[47]

Anionic surfactants containing heterocyclic ring:

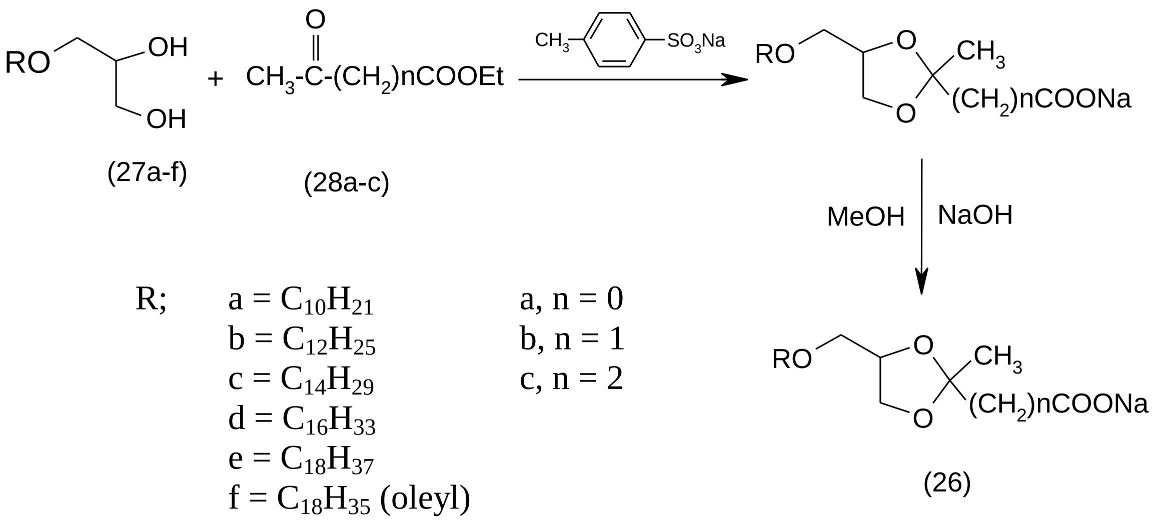
2.2.3 Surfactants bearing 1,3-dioxalane ring.

Dioxalane ring (25) was prepared from the reaction of fatty ketones with fatty epoxy esters in presence of ethylene oxide and boron trifloride followed by alkaline hydrolysis.[48]



(25)

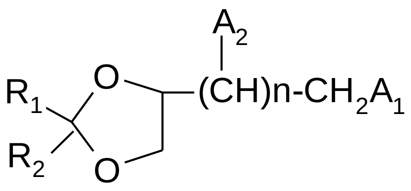
Dioxalane (26) as new soap - type of surfactants was prepared in a good yield by the acid catalyzed condensation of 1-o-alkyl glycerol; alkyls: decyl, dodecyl, tetradecyl, heptadecyl, octadecenyl or cis 9-octadecyl (27) with ketocarboxylic acid ester (28), followed by-alkaline hydrolysis without any expensive reagent, or special equipment.[49]



(27a-f) (28a-c) (26)

R; a = $C_{10}H_{21}$ a, n = 0
b = $C_{12}H_{25}$ b, n = 1
c = $C_{14}H_{29}$ c, n = 2
d = $C_{16}H_{33}$
e = $C_{18}H_{37}$
f = $C_{18}H_{35}$ (oleyl)

