

Fatty Acids:

Fatty acid is a carboxylic acid often with a long aliphatic chain, which is either saturated or unsaturated. Fatty acids and their derivatives are consumed in a wide variety because they are used as raw materials for a wide variety of industrial products like, paints, surfactant, textiles, plastics, rubber, cosmetics, foods and pharmaceuticals.

Industrially, fatty acids are produced by the hydrolysis of triglycerides, with the removal of glycerol moiety.

As mentioned before, fatty acids can be classified into two classes, the first is unsaturated fatty acid with one or more double bonds in the alkyl chain and the other is saturated fatty acid.

Long chain 3-alkenoic acids are a family of polyunsaturated fatty acids which have in common a carbon-carbon double bond in the position 3. They are used as key precursors for synthesis of many organic compounds. There are many methods for the synthesis of such acids; here we will mention two of these methods.

Nucleophilic substitution of allylic substrates with organometallic reagents, treatment of β -vinyl- β -propiolactone with butylmagnesium bromide in the presence of copper(I) iodide in THF at -30°C , gave 3-nonenoic acid as a major product and 3-butyl-4-pentenoic acid with the ratio 98:2 respectively⁽¹⁾.

Knoevenagel condensation of an aldehyde with malonic acid in the presence of organic bases was considerable value for the synthesis of unsaturated fatty acids. This reaction is mainly related to its application for the synthesis of α - β -unsaturated fatty acids. For the synthesis of β - γ -unsaturated fatty acids the Linstead modification ⁽²⁾ of the Knoevenagel condensation, in which triethanolamine or other tertiary amines are used. It gives modest yield of 3-alkenoic acid.

Corey^(3, 4) has postulated the possibility to orient the Knoevenagel condensation for the synthesis of 2- or 3-unsaturated acids in a predictable way, by modifying the base strength and polarity of the medium. On the other hand, 3-alkenoic acids of high stereochemical purity were prepared by Ragoussis⁽⁵⁾ in good yield by reaction of various aliphatic aldehydes with a three-molar excess of malonic acid and piperidinium acetate as a base in xylene.

Also, Rao *et al*⁽⁶⁾ used equimolar ratios of malonic acid and aldehydes with triethylamine as a base as well as solvent to give (E) 3-alkenoic acids in good yield, ranging from 80-88%. This method avoids the use of large molar excess of expensive malonic acid, and the reaction conditions are easily attained.

Recently 3-alkenoic acids were obtained in high yields and stereochemical purity when equimolar quantities of aliphatic aldehydes with a α -hydrogen atom and malonic acid adsorbed on SiO₂ were subjected to microwave irradiation⁽⁷⁾.

The following investigation deals, with the surface active agents which are one interesting applications of fatty acids.

Surface active agents:

A member of the class of materials that, in small quantity, markedly affect the surface characteristics of a system; also known as surface active agent (surfactants). In a two-phase system, for example, liquid-liquid or liquid-gas, a surfactant tends to locate at the interface of the two phases, where it introduces a degree of continuity between the two different materials. These substances consist of a hydrophobic tail portion, usually a long-chain hydrocarbon, and a hydrophilic polar head group, which is often ionic or strongly polar groups. A material possessing these characteristics is known as an amphiphile. It tends to dissolve in both aqueous and oil phase and to locate

at the oil-water interface. Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water.

On the other hand, when surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil.

Surfactants are employed to increase the contact of two materials, sometimes known as wettability. Surfactants and surface activity are controlling features in many important systems, including emulsification, detergency, foaming, wetting, lubrication, water repellance, waterproofing, spreading and dispersion, and colloid stability.

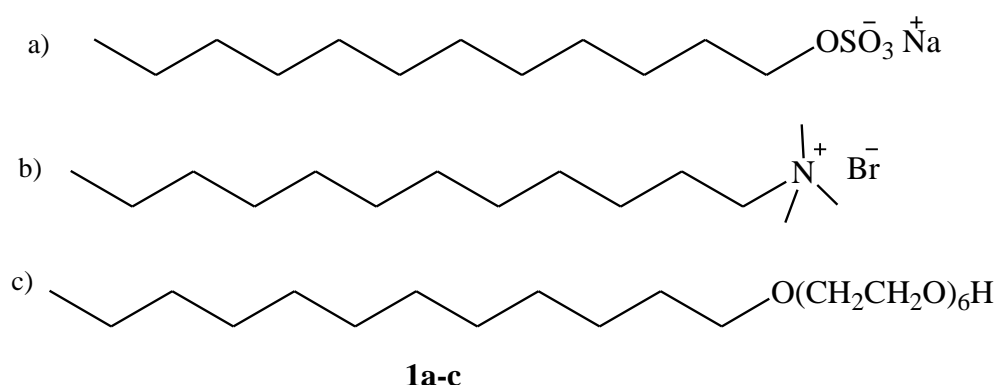
In general, it's necessary that the surfactant molecule should contain two kinds of groups one lipophilic or oil-soluble and the other hydrophilic or water-soluble, these groups can occur in different forms, that such a wide variety of surface active agents exists. Thus the surfactants are divided into four classes: amphoteric, with zwitterionic head groups; anionic, with negatively charged head groups include long-chain fatty acids, sulfosuccinates, alkyl sulfates, phosphates, and sulfonates; cationic, with positively charged head groups may be protonated long-chain amines and long-chain quaternary ammonium compounds; and nonionic, with uncharged hydrophilic head groups, while nonionic surfactants include polyethylene oxide, alcohols, and other polar groups.

Classification of surfactants:

The primary classification of surfactants is made on the basis of the charge of the polar head group. Thus surfactants are classified into the class's nonionic, anionic, cationic, and amphoteric surfactant. Recently surfactants can be classified according to the number of hydrophobic tails and hydrophilic head groups, into conventional and gemini surfactants.

1- Conventional surfactants:

In this type of surfactants the surface active compound is a molecule with hydrophilic head group and a one hydrophobic tail. The head group may be ionic, zwitterionic or nonionic, while the tail is typically a linear hydrocarbon chain of 10 to 18 carbons atoms. Compounds 1a-c are examples of common conventional surfactants.



a) anionic surfactant sodium dodecyl sulphate (SDS), b) cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) and c) nonionic surfactant hexaethylene glycol monododecyl ether (C12E6).

The conventional surfactants can be classified into four major groups as follow:

A- Nonionic surfactants:

Nonionic surfactants differ from both cationic and anionic surfactants in that the molecules are actually uncharged and the hydrophilic group is made up of some other very water soluble moieties. They don't ionize

in aqueous solution, because their hydrophilic group is of non dissociable type, such as alcohol, phenol, ether, ester, or amide. A large part of these nonionic surfactants are made hydrophilic by the polycondensation of ethylene oxide or propylene oxide.

Traditionally, nonionic surfactants have used poly (ethylene oxide) chains as the hydrophilic group. However, the two common classes of surfactants that use poly (ethylene oxide) chains as their hydrophilic group are the alcohol ethoxylates and the alkylphenol ethoxylates.

Another class of nonionic surfactants is the sugar surfactants. In which the hydrophilic group is sugar. (monosaccharides, disaccharides and trisaccharides).

The nonionic surfactant molecules contain a hydrophobic unit usually derived from fatty acids, fatty alcohols, alkylphenols, mercaptanes, amines and amides combined with a hydrophilic group which is, in most cases, a polyethylene or polypropylene chain introduced into the structure by condensation of ethylene oxide and/or propylene oxide with the hydrophobic base ⁽⁸⁾. This process for preparation of nonionic surfactants is called alkoxylation, for ethylene oxide is ethoxylation and for propylene oxide is propoxylation. This reaction is catalytic one and usually is alkaline catalyst. Conventional alkaline catalysts such as KOH or NaOMe give a relatively broad distribution ⁽⁹⁾.

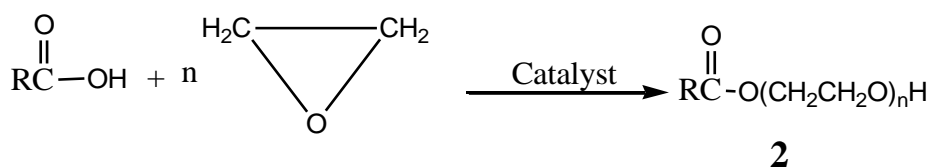
On the other hand, These materials are not ionizable and their characteristics are dependent on the balance between hydrophobic and hydrophilic groups. The reaction with ethylene oxide is used most frequently in order to increase hydrophilicity while the reaction with propylene oxide gives the molecule a more hydrophobic character.

Nonionic surfactants can be classified according to the hydrophobic part used in their preparation into the following items:

a- Alkoxylated fatty acids:

The esterification of a fatty acid by hydroxyl group from polyethyleneoxide chain gives an important family in nonionic surfactants, because of their compatibility with biological tissues which make them suitable for pharmaceuticals, cosmetics and food stuffs. Ethoxylated fatty acids can generally be obtained by two different methods: the first one is the esterification of fatty acids with polyethylene glycol and the second is ethoxylation of fatty acids. In the esterification process, mixtures of mono- and diesters are formed because of the two hydroxyl groups in the polyethylene glycol that exhibit the same reactivity⁽¹⁰⁾.

The formation of monoester or diester depends on the ratio of the reactants. An equal molar ratio of fatty acid and polyethylene glycol in the presence of boric acid as catalyst resulted in monoester **2** which is similar to that resulting from base catalyzed reaction of ethylene oxide and fatty acid⁽¹¹⁾.

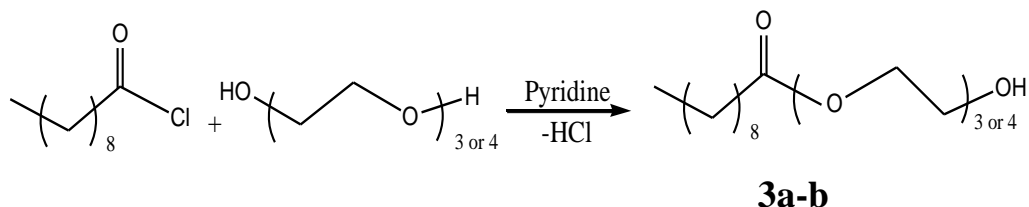


Where R = Alkyl fatty chain

Furthermore, polyethylene glycol ester can be prepared from the reaction of ricinoleic acid and/or 12-hydroxystearic acid with ethylene oxide and/or polyethylene glycol (Mol. wt. 1000); to give ricinoleic polyethylene glycol ester and/or 12-hydroxystearic acid polyethylene glycol, the product is useful as defoamer in sugar solution and laundry detergent⁽¹²⁾.

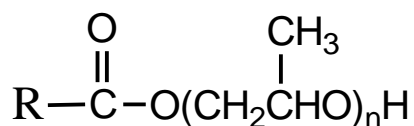
While, the diesters of fatty acids with polyethylene glycol (Mol. wt. 600) are used as emulsifiers in pharmaceuticals, cosmetics and food industry, and as wetting agents in the manufacture of fibers and paints, and also, as plasticizers in plastic industry according to their type and purity degree^(13, 14).

Deconyl triethylene glycol ester and deconyl tetraethylene glycol ester **3a-b** were synthesized by esterification of corresponding polyethylene glycol by decanoyl chloride in the presence of pyridine.



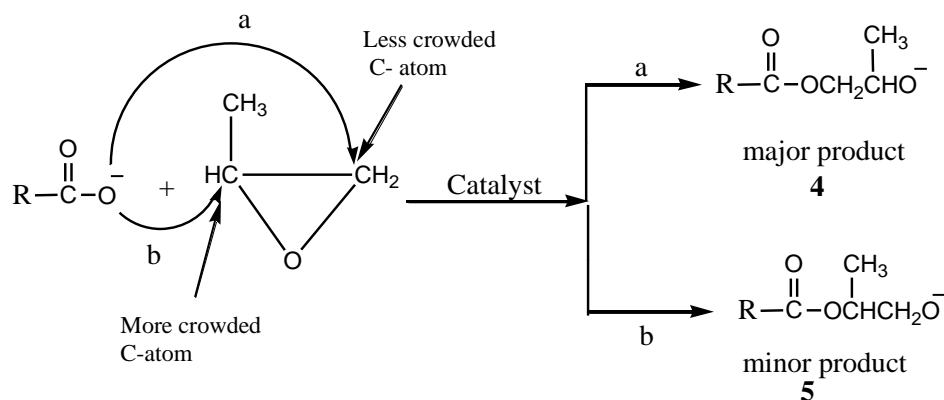
The physicochemical properties (e.g. critical micelle concentration, cloud point, and equilibrium surface tension) for these compounds were determined. It was found that critical micelle concentration, cloud point, and equilibrium surface tension are roughly the same for corresponding ethers and esters^(15, 16).

Also the esterification of fatty acids with propylene oxide was reported^(17, 18). This reaction was completed in the presence of base catalyst to give broad range distributions and the general formula for fatty acid propoxylated compounds is shown below

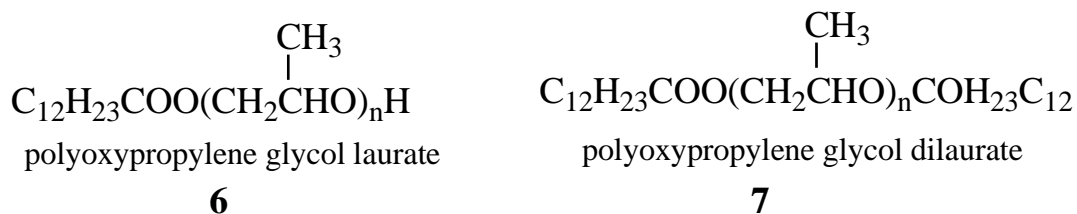


where R= alkyl fatty chain, n= number of moles of propylene oxide.

Due to that the propylene oxide molecule is not symmetrical; the products of propoxylation process give isomeric mixtures of primary and secondary products 4, 5 respectively⁽¹⁹⁾.



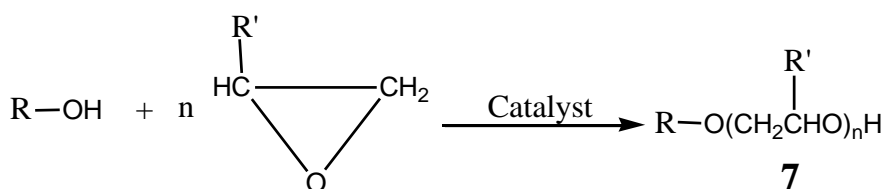
The propoxylation reaction of lauric acid was investigated in the presence of base catalyst (KOH). Polyoxypropylene glycol laurate **6** and polyoxypropylene glycol dilaurate **7** were produced^(20, 21). Such these products have broad range distribution in their molecules.



Also, propoxylated products of mixed fatty acids isolated from rice bran oil were obtained by the alkali catalyzed reaction of propylene oxide with the isolated fatty acids⁽²²⁾. Another way for synthesis of like these products is the preparation of oxypropenoxylated diol monoester of palmitic and oleic acids from the reaction of oxypropylated diol with boric acid, esterifying the resultant borate with fatty acids, and selectively hydrolyzing the borate ester followed by evaluation of their surface active properties⁽²³⁾.

b- Alkoxylated fatty alcohols:

Fatty alcohols ethoxylation and propoxylation are the most important source for nonionic surfactants widely used in many compounds formulations⁽²⁴⁾. The alcohols are derived either from natural fats and oils or from petrochemical raw materials. The fatty alcohols have active hydrogen and can react with ethylene or propylene oxides easily in the presence of catalyst. The general formula of alkoxylated Fatty alcohol **7** is presented in the following: reaction.

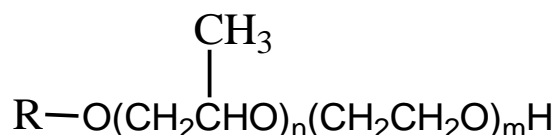


where R= alkyl fatty chain, n= number of moles of Ethylene oxide or Propylene oxide,
R' = H or CH₃

An important physical chemical property of alkoxyated fatty alcohols is the cloud point. Whereas the solubility of ionic surfactants increases with temperature, polyoxyethylene alcohols become insoluble at high temperatures. The temperature at which the aqueous surfactant solution becomes cloudy is called the cloud point and is also a characteristic of the relation of the hydrophilic ethylene oxide chain to the hydrophobic alkyl chain. This phenomenon can be explained by the breaking of hydrogen bonds that cause insolubility at high temperatures and is used as an important specification of alkoxyated fatty alcohols. The fatty alcohol with alkyl chain contains C₈₋₁₀ and C₁₆₋₁₈ were ethoxylated by using ethylene oxide to prepare a nonionic surfactant⁽²⁵⁾. Three nonionic surfactants were synthesized with polyethylene oxide and diols such as 1, 6-hexanediol and 1, 10-decanediol as the main starting materials⁽²⁶⁾. Where as the most used alcohol is the tridecanol, actually a mixture of C₁₂- C₁₆, the (chloro) oxypropyl derivatives of tridecanol have been synthesized from tridecanol, propylene oxide, and epichlorohydrin in the presence of aqueous NaOH⁽²⁷⁾.

A nonionic surfactant was prepared by addition reaction of lauryl alcohol with propylene oxide and ethylene oxide, the surfactant showed highest surface active properties when the addition moles of propylene oxide and ethylene oxide is 8-10, and 20-25 respectively⁽²⁸⁾.

Ethoxylated and propoxylated fatty alcohol with the formula:



Where R = C₈ alkyl (2-ethyl hexyl) and n = 0.8-2.0_(av.) and m = 2.0-5.0_(av.)

They are useful low foam and as wetting agent for hydrophobic polymers surfaces such as cellulose, polyethylene, polypropylene and rubbers⁽²⁹⁾.

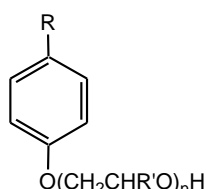
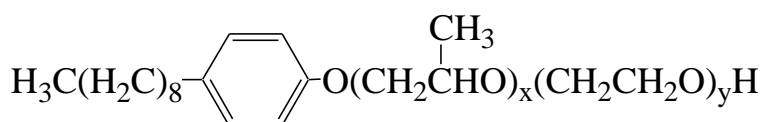
Propoxylated rice bran fatty alcohol were obtained from reduction of fatty acids of rice bran oil by LiAlH₄ to the corresponding alcohols,

followed by alkali catalyzed reaction of the latter with propylene oxide ⁽²²⁾, and by comparison with the corresponding propoxylated mixed fatty acids of rice bran oil it was found that the reaction rate of the alcohols was higher than that of acids. The most important technical point in the ethoxylation process is easiest of separation of catalyst from the product, Sr-phosphate catalyst was removed from the product by filtration, and Zirconium alkoxide sulfate, and Zirconium dodecanoxide sulfate catalysts are very active catalyst and can be easily separated from products ^{((30, 31)}.

On the other hand, the ethoxylated or propoxylated fatty alcohols are useful for detergents, emulsifiers, perfumes, and dry cleaning agents ⁽³²⁾. Alkoxyated fatty alcohol with propylene oxide then with ethylene oxide in the presence of double metal cyanide catalyst were useful as emulsifiers, foam regulators and wetting agent in detergents, hard surface cleaners, coatings, adhesives, fatliquoring agents, textile, finishing agents and in cosmetic and pharmaceutical ⁽³³⁾. Also the ethoxylated isodecanol and 1-decanol showed low critical micelle concentration and high detergency for dishwashing and laundering ⁽³⁴⁾.

c - Alkoxyated Alkyl Phenols:

Alkoxyated Alkyl Phenols **8** have played an important role in the nonionic surfactant market. The most common of these products are based on nonyl phenol **9**, or octyl phenol. Their application is almost universal because of their good performance characteristics ⁽³⁵⁻³⁸⁾.

**8****9**

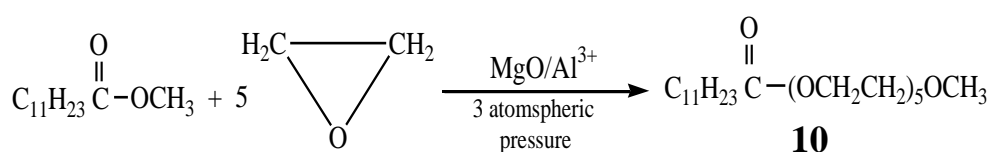
Where R= alkyl fatty chain, R' = H or CH₃

Alkyl phenol alkoxyated have been widely used in number of different applications e.g. detergent, detergent additive, cosmetic agent, pharmaceutical agent and disinfectant⁽³⁹⁻⁴¹⁾.

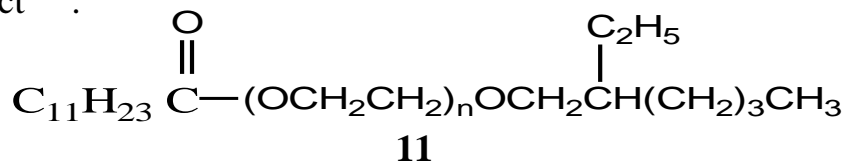
d-Alkoxyated Fatty Acid Ester:

Materials that contain an active hydrogen atom in their configuration, e.g., fatty alcohol and fatty acids, can easily be converted with ethylene oxide to the corresponding ethoxylates using standard alkaline catalysts. Therefore, direct conversion of methyl esters is not possible if these conventional catalysts are used, but another new catalysts based on solid catalyst modified by metal cations were used⁽⁴²⁾.