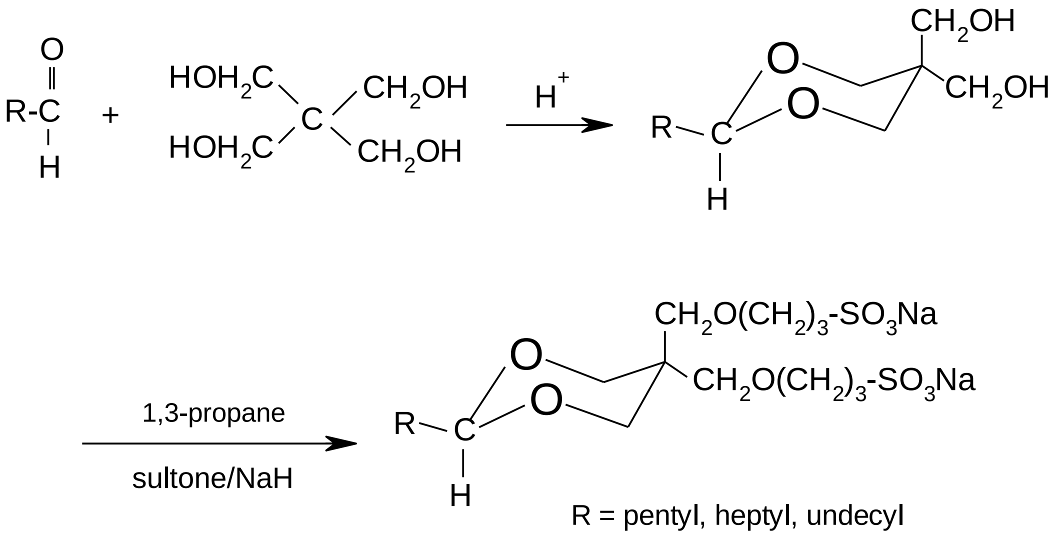
Dioxalanes (29) were prepared by condensation of 2-undecanone with glycerine followed by sulfonation.[50]



(29)

R_1 = nonyl   A1 = OSO_3Na
R_2 = Me A_2 = OH
n = 0, 1

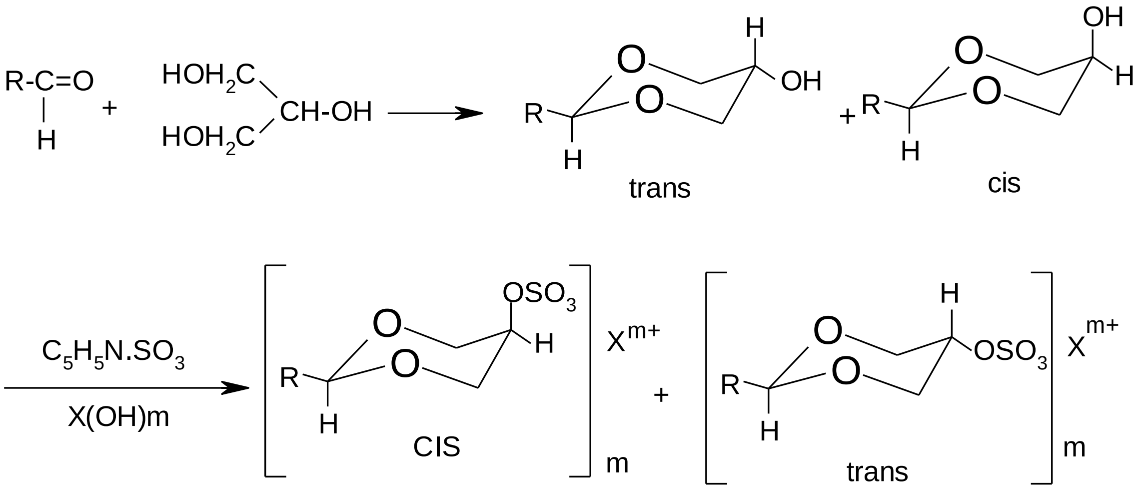
Dianionic cleavable surfactants (30) were prepared by the condensation of aldehydes with 2,2-bis (hydroxymethyl)-1,3-propandiol, followed by reaction with 1,3-propane sultone in presence of NaH[51]. The critical micelle concentration, kraft point and acid hydrolysis of these surfactants were determined and show a good results to make them for choice in industrial applications.



R = pentyl, heptyl, undecyl

(30)

Recently[52,53] synthesis and surface properties of chemodegradable anionic surfactants (31a,b) were described. These surfactants were prepared form the reaction of aliphatic aldehydes with glycerol followed by separation in high yields of individual geometric cis and trans 2-n-alkyl-5-hydroxy-1,3- dioxanes, followed by sulfation with sulfur trioxide-pyridine complex and finally neutralization with NaOH, KOH, LiOH, $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$ and / or NH_4OH. It was shown that the surface activity of these compounds is influenced by both their geometric structures and mono-and di-valent counterion.

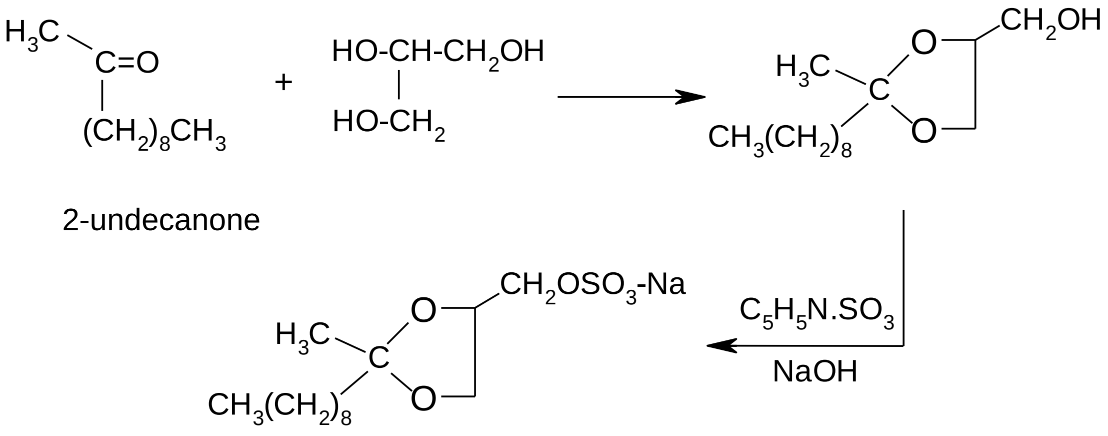


(31a) (31b)

R = C_nH_{2n+1}
n = 7-13, m = 1,2
x = Na, K, Li, Mg, Ca, Ba, or NH_4

An anionic dioxalane surfactant prepared from condensation of 2-undecanone with glycerin and sulfated to give (32) with surface tension sat (CMC) 39.6 dyne /cm, kraft point (1%) < 0^{o}, and (CMC) 1.0 x 10^{-2} mol^{-l}.

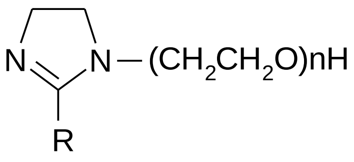
Anionic surfactants (32) was completely decomposed by 10N HCL at 25^{O}C for 1 hr due to the presence of easily degradable dioxalane ring[54].



(32)

2.2.4 Surfactants bearing imidazoline ring:

Acylation of imidazoline derivatives (33) with maleic anhydride in the presence of water and sulfation with Na_2SO_3 to give foaming synthetic detergents[55].

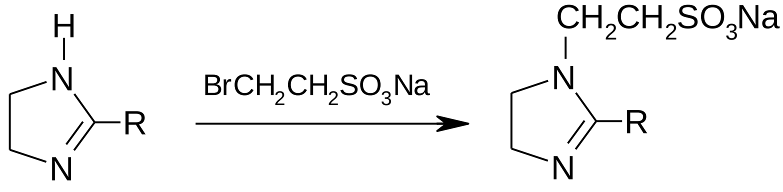


R = C_9-$_{17}$ alky

n = 1-30

(33)