However, methylpolyoxyethylene ether laurate ester **10** is prepared from methyl laurate and ethylene oxide at 180 °C and 3 atmospheric pressure, using Al³⁺ ion containing MgO as catalyst⁽⁴³⁻⁴⁶⁾.



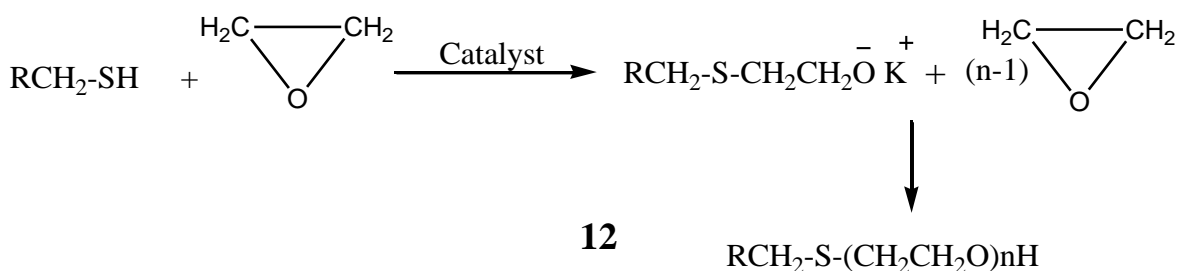
The long chain aliphatic esters (2-ethylhexyl laurate) are used as raw material for ethoxylation in the presence of appropriate catalyst (calcium based catalyst); they react with ethylene oxide to give polyethylene glycol 2-ethyl hexyl ether laurate **11** without formation of excessive amount of by product⁽⁴⁷⁾.



Ethoxylated fatty acid methyl ester showed excellent distributions in large variety of application, e.g. laundering and dishwashing detergent, fabric and hard surface cleaners⁽⁴⁸⁾.

e-Alkoxyated mercaptans:

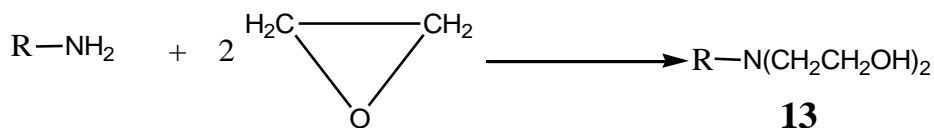
Mercaptanes RSH are organosulfur compounds called thiols or thio alcohols containing mercapto group attached to alkyl chain. Polyoxyethylene mercaptans **12** are prepared by the catalyzed addition of ethylene oxide to the mercaptans.



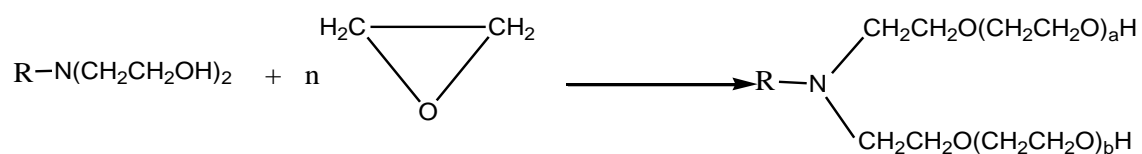
Usually the alkyl mercaptans of the C₁₀ to C₁₈ branched chain types are employed for condensation with ethylene oxide. The mercaptan adducts have a limited use because their smell, they can be used as emulsifiers and exhibit better detergency in laundry at high temperature with higher cloud point and lower turbidity. Also, they are excellent thermally stable surfactants, and their alkaline salts exhibit good surface activity^(49, 50).

f- Alkoxyated amine:

The ethoxylation of higher amines with ethylene oxide produce a nitrogen- based polyoxyethylene surfactant. The synthesis of ethoxyated amines **14** take place through two steps, the first one is the conversion of an amine with ethylene oxide to an amino alcohol **13**:



The second step is the growth of the polyoxyethylene chain through reaction of more ethylene oxide with the hydroxyl groups of the amino alcohol.



Where a + b = n : number of ethylene oxide group

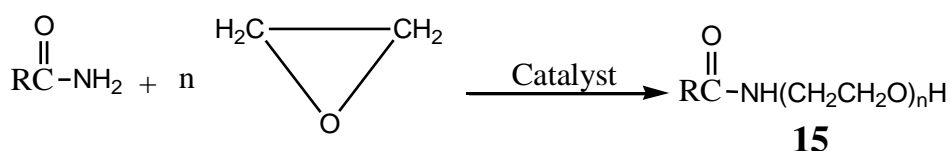
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Whereas in the first reaction step no catalyst is necessary, the second step requires a catalyst such sodium or potassium hydroxide ^(51, 52). The ethoxylation of 4-(methyl, octyl, decyl or dodecyl) aniline carried out with ethylene oxide in the presence of KOH as catalyst ⁽⁵³⁾.

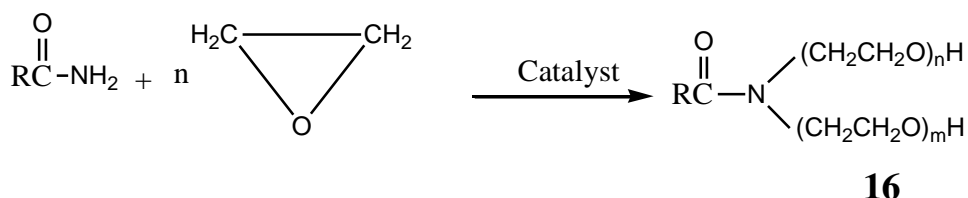
Ethoxylated amines have a wide range of applications. They are used as emulsifiers, solubilizers, and in cleaning and detergent formulations.

g- Alkoxylated amide :

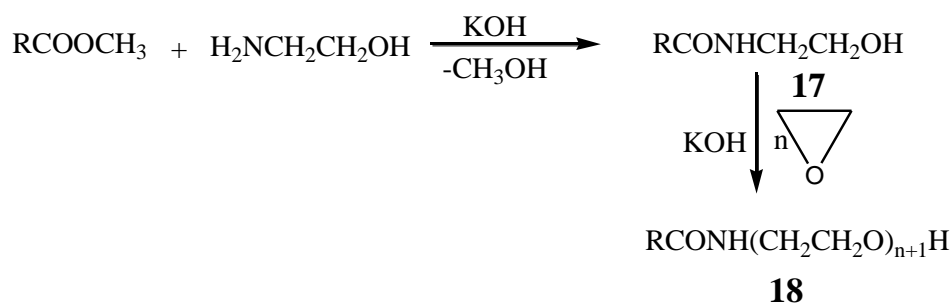
The ethoxylated amide **15** obtained by the addition of ethylene oxide to acid amides as follows:



Furthermore, ethylene oxide can be condensed with each of the two hydrogens in higher alkyl amides to form N,N- disubstituted polyoxyethylene acid amides **16**.



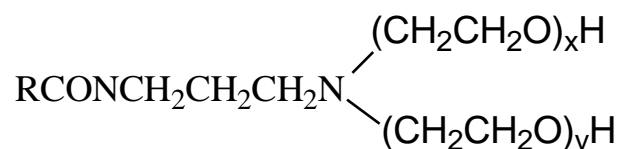
Monoethanolamide **17** prepared from the reaction of methyl ester of fatty acids with monoethanolamine was ethoxylated with ethylene oxide to give nonionic surfactant **18** ⁽⁵⁴⁾.



Where, RCO = stearyl, oleyl, elaidyl and linoleyl; n = 10,15 and 20 moles of EO

Also, lauric acid monoethanolamide prepared from the reaction of lauric acid with monoethanolamine was ethoxylated with ethylene oxide under pressure, and the product was used for cosmetics and cleaning compositions⁽⁵⁵⁾. The fatty acid monoethanolamide ethoxylates have a wide range of applications such as in paint, drug, antistatic agents and detergent⁽⁵⁶⁾.

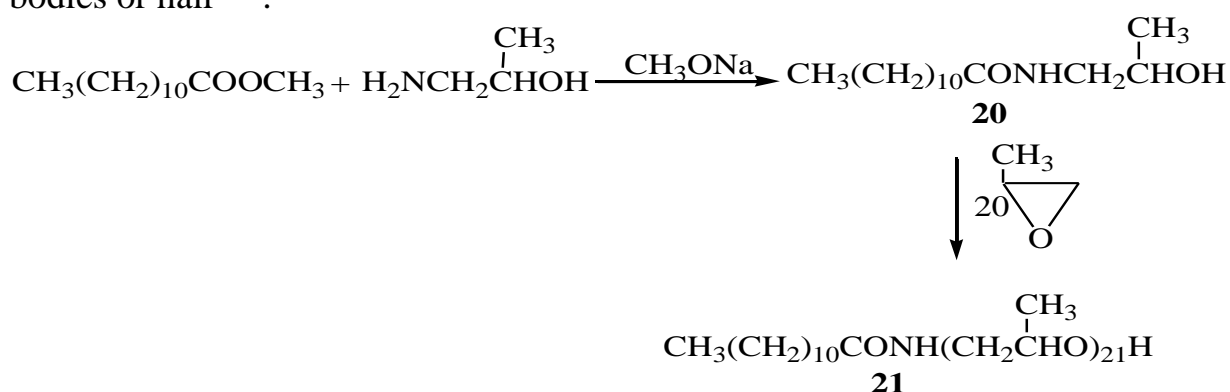
N-propyl amino lauryl amide can be ethoxylated with ethylene oxide in presence of tri-ethylamine, the N-propyl amino lauryl amide and three of its ethoxylated derivatives **19** can be used as corrosion inhibitors of carbon steel⁽⁵⁷⁾.



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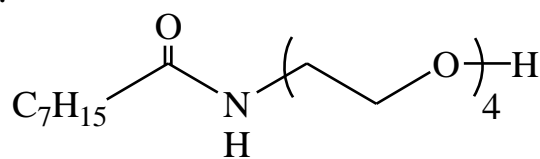
where $(X + Y) = 2, 8, 15$ moles of ethylene oxide.