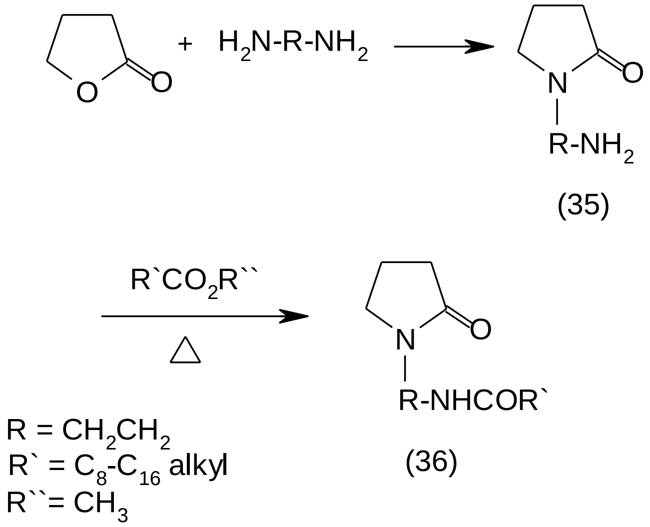
Sulfo-imidazline betaine anionic surfactants (34) were synthesized by the reaction of hydrophilic material Na 2-bromoethyl sulfonate with alkyl imidazline (alkyl in surfactants range). The surfactants have low surface tension, good foaming and low (CMC)[56].



(34)

2.2.5 Surfactants bearing pyrrolidone nucleus

The reaction of butyrolactone with primary diamines at high temperatures produced N-alkyl substituted pyrrolidones which react with excess of diamines, to afford N-amino-alkyl pyrrolidones (35), which can be further condensed with fatty acids, anhyrides, acid chorides, or esters to produce amidoalkyl pyrriolidones (36). When the fatty acids are in the surfactant range (C_8-C_{16}), a highly surface active compounds are formed[57].

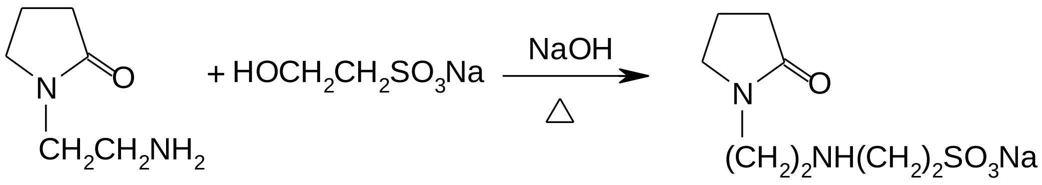


(35)

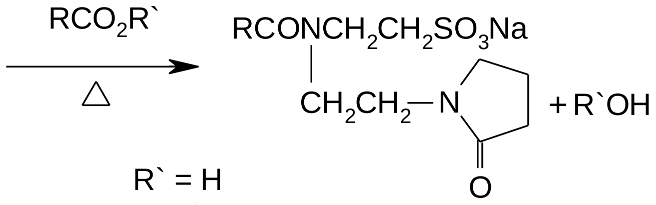
(36)

$R = CH_2CH_2$
$R` = C_8$-C_{16} alkyl
$R`` = CH_3$

N-Amino-alkyl pyrrolidones condensed with sodium isothionte to form the N- (pyrrolidonyl-ethyl) taurine sodium salt (37), which can be further condensed with lauric acid to form the N-(pyrrolidonyl-ethyl) N-lauroyl taurine salts (38)[58].



(37)

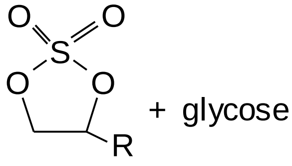


R` = H
R= $C_{11}H_{23}$

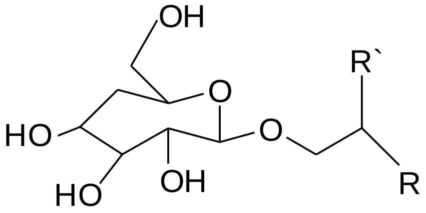
(38)

2.2.6 Surfactant bearing pyrane ring:

New surfactants of glucose were synthesized from cyclic sulfates as alklating agents in anomeric-o-alkylation of glucose, where the reaction of sulfate (39) with glucose directly furnished the corresponding gluciopyranosyl-oxymethyl sulfates (40)[59].