On the other hand, the fatty acid amide propoxylation can be achieved. Thus, the lauric acid methyl ester reacted with isopropanolamine in the presence of sodium methoxide as catalyst to give **20**, the latter is propoxylated with propylene oxide to give propoxylated lauric isopropanolamide **20**⁽⁵⁸⁾, which used as emulsifiers, cleaning disches and bodies or hair⁽⁵⁹⁾.



A pure nonionic surfactant, tetra (ethylene glycol) mono-n-octaneamide **22**, was synthesized. The surface active properties of this surfactant were determined. Hydrolysis catalyzed by an acid, an alkali, a

peroxide, and enzymes were also studied. The fatty acid monoethanolamide ethoxylates are used in applications such as personal care products, detergents, and emulsifiers⁽⁶⁰⁾.

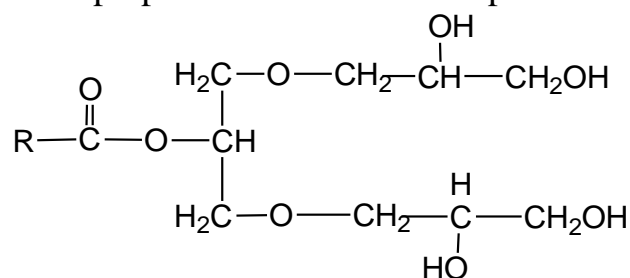


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h- Alkoxylated Oils and Glycerides:

Partially esterified glycerol with fatty acids, monoesters (monoglycerides), and diesters (diglycerides) can be ethoxylated by using standard alkaline catalysts. While purified triglycerides do not possess any active hydrogen atom in the molecule to react with ethylene oxide.

Highly Purified triglycerol mono-n-fatty acid esters, 1, 3-O-bis (glyceryl) glycerol-2-O-monododecanoate, 1, 3-O-bis (glyceryl) glycerol-2-O-monotetradecanoate, 1,3-O-bis (glyceryl) glycerol-2-O-mono-hexadecanoate **23a-c** respectively were prepared and these compounds have excellent surface activity^(61, 62).

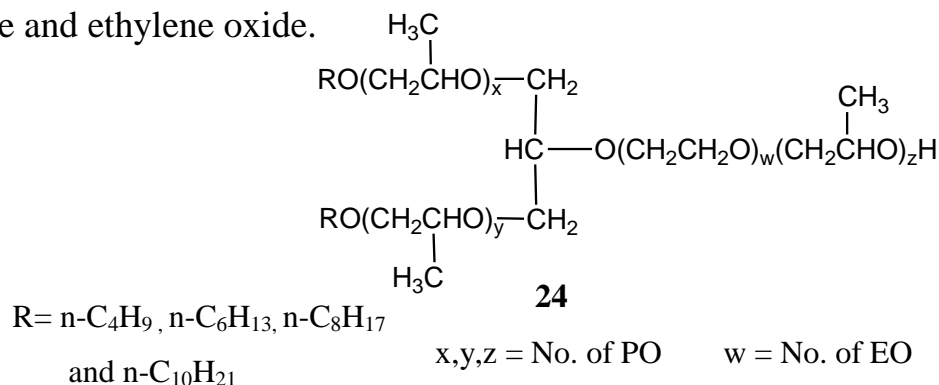
**23a-c**Where R = C₁₁H₂₃, C₁₃H₂₇ and C₁₅H₃₁

Ethoxylated glycerol esters and their derivatives are used widely in the cosmetic industry. Partial esters of polyols such as glycerol, polyglycerol and sorbitol are nonionic surfactants that are used as emulsifiers in the food, detergent and are used widely in the cosmetic industry^(63, 64).

i- Polyol based nonionic surfactant:

This class of surfactant is based on polyhydroxy compounds, it can be esterified with long chain fatty acid, and the polyhydroxy compound act as hydrophilic part and the fatty chain as hydrophobic one.

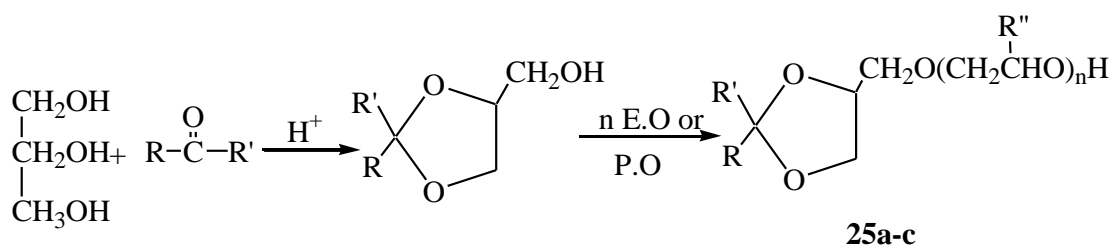
1,3-dialkoxy-2-propanols and 1,3-dialkoxy(oligooxypropylene)-2-propanols and their oligooxyethylenated **24** were synthesized using propylene oxide and ethylene oxide.



The surface active properties of the prepared compounds such as cloud point, wetting ability, and contact angle foam height and emulsion stability were studied⁽⁶⁵⁾.

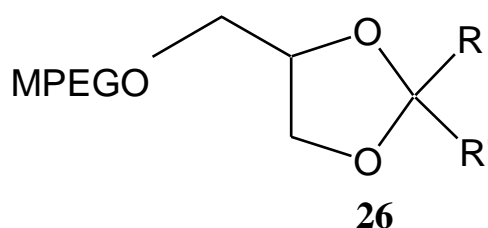
Another surface-active compounds known as cleavable surfactants which are readily biodegradable surfactants, they have into their structure a bond with limited stability. Most cleavable surfactants contain a hydrolysable bond, which can chemically hydrolyzed under acid or alkali condition. In the environment, bonds susceptible to hydrolysis are often degraded by enzymatic catalysis. Cyclic 1,3-dioxolanes are a type of acid cleavable surfactants. They are typically synthesized from a long chain aldehyde by reaction with a diol or a higher polyol to give compounds contain a dioxolane or dioxane rings. Reaction with a vicinal diol gives the dioxolane and with 1,3-diols yield dioxanes. These compounds are cleavable or degradable nonionic surfactants. In case of glycerol vicinal hydroxyl groups give dioxolane and the remaining hydroxyl group may also be ethoxylated to give nonionic surfactant.

Nonionic surfactants bearing 1,3-dioxolane ring **25a-b** were prepared by the acid-catalyzed condensation of ketones and glycerol, followed by ethoxylation or propoxylation. These surfactants had good surface activity, excellent detergency and easily hydrolyzed under acidic condition⁽⁶⁶⁾.



Where R,R' = alkyl chain (in surfactant ring) , R''= H or CH₃ and n= 3-8

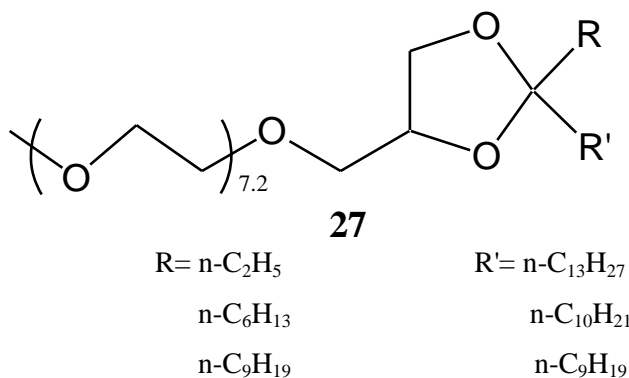
An oil-soluble pH-degradable nonionic surfactant **26** with poly (ethylene glycol) monomethyl ether as the hydrophile and a cyclic ketal as the hydrophobe was synthesized for use in microemulsion-based protein extraction.



Where R = C₁₃H₂₇ , R' = C₂H₅ and MPEG = CH₃O(CH₂CH₂O)_nOH, n = 7,8

The cyclic ketal linkages hydrolyzed under mildly acidic conditions (pH₅ or less), yielding two non-surface-active species, one of which resides in the aqueous phase (MPEG) and the other in the oil phase (ketone) ⁽⁶⁷⁾.

A series of three nonionic surfactants which undergo acid-catalyzed hydrolysis, O-[(2,2-dialkyl-1,3-dioxolan-4-yl)methoxy]-O-methoxy poly (ethylene glycol), or cyclic ketal **27**, were synthesized. The surfactants shared similar HLB values but differed in the relative length of their two alkyl tails. These compounds can be used successfully to form microemulsion systems as single surfactants or components of a surfactant mixture ⁽⁶⁸⁾.



j- Sugar based nonionic surfactant :

The carbohydrate polar head has multiple hydroxyl groups with defined orientations, allowing for the formation of strong cooperative hydrogen bonds between the surfactant molecules. This fact, together with the hydrophobic interactions between the long hydrocarbon chains, leads to spontaneous association in water.

Surfactants containing sugar components and fatty acids ⁽⁶⁹⁻⁸⁴⁾ satisfy the quality standards for food application, emulsifiers in pharmaceuticals, and cosmetic products. The most common sources of carbohydrates which used are sugar beet or sugarcane, glucose derived from starches, and sorbitol as the hydrogenated glucose derivative.

B-Anionic surfactant:

Anionic surfactants are surface active substances dissociated in water to give a linear or branched chain with hydrophilic negatively charged head group such as carboxylate, sulfate, sulfonate and phosphate in addition to a metallic cation. The anionic surfactants have the advantage of being high and stable foaming agents. The most common used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps. Furthermore, they are the most widely used types of surfactant for laundering, dishwashing liquids and shampoos because of their excellent cleaning properties and high foaming properties.

It is the most widely used type of surfactant for laundering, dishwashing liquids and shampoos because of its excellent cleaning properties and high performance. The major subgroups of this class are the alkali carboxylates or soaps, sulfates, and sulfonates.

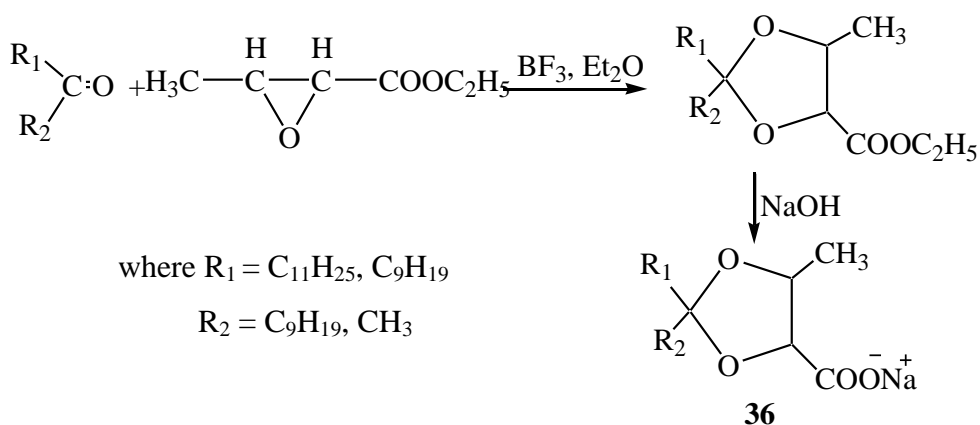
a. Carboxylates :

Soaps are considered the oldest known class of surfactants, they are alkali salts of long-chain fatty acids. The term soaps are mainly applied to

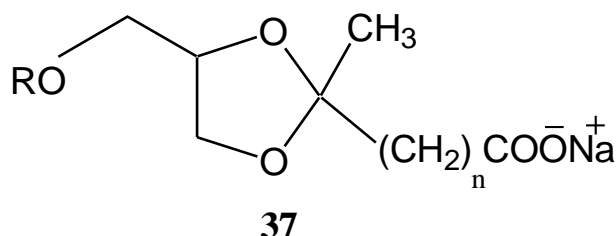
the water-soluble alkali metal salts of fatty acids, or heavy metals salts and alkaline earth metals salts of fatty acids that are water insoluble and are termed 'metallic soaps'. These salts are produced from saponification process, a chemical process of splitting fat into the alkali salt of fatty acid and glycerine⁽⁸⁵⁾.

The main application of soap is in the personal care industry, followed by the detergent industry.

New soap-type surfactants **36** bearing a 1,3-dioxolane ring were prepared from the reaction of fatty ketones with epoxy esters in the presence of ethylene oxide and boron trifluoride followed by alkaline hydrolysis⁽⁸⁶⁾.



Another soap surfactant contain 1, 3-dioxolane ring **37** were prepared in good yields by the acid-catalyzed condensation of 1-O-alkylglycerols (alkyl: decyl, dodecyl, tetradecyl, heptadecyl, octadecyl, or cis-9-octadecenyl) with oxocarboxylic acid esters, followed by alkaline hydrolysis.

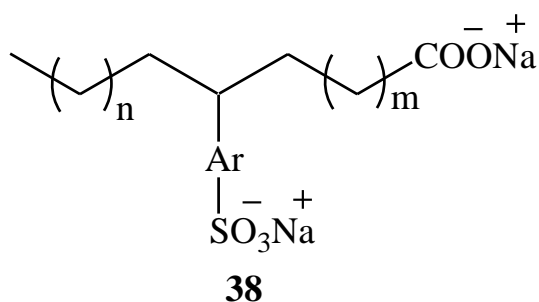


Where: $R = C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}, C_{18}H_{37}, C_{18}H_{35}$ (oleyl), and $n = 0,1,2$.

These surfactants were soluble in alkaline water at room temperature. And because these surfactants contain a 1,3-dioxolane ring, they can be utilized as a

new acid-decomposable type of cleavable surfactant. At pH=1, they decompose almost completely into nonsurface-active species after 80 min⁽⁸⁷⁾.

Three unsymmetrical surfactants 38 with different aromatic rings and a carboxyalkyl chain were synthesized and the aromatic rings were sulfonated. These compounds have some improved surface properties.



Where Ar = phenyl, dimethylphenyl and naphthyl and $m + n = 13$ and $R' = H, CH_3$

The structure of the product is quite similar to alkylbenzene sulfonate, which is one of the most important detergents, so it is expected that this surfactant will also be a good detergent. In addition, a hydrophilic group (carboxyl group) was linked at the end of the alkyl chain of the novel surfactant⁽⁸⁸⁾.

b-sulfonated compounds:

It's a compound which the sulfur is attached directly to the carbon chain (C—S coupling reaction). Materials that are related through the sulfonate group include the aliphatic paraffin sulfonates produced by the photochemical sulfonation of refinery hydrocarbons, petroleum sulfonates derived from selected petroleum distillate fractions, olefin sulfonates, sulfosuccinate esters and related compounds, alkylaryl sulfonates, and ligninsulfonates, which are a byproduct of the paper manufacturing process, the most important types will be described below.

1- Aliphatic Sulfonates:

The simple aliphatic sulfonic acids and their salts are represented by the general formula $R-SO_3^- M^+$ where R is normal or branched-chain, saturated or unsaturated alkyl or cycloalkyl group of a sufficient size to impart surface activity, and M is hydrogen or an alkali metal ion. There are various methods for the preparation of the alkyl sulfonate. Paraffin sulfonates, or secondary n-alkylsulfonates, are prepared by the sulfoxidation of paraffin hydrocarbons with sulfur dioxide and oxygen under ultraviolet irradiation, or by chlorosulfonation⁽⁸⁹⁻⁹¹⁾.

Alkane sulfonates are highly soluble surfactants and the typical applications are in detergents, personal care products, cleaners, and dishwashing detergents⁽⁹²⁾.

2- Alkylaryl Sulfonates:

When the aromatic ring is substituted with one or more alkyl groups, the surface-active character of this sulfonated compounds is greatly enhanced than the sulfonated aromatic compounds. This class of materials has become important anionic surfactants⁽⁹³⁻⁹⁸⁾.

3- α -Sulfocarboxylic Acids and Their Derivatives:

The α -sulfocarboxylic acids are represented by the general formula:



in which R is CH_3 or a longer alkyl chain and M is hydrogen or a normal surfactant cation. However, if the free carboxylic acid is esterified with an alcohol of proper length, the resultant esterified compound will generally perform well as surfactants⁽⁹⁹⁻¹⁰⁴⁾.

c- sulfated compounds:

Compounds in which the sulfur is attached to the carbon chain through an oxygen atom (C—O—S) are known as sulfated compounds. The surfactant properties of sulfated materials is sensitive to the starting material composition and conditions of reaction. They have good water solubility and surface activity and readily available starting materials from a number of agricultural and petroleum sources, these compounds can be classified as follow:

1-Sulfated Fats and Oils:

Sulfated oil is a reaction product of a sulfation, between sulfuric acid and fatty oil. The sulfate esters are obtained by the treatment of a variety of hydroxylated or unsaturated natural fats and oils with sulfuric or chlorosulfonic acids. These materials represent as the oldest types of commercial synthetic surfactants, They will contain not only sulfated glycerides but also sulfated carboxylic acids and hydroxycarboxylic acids produced by hydrolysis of the starting materials. Thus the uses of the sulfated fatty oils has decreased considerably, they are used as detergents, wetting agents, or both, with good detergency⁽¹⁰⁵⁾.

2-sulfated monoglyceride:

The sulfated monoglycerides^(105, 106) are generally prepared by the controlled hydrolysis and esterification of triglycerides in the presence of sulfuric acid or oleum. Because of the natural availability of the starting materials for such processes, the sulfated monoglycerides have a great deal of commercial potential, where triglycerides from plant and animal sources may be more readily available than the more expensive petroleum-based raw materials.

3- Sulfated Fatty Alcohol:

Fatty alcohols were obtained from the catalytic hydrogenation of natural fatty acids derived from vegetable and animal byproducts. The alcohol was then sulfated by reaction with chlorosulfonic acid and neutralized with alkali to give fatty alcohol sulfates which are among the most widely used surfactants.

Long chain alkane-1,2-diol were prepared by the reduction of corresponding 2-hydroxy myristic, plamitic and stearic methyl esters by LiAlH_4 , the 2-hydroxy acids, methyl esters and alkane 1,2-diol were sulfated by chlorosulfonic acid then neutralized by NaOH to give the following sulfated products **39,40** and **41**:

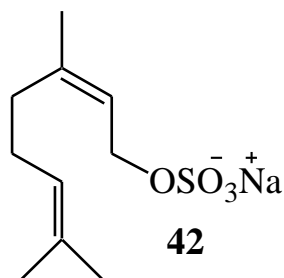


Also the 2-hydroxy fatty acids reacted with mono and diethanol amine to give the corresponding fatty alkanolamides, these products were sulfated too, and the surface active properties of all the prepared compounds were evaluated⁽¹⁰⁷⁾.

Simple lipase-mediated synthesis of alkyl ricinoleates and 12-hydroxy stearates was performed by transesterification of methyl ricinoleate, 12-hydroxy stearate and various alcohols in a solvent-free system. On the other hand, sulfates of alkyl ricinoleates and 12-hydroxy stearates were evaluated for surfactant properties such as surface tension, critical micelle concentration, emulsifying properties, foaming power, and calcium tolerance. The surfactant properties of sulfated alkyl ricinoleates were found to be superior to the sulfated alkyl 12-hydroxy series⁽¹⁰⁸⁾.

An anionic surfactant, sodium geranyl sulphate (sodium 3,7-dimethyl-2,6-octadienyl sulphate) **42** derived from geraniol, was synthesized by chlorosulfonation of geraniol in pyridine, then neutralized by sodium

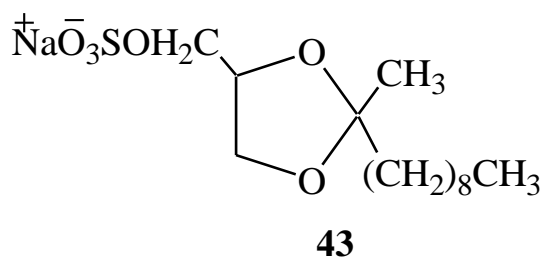
carbonate and sodium bicarbonate. The surface tension critical micelle concentration for the product was determined⁽¹⁰⁹⁾.



sodium geranyl sulphate

Because of the good foaming power of the alcohol ether sulfates, they are preferably used in foam baths, shampoos, and manual dishwashing detergents.

However, an easily biodegradable dioxolane surfactant **43** was prepared from the condensation of undecanone with glycerin followed by sulfation with sulfur trioxide-pyridine complex, and finally neutralization with NaOH, KOH, and NH₄OH, respectively to give an anionic surfactant with critical micelle concentration 1.0×10^{-2} mol/L, surface tension at critical micelle concentration 39.6 dyne/cm and kraft point (1%) < 0°C.



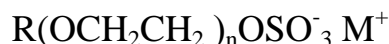
This type of anionic surfactant was completely decomposed by 1.0 N hydrochloric acid at 25°C for 1 hour⁽¹¹⁰⁾.

4-Sulfated Ethers:

Nonionic surfactants of the polyoxyethylene type, generally exhibit excellent surfactant properties, but they have two primary disadvantages, however, in that they are seldom good foam producers and give cloudy solutions at higher temperature, which may lead to phase separation. Fatty

alcohol sulfates, on the other hand, generally have good foaming properties, but their more common sodium salts sensitivity to water hardness is a big disadvantage for many applications.