(39)

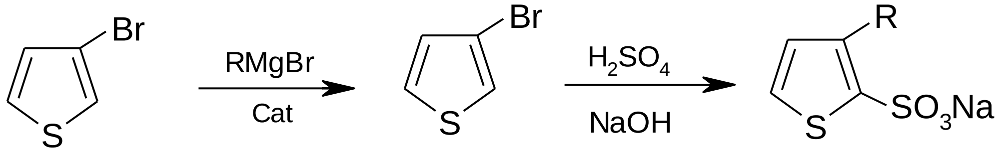


(40)

R = decyl, dodecyl, tetradecyl
R` = OSO_3Na

2.2.7 Surfactant bearing thiphene ring:

The sodium salts of 3-n-alkyl thiphene were obtained[60,61] from the reaction of 3-bromo thiphene and n-alkyl magnesium bromides in presence of a catalyst[62]. The alkyl thiphene easily underwent sulfonation reaction with sulfuric acid in neutral solvent and neutralization with aqueous NaOH solution to obtain the sodium salts (41).



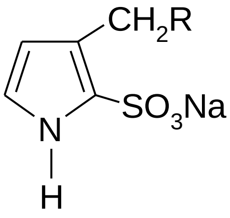
R = n-alkyl

(41)

2.2.8 Surfactant bearing pyrrole ring:

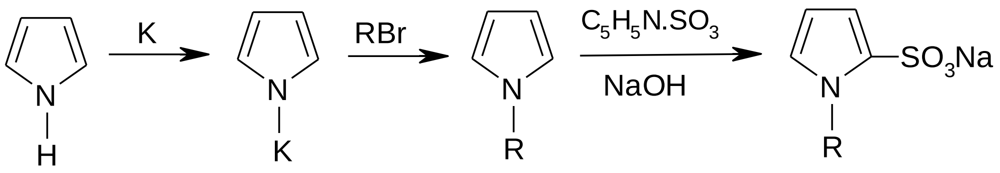
Sodium salts of 3-n-alkyl- or 3-n-alkanoyl pyrryl-2-sulfonic acids were synthesized**[63-65]**. The sulfonation of the 3-n- alkyl pyrrole was carried out with SO_3-pyridine complex to produce the sodium salts (42).

R = alkyl or alkanoyl



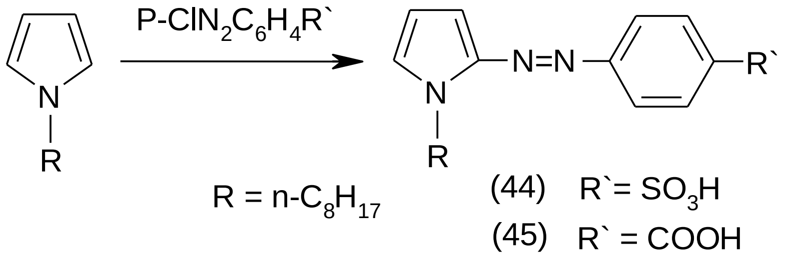
(42)

Sodium salts of 1-n-alkyl pyrryl-2-sulfonic acids (43) were synthesized in a convenient way by reaction of pyrryl potassium salt with n-alkyl bromides to give the hydrophobes which underwent easily sulfonation with SO_3-pyridine complex resulting in sodium salts**[66]**.