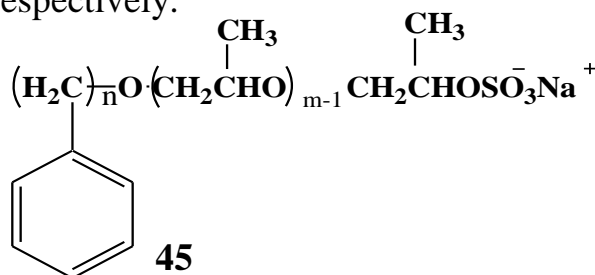
The water-insoluble nonionic material, however, can then be sulfated with chlorosulfonic acid or SO₃ and neutralized, usually with sodium hydroxide, to give the alcohol ether sulfate **44**:



44

This class of surfactant combines the advantages of both the anionic and nonionic surfactant types. Because of their good foaming power, alcohol ether sulfates are preferably used in foam baths, shampoos formulations, and manual household dishwashing detergents.

Anionic surfactants **45** prepared from hydroxypropylated aralkyl alcohols were prepared by propoxylation of three aralkylalcohols (benzyl, β-phenylethyl and γ-phenylpropyl) alcohols by using base catalyst (NaOH) and Lewis catalyst (SbCl₃) respectively.

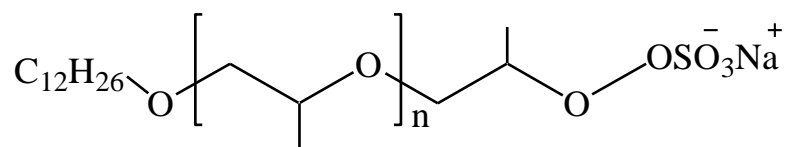


Where n= 1,2 and 3 and m= 5,7,9,11 and 14 moles of propylene oxide

The prepared hydroxylpropylated compounds were sulfated to give anionic surfactant, the surface active properties of the prepared anionic surfactant were evaluated, and the results indicate that the surface active properties of the new anionic surfactants were improved by increasing the hydrophilicity in the starting molecule⁽¹¹¹⁾.

On the other hand, new anionic surfactants with a carboxylate or sulfate polar head group **46** were synthesized from polypropoxylated alcohols,. The surface active properties of these compounds were determined and the

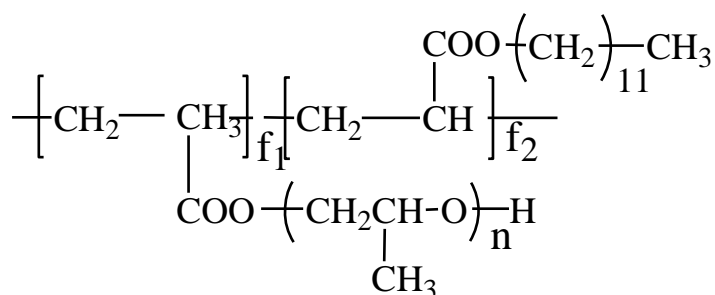
critical micelle concentration was found to decrease with the length of the polypropylene glycol spacer⁽¹¹²⁾.



46

Where n = 6, 10 and 14 moles of PO

A series of anionic copolymeric surfactants **47** based on n-dodecylacrylate ester as hydrophobe, and oxypropylated acrylate ester as hydrophiles, were prepared by copolymerization of n-dodecylacrylate and oxypropylated acrylate ester with molar ratio's (0.3:0.7, 0.4:0.6 and 0.5:0.5, respectively) in the presence of benzoyl peroxide as initiator followed by sulfation and neutralization, the surface activity, and biodegradability were evaluated⁽¹¹³⁾.



47

Where n = 4 and 6 mol. propylene oxide, $f_1 = 0.7, 0.4$ and 0.5 and $f_2 = 0.3, 0.6$ and 0.5

C- Cationic surfactants:

This type of surfactants ionizes in solution giving an oil soluble cation (active part of the molecule) and an anion. A very large proportion of this class corresponding to nitrogen compounds such as fatty amine salts and quaternary ammonium salts, with long chain of the alkyl group, often comes from natural fatty acids. These surfactants are in general more expensive than anionic and they used in fabric softeners and in laundry detergents.

D- Amphoteric surfactants:

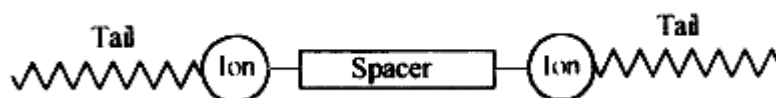
When a single molecule exhibit both anionic and cationic dissociation it is called amphoteric or zwitterionic. These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). They are frequently used in shampoos and other cosmetic products, and also in hand dishwashing liquids because of their high foaming properties.

2- Gemini surfactants:

In recent years novel forms of surfactants consisting of two conventional surfactants joined chemically at the head group have generated much interest. This new class of amphiphilic molecules called gemini or dimeric surfactant. Gemini surfactants are new family of surfactant molecules possessing more than one hydrophobic tail and hydrophilic head group. These surfactants usually have better surface-active properties and lower critical micelle concentrations than corresponding conventional surfactants of equal chain length ⁽¹¹⁴⁾. Gemini surfactants are also classified according to the hydrophilic head groups according to anionic, cationic, nonionic and amphoteric gemini surfactants. They are used as promising surfactants in industrial detergency and have shown efficiency in skin care, antibacterial property.

In general, the hydrophobic part of the surface active agents is usually a long chain hydrocarbon, whatever its one or more hydrophobic tail and the water soluble grouping can be sulphate, sulphonate, carboxylate, and quaternary ammonium salt and hydroxyl groups. In this work will present the necessary knowledge on the concerned subject which is the nonionic, anionic and gemini (nonionic, anionic) surfactant.

The gemini surfactant consists of two conventional surfactant molecules chemically bonded together by a spacer. The two terminal hydrocarbon tails can be short or long; the two polar head groups can be ionic, zwitterionic or nonionic as with conventional surfactants. The spacer can be short or long, flexible or rigid. Geminis are considerably more surface-active than conventional surfactants. A schematic representation of gemini is shown below.



All gemini surfactants possess at least two hydrophobic chains and two ionic or polar groups, and a great deal of variation exists in the nature of spacers⁽¹¹⁵⁾. Short or long chain of methylene groups, rigid (stilbene), polar (polyether), and nonpolar (aliphatic, aromatic) groups may be used as spacers.

Gemini surfactants have been synthesised with two head groups such as sulphate, carboxylate, phosphate^(116,117), dimethylammonium⁽¹¹⁸⁻¹²¹⁾, and polyoxy-ethylene. On the other hand have symmetrical or nonsymmetrical structure. The great majority of geminis have symmetrical structures with two identical polar groups and two identical chains and nonsymmetric structure, both amphiphilic moieties can be different in terms of chain length and head group nature for example, one head group is sodium sulphonate and the other a polyoxyethylene.

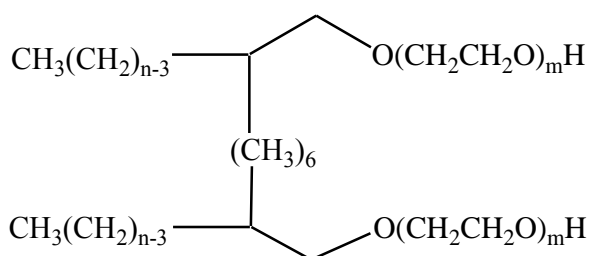
Furthermore, gemini surfactants have attracted considerable interest, since these compounds have much smaller critical micelle concentration (CMC) values, much greater efficiency in reducing surface tension than expected, and other unusual behaviors. Also, they have been generating increasing interest owing to their superior performance in applications and their tunable molecular geometry.

As conventional surfactant molecules the Gemini surfactants can also be classified into, anionic, cationic and nonionic Gemini surfactants. This study is concerned with anionic and nonionic Gemini surfactants.

-Nonionic Gemini surfactants:

Till now the majority of Gemini surfactant studies have been on ionic systems, although nonionic Gemini surfactants have also been studied, they are always synthesized with hydrophobic moieties containing additional atoms (such as O, N, and S) in order to avoid the difficult, multistep synthesis necessary to produce exact Gemini surfactant analogues of conventional poly(ethylene oxide) surfactants. Further, the majority of studies of these nonionic geminis have concentrated on synthesis and surface properties, while the physical chemistry has been virtually ignored.

A series of nonionic Gemini surfactants **48** that are direct dimeric analogues of conventional and widely used poly(oxyethylene) alkanol surfactants were synthesized.

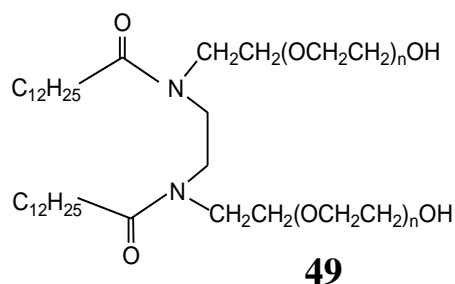


48

The nomenclature used here is Gem_nE_m , where n ($= 12, 14, \text{ and } 20$) is the number of carbons per tail and m ($= 5, 10, 15, 20, \text{ and } 30$) is the average number of ethylene oxide units per head group. The surfactants described are all polycondensates of ethylene oxide, analogous to commercial nonionic surfactants. The water-solubility, clouding behavior, and critical micelle concentrations of these surfactants were evaluated and compared with the conventional analogues. Cloud temperatures increase with m and decrease with

n , as observed for conventional surfactants. Critical micelle concentrations have lowest values from the conventional surfactants⁽¹²²⁾.

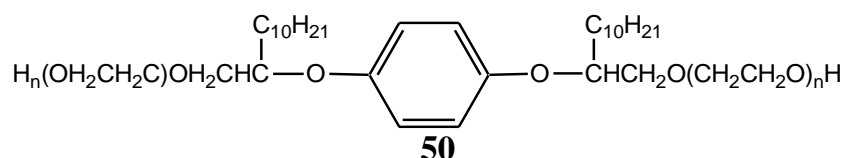
Also, two nonionic surfactant dimers (gemini surfactants) of the dimethylene 1,2-bis(*N*-polyethyleneglycol dodecylamide) **49** type and the corresponding surfactant monomers of the *N*-methyl, *N*-polyethyleneglycol dodecylamide type have been synthesized with an increasing number of ethyleneglycol (EG) units (3, 6, or 9 ethylene glycol units) in the head group.



dimethylene-1,2-bis(*N*-polyethyleneglycol dodecylamide) Where $n = 2, 5$ or 8 ethylene oxide units

Their micellization behavior in aqueous solution has been investigated. The cloud temperature, critical micelle concentration, and micelle aggregation number have been measured using turbidity, surface tension. These results permit comparison of the micellization behavior of nonionic surfactant monomers and dimers with polyethylene glycol head groups. The nonionic surfactant dimers have been found to be more effective and efficient than the corresponding monomers at lowering the surface tension of water and have lower critical micelle concentration. But the cloud temperatures of the dimers are lower than those of the monomers⁽¹²³⁾.