(43)

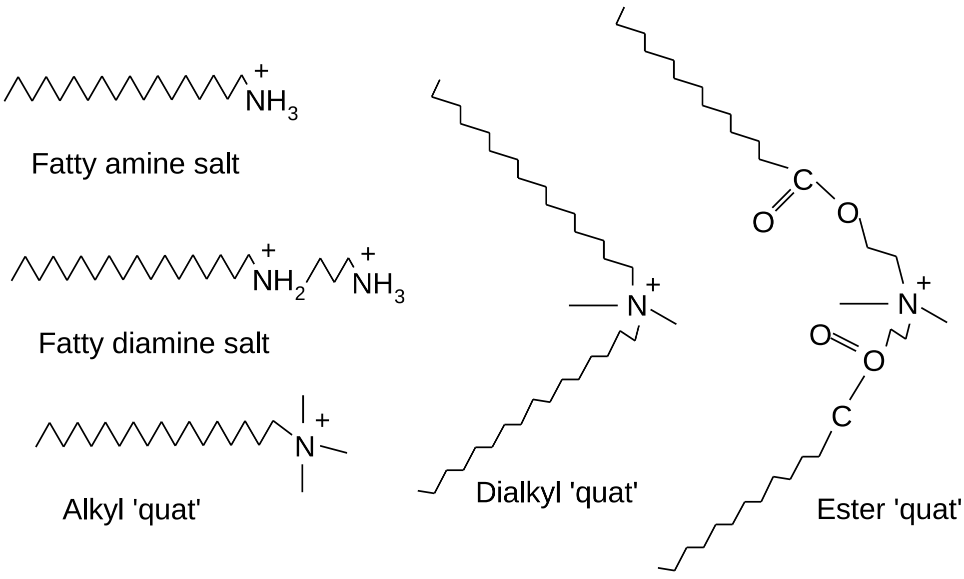
p-(1-n-alkylpyrryl-2-azo) benzene sulfonic acid and/or benzoic acid were synthesized[32,67] from p-aminobenzene sulfonic acid and/or benzoic acid with $NaNO_2$/HCL to form the diazonium salt which treated with 1-n-alkyl pyrrole to give the products (44and/or 45).



2.3 Cationic surfactants:

Most cationic surfactants have a nitrogen atom carrying the positive charge, which is the carrier of the surface character of this type.

Examples of cationic surfactants (46):



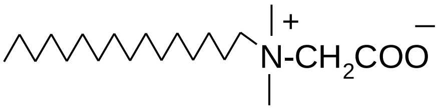
(46)

Important points: they are the third largest class, not compatible with anionic, show higher aquatic toxicity than other classes.

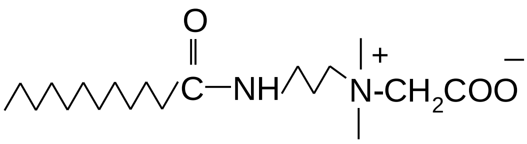
2.4 Amphoteric surfactants:

Amphoteric surfactants are characterized by a molecular structure containing two different hydrophilic groups, one with anionic and one with cationic character. Most amphoteric surfactants are able to behave in acidic media like cationic and in alkaline media like anionic surfactants.

Examples of amphoteric surfactants (47):



Betaine



Amidobetaine

Amino oxide

(47)

3. SURFACE PROPERTIES OF NONIONIC SURFACTANTS

The ethylene oxide adducts form molecular aggregates owing to the effect of association forces. The ether oxygen atom of the ethylene oxide groups has the ability of forming associated compounds, water molecules can be added owing to hydrogen bonding, and this is responsible for the water solubility of the products.

3.1 Cloud point:

When heating a non-ionic aqueous solution a separation into two phases occurs at a certain temperature, this temperature is called the cloud point. The cloud point of non-ionic arises because the solubility of the polyethylene oxide entity is due to hydrogen bonding. It increases with increasing EO content and decreases with increasing hydrophobicity of the surfactants[68]. The surface activity of the surfactant solution is affected just below and high the cloud point. Cloud point temperatures are an excellent means of characterizing many of the non-ionic surfactants. In fairly diluted solutions, it is independent of concentration and is a characteristic of a particular surfactant. For laundry and cleaning applications optimal cleaning generally occurs with ethoxylated has high cloud point[69].