A series of nonionic dimeric poly(ethylene oxide) surfactants **50** were synthesized from ethoxylated hydroquinone bislauryl alcohol.



where $n = 9, 20$ and 80

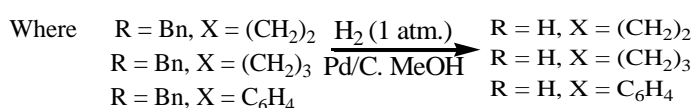
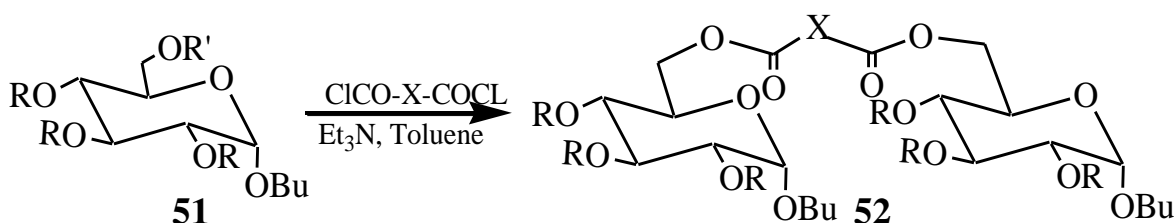
Also, the surface properties, such as the critical micelle concentration, minimum surface tension, surface excess concentration, and

surface area per molecule, have been determined by means of surface tension measurements. Effects of salt and pH on the surface properties for these gemini surfactants in aqueous solution systems were investigated⁽¹²⁴⁾.

The nonionic gemini surfactants based on carbohydrates is considered to be the most known kind in this type of gemini surfactants. Because of their biodegradability and the fact that they can be easily prepared starting from renewable raw materials such as carbohydrates and long-hydrocarbon-chain alcohols. Most of these surfactants composed of two alkyl glucosides linked through a spacer.

The alkyl glycosides were prepared starting from D- glucose and long hydrocarbon chain alcohols, two molecules of alkyl glucosides linked through their primary hydroxyl groups may be suitable to improve their surfactant properties producing a nonionic gemini surfactant. Thus, 1,5-bis-[6-O-(n-butyl α -D-glucopyranoside)] glutarate were synthesized from n-butyl α -D-glucopyranosid using n-butyl 2,3,4-tri-O-benzyl α -Dglucopyranoside to protect butyl glucoside through the reaction⁽¹²⁵⁾.

Carbohydrate containing dimeric (or gemini) surfactants **52** were synthesized starting from D-glucose. These gemini surfactants prepared from butyl- α -D-glucopyranoside **51** with three different spacers (glutaryl, succinyl and terephthaloyl) were used to link the sugar moieties through 0-2 or 0-6. The critical micellar concentration (CMC) for these new compounds was ten-fold smaller than that of their monomeric counterpart⁽¹²⁶⁾.

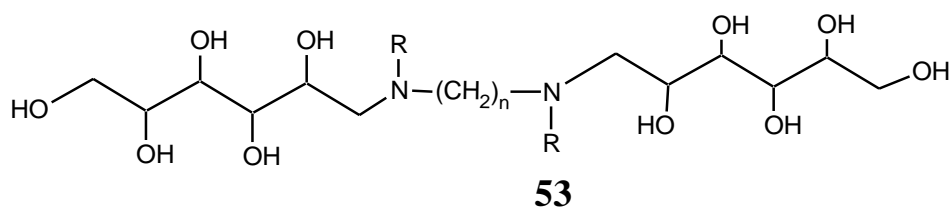


On the other hand, the interfacial properties of this new family of gemini nonionic surfactants derived from alkyl glucosides were studied and the physicochemical parameters of these dimeric compounds were compared with those of their monomeric counterparts. The effect of the position of the linkage, the anomeric configuration, the spacer functionality, and the spacer type (rigid or flexible) on the behavior of these surfactants was analyzed and it was found that the slight structural variations have a significant influence on their properties. The maximum length of the hydrophobic chains for obtaining gemini surfactants with improved efficiencies compared to those of the starting monomeric alkyl glucosides⁽¹²⁷⁾.

Another gemini surfactant synthesized starting from D-glucose and a commercial mixture of dodecyl and tetradecyl alcohols. Three different spacers (glutaryl, succinyl, and terephthaloyl) were used to link the sugar moieties. The interfacial properties of these nonionic gemini surfactants were studied⁽¹²⁸⁾.

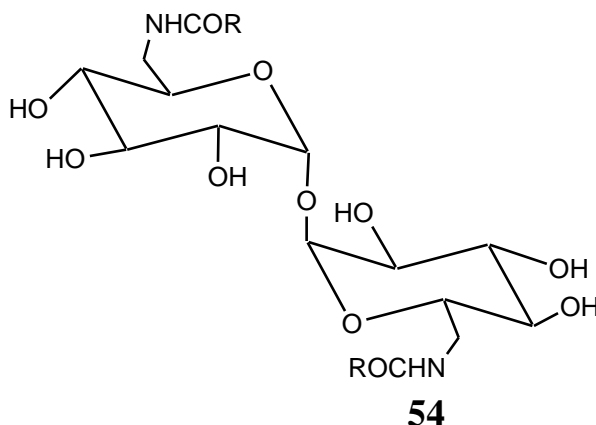
A large variety of xylose, glucose, galactose, and lactose derived gemini surfactants, with different chain and spacer lengths, have been prepared from partially protected sugars (isopropylidene derivatives), using enzymes to introduce fatty acids regioselectively into carbohydrate moieties⁽¹²⁹⁾.

Also, series of nonionic gemini surfactants interesting aggregation behavior was synthesized. Bis(1-amino-1-deoxy-D-glucityl)alkanes and bis(N-tetradecanoyl-1-amino-1-deoxy-D-glucityl)alkanes **53** were prepared with different spacer length.⁽¹³⁰⁾



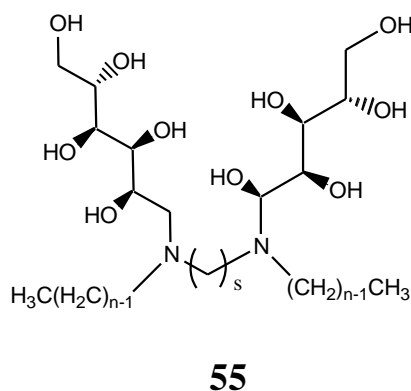
Where R = H, C(O)-C₁₃H₂₇; and n = 6,8 and 10

Nonionic gemini surfactants have amide groups having trehalose as the spacer **54**. This series consists of trehalose having the 6- and 6'-hydroxyls replaced by long-chained amides. These geminis are water insoluble despite the two amides and multiple hydroxyls ⁽¹³¹⁾.



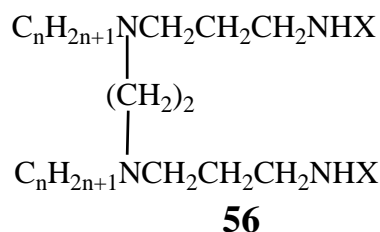
Where R = C₇H₁₅, C₉H₁₉, C₁₁H₂₃, C₁₃H₂₇, C₁₅H₃₁, C₁₇H₃₅, C₁₇H₃₃ (cis 9).

Novel reduced sugar gemini amphiphiles linked through their tertiary amino head groups via alkyl spacers of 4 or 6 carbons, and with varying (unsaturated) alkyl tail lengths of 12-8, bis- α,γ -(alkyl-10-deoxyglucitylamino)-alkanes **55** have been synthesized and tested for using in pharmaceutical ⁽¹³²⁾. Also a series of novel nonionic gemini surfactants with identical head groups and α,ω -diamino-(oxa)alkyl spacers were synthesized by reductive aminations involving α,ω -diaminoalkanes and the appropriate sugars or aldehydes. The new gemini surfactants which synthesized were characterized ⁽¹³³⁾.

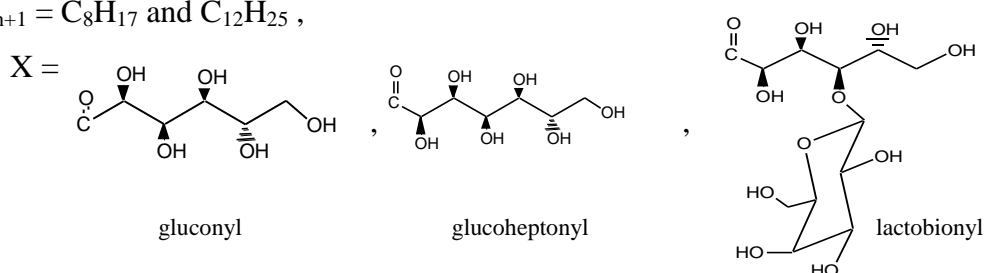


where s = 4 or 6 and n = 12,14,16,18,18:1(oleyl)

A new group of gemini aldonamide type surfactants *N,N'*-Bisalkyl-*N,N'*-bis[(3-aldonamide)propyl] ethylenediamines **56** represent a new class of gemini saccharide derived surfactants exhibiting profound surface properties.