3.2 Surface and interfacial tensions:

The surfactants accumulate at the surface of their aqueous solutions and reduce the surface tension. The hydrophobic group lies parallel to each other and point outwards, while the hydrophilic groups are oriented towards the interior of the liquid. The surface tension is determined by using the DU NOUY tensiometer or the Traube stalagmometer. The surface tension of solutions of oxypropylated diol monoesters of palmitic and oleic acids were determined, the surface tension decreases as the mass of the hydrophilic groups decrease. It is also found that an increase in the molar mass of the hydrophobic base has the same effect.

3.3 Foaming power:

Most surfactants give rise to foam, which can be desirable or undesirable depending upon their applications. Whether high foam, defoam or antifoam is needed[70-71], the formulator wishes to control the level of foam and to know which outside factors can affect the foam. As a general rule, foam is not generated in a pure liquid phase and a surfactant that strongly adsorbs at the air interface is necessary in order to produce foam in aqueous solution[72].

Alkyl glucosides have high foam but on blinding with other matters show low foam[73]. Ethoxylated with straight hydrocarbon chains show better foaming than those with branched chains and the foam amount goes through a maximum when the chain length of EO is increased[74,75]. The easiest way to control foam is by choosing a suitable surfactant. However, in many practical applications there will be limitations on the choice of surfactant with respect to its foaming ability. The primary reason for using a surfactant, e.g. detergency, may give higher foaming products than wanted, the ideal surfactant may be very costly or the interaction with other components may change the foam performance. Therefore there can be a need to control the foam by adding a foam control agent. Such foam control agents are called antifoamers (tallow oil with 1-4 moles EO)[76], or defoamers (branched alcohol ethoxylated). (can sugar fatty acid ester HLB 3.0-4.5)[77]. The two terms are not synonymous, as an antifoamer will prevent foam from being produced, whereas a defoamer will collapse produced foam[78-80].

3.4 Emulsification power:

An emulsifier is usually added to make the preparation of an emulsion easier and to increase its stability. The emulsifying efficiency of a surfactant was related to the polarity of the molecule or the relation between the contribution of the polar hydrophilic head and the nonpolar lipophilic tail. Griffin[81] found that, it is possible to define this polarity for nonionic agents in terms of an empirical quantity termed "the hydrophile-lipophile balance", or HLB. This is represented by an arbitrary scale in which the least hydrophilic materials have low HLB number, and increasing HLB corresponds to increasing hydrophilic characters. The nature of the emulsifier is inferred from its chemical composition. Linear, long saturated hydrocarbons are strong hydrophobic.

The introduction of halogens increases the hydrophobic characteristics. Hydroxyl, carbonyl, ether and ester groups, give the compounds a more hydrophilic nature. Aromatic groups are more hydrophilic than paraffin with the same number of hydrocarbon atoms. Aliphatic adducts commonly used as emulsifiers have usually 12-18 carbon atoms in the hydrophobic portion of the molecule. The emulsification power was estimated by stirring vigorously equal volumes of the surfactant solution (0.5% by weight) and a flushing oil for 5 minutes at 25 ± 3 °C and measuring the depth of the oil emulsion and the aqueous layer after 24 hours. The results are expressed in % emulsion[82].

Emulsion was prepared from 10 ml of a 20m mol aqueous solution of the surfactants and 5 ml of toluene at 40 °C. The emulsifying property was determined by the time it taken for an aqueous volume separating from the emulsion layer to reach 9 ml counting from the moment of the cession of shaking[83].

4. FIELD OF APPLICATIONS

Nonionic surfactants find diverse applications, both in industry and home. Their moderate foaming and good detergency make them very suitable for washing purposes. The good dispersion, emulsification and leveling capacities of ethoxylated surfactants made them very useful in the pulp, viscose and textile industries, and also in those concerned with metals, paints, plastics and mineral oils. A number of ethylene oxide adducts especially the linear ester and ether adducts have been biologically tested and found to be well suited for pharmaceutical and cosmetic preparations.

Nonionic surfactants are used extensively, because of their good detergency, easy rinsing and low foaming in cleaning of milk and beer bottles. Surfactants of ester and ether adducts in combination with anionics are also used in the cleaning of buildings and floors. In addition, ethoxylated surfactants are used to clean the tanks of ships and to break emulsion in cases where water / oil emulsions have been produced by contamination of the oils, especially fuel oils by water. In the textile industry, nonionics are used also for solvent scouring and desizing, carbonizing; kier boiling dye leveling. The ethylene oxide adducts were also used as additives to pesticides present in powder form, to facilitate rapid wetting and spreading of the pesticide[84]. Fungicides are generally not used in the form of emulsions, but addition of nonionics to fungicide concentrated spray mixes has greatly improved their effect. Ethylene oxide adducts were used as base for suppositories and as a water soluble base in ointments. It can also be used as solubilizers for lipophilic compounds in water, and can be applied in the case of oil-soluble vitamins[85-87].

Esters and alkyl ether adducts are widely used in cosmetic preparations. Nonionic surfactants are employed in a variety of ways in leather industry. It is used to accelerate soaking and liming is improved by the addition of wetting agents. Adducts incorporated in an organic solvent such as paraffin oil may be used to aid in the degreasing of skin.

The dying of fiber with aniline dyes and also bleaching, becomes more uniform when alkyl phenol adducts are used. In the paint industry, the addition of surfactants makes the wetting of pigments easier, stabilizes the binder containing dispersions and improves the compatibility of the binder in polar-non polar solvent combinations[88-90].

Surfactants were extensively used in the production of mineral oil. They studied the application of synthetic detergents for the crude oil recovery from sand or other minerals. In the mineral technology, the ethoxylated compounds were used as furthers while their xanthate and dithiophosphate derivatives were applied as collectors[91-92].

Ethylene oxide adducts were applied as emulsifiers for chemicals used in floatation. Alkyl phenol adducts in combination with sodium salts of fatty acids were used in the flotation of uranium ore. The addition of surfactants to the concrete improves the workability, strength and frost resistance for heavy concrete, for light-weight concrete, the addition of surfactants lowers the density and the thermal conductivity[84, 93].

Nonionic surfactants are frequently employed in the dust control for removing the highly dispersed lead dioxide dust from the air. Ermilor studied the relation between the structure of alkyl phenol adducts as wetting agents and their dust-removing efficiency.

Nonionic surfactants are used in many textile applications for the purpose of wettability, emulsification and detergency. For example, in the desizing of cotton, selected nonionic surfactants are suitable, as they resist the electrolyte effect and the high temperature and they facilitate the removal of starch and spinning lubricant additives. The use of these surfactants in scouring bleaching and finishing operations enables wetting out the fabric emulsifying natural fats and waxes, and removing soiled dirt and additional impurities during fabric manufacture[94].

Anionic surfactants are very widely distributed throughout science, technology, and every day life. Examples which at once come to mind are the washing, wetting out of textile materials, the preparation of dispersions and emulsion, the application of agricultural and horticultural sprays, and a wide variety of special uses, the number of which is continually increasing.

Surface active agents find extensive usage in agriculture. They are added to insecticides, fungicides and herbicides to make them easier to apply and improve their retention on the sprayed surface. For example, alkyl sulphates and alkyl aryl sulphontes are added to arsenious herbicides and fungicides. Some detergents are themselves good insecticides and can be used without the addition of other poisons, for instance, the potassium soaps of fatty acids, nonionic substances such as fatty acid esters[80, 95].