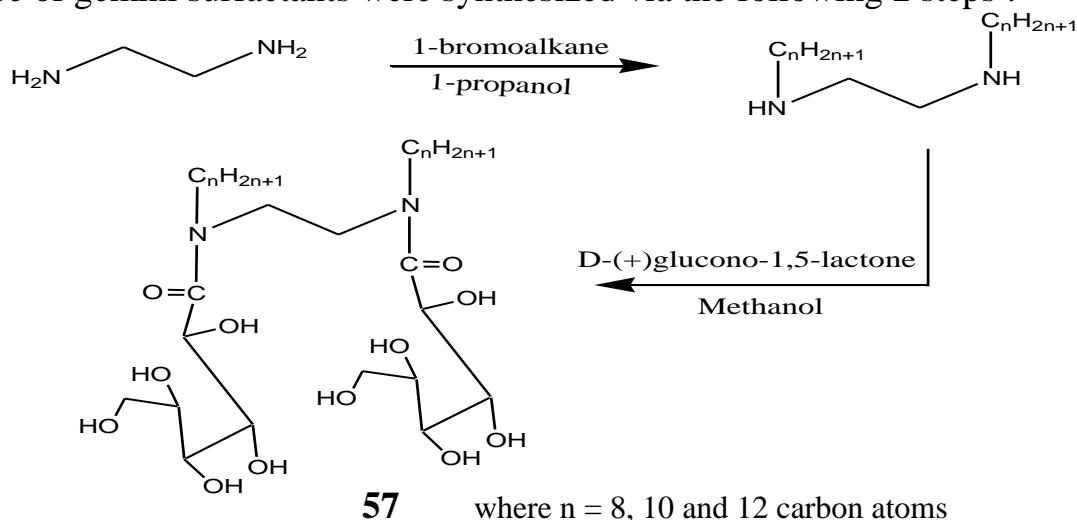


Where $\text{C}_n\text{H}_{2n+1} = \text{C}_8\text{H}_{17}$ and $\text{C}_{12}\text{H}_{25}$,



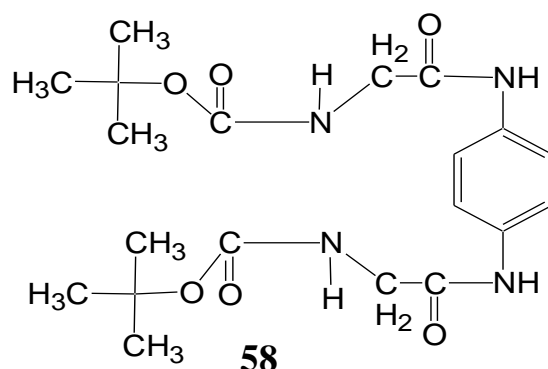
These surfactants were synthesized and characterized. The surface properties were measured for these gemini surfactants. They are very efficient at adsorbing at the free surface and at forming micelles in water and their critical micelle concentration values are remarkably low⁽¹³⁴⁻¹³⁶⁾.

Also, a novel sugar-based gemini surfactants synthesized from glucono-lactone (monosaccharide), *N,N'*-dialkyl-*N,N'*-digluconamide ethylenediamine **57**, where *n* is the hydrocarbon chain length of (8, 10 and 12). This type of gemini surfactants were synthesized via the following 2 steps :



The physicochemical properties of aqueous solutions of novel sugar-based gemini surfactants have been presented. The monosaccharide head groups of the surfactants are directly bound to the tertiary amine group at the level of an ethylene spacer. This means that the chemical structure of the gemini surfactants is molecularly restricted when compared the corresponding monomeric surfactants with these synthesized gemini surfactants found that the nonionic gemini surfactant have a greater ability in lowering the surface tension and a remarkably lower critical micelle concentration ⁽¹³⁷⁾.

On the other hand, a new class of unusual nonionic gemini surfactant, viz. the bis-amide *p*-phenylenediamine Boc-bisglycamide **58** was synthesized. A new bis-amide compound has a complex arrangement of hydrophobic and hydrophilic segments and the *p*-phenylenediamine group is considered to be a spacer group that connects two amide functional head groups with the hydrophobic moieties; hence, the molecule has been considered to be a double-head-double-tail gemini surfactant.



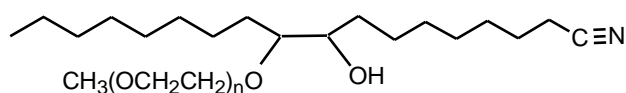
The surface tension, monolayer, and theoretical Connolly surface treatment, including computer simulation techniques were determined. Also, the bis-amide forms a smooth, stable monolayer even at low concentration. The critical micelle concentration values were also obtained by various techniques ⁽¹³⁸⁾.

The majority of work on gemini surfactants has been made with symmetrical geminis that contain identical polar head groups and identical

hydrophobic tails. Also, gemini surfactants can be nonsymmetrical, this means that the two amphiphilic moieties can differ either in the length of the hydrophobic tail or in the nature of the head group.

There are several reasons as to why symmetrical geminis dominate; the simplest being that they are usually easier to synthesize than their unsymmetrical counterparts. Ease of preparation is probably the main reason why most research has been made on symmetrical geminis ⁽¹³⁹⁾.

Another series of novel heterogemini nonionic **59** surfactants based on fatty acids was studied. The hydrophobic part of the surfactant, made from oleylnitrile, has a double bond in the middle of the chain to which the hydrophilic part is attached.



59

Where n = 11 or 16 moles of ethylene oxide

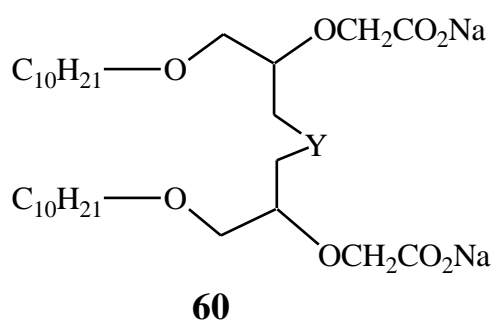
One of the hydrophilic groups is a methyl-capped polyoxyethylene chain with 11 or 16 oxyethylene units, whereas the other is a secondary hydroxyl group. The reason for using the nitrile derivative of the fatty acid instead of a more conventional derivative such as an ester or amide is to achieve good hydrolytic stability, which is often demanded for cleaning applications ⁽¹⁴⁰⁾.

- Anionic gemini surfactants:

The majority of gemini surfactant studies have been on ionic systems. A large variety of anionic gemini surfactants are sulfonate, sulfate, phosphate and carboxylate.

-Carboxylated gemini surfactants :

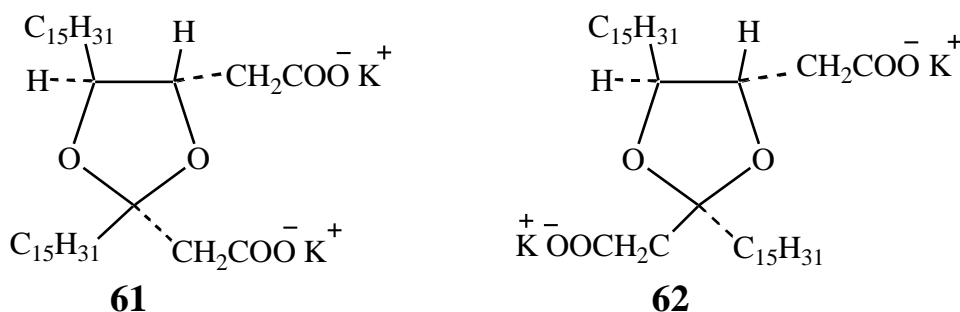
The soap type surfactants attracted special attention because of their higher biodegradability than many types of surfactants, but their application is restricted because their solubility in hard water is low due to the formation of calcium soap. Incorporation additional hydrophilic groups into soap type molecule improve their solubility in hard water results in dispersion of their surface active properties, therefore that the double chain bis(carboxylate) types surfactants **60** will have a good solubility in hard water and excellent surface active properties, some double chain surfactants with two carboxylic groups were prepared, and their surface active properties in alkaline aqueous solution were measured and found that these compounds have excellent micelle forming and high wetting ability and have higher solubility in hard water than the conventional soap ⁽¹⁴¹⁾.



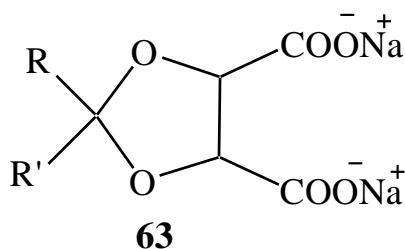
Where Y = -O-, -OCH₂CH₂O-, -O(CH₂CH₂O)₂-, -O(CH₂CH₂O)₃-, -O(CH₂)₄O-.

Another double-chain, double-head group (dicarboxylate) surfactants **61**, **62** of a 1:1 mixture of diastereomeric were prepared containing 1,3-dioxolane, using carbonate buffers with K⁺ rather than Na⁺ for neutralization, the potassium carbonate were used because the potassium surfactants were much more

soluble than the sodium surfactants, also the surface active properties were determined⁽¹⁴²⁾.



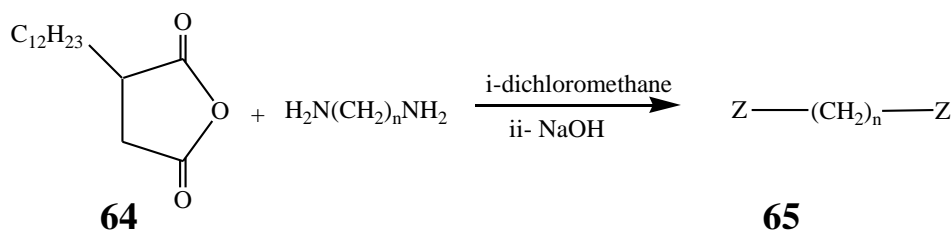
For another type of cleavable surfactant, 2-(long-chain alkyl)-1,3-dioxolane-4,5-dicarboxylate **63**.

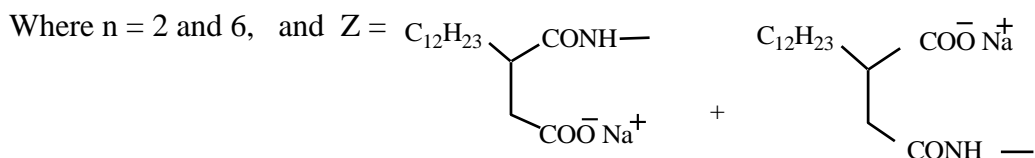


Where R = C₁₁H₂₃ and R' = H, CH₃

The biodegradability of these carboxylate types of “acid-sensitive” cleavable surfactants bearing a 1,3-dioxolane ring was measured by the biochemical oxygen demand (BOD) method in the presence of activated sludge. The biodegradation rate for the compound, bearing a proton at position 2 in the dioxolane ring, is faster than that for the corresponding compound bearing a methyl group at position 2⁽¹⁴³⁾.

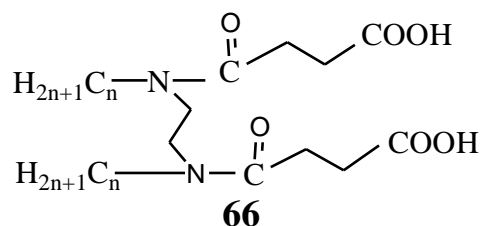
New anionic gemini surfactants with low critical micelle concentration values can be synthesized by a simple synthetic route using readily available reagents. The synthesis involves the reaction of a diamine with 2-dodecen-1-ylsuccinic anhydride **64** to form a bis(1-dodecylsuccinamic acid) **65**, which is neutralized to form the sodium salt⁽¹⁴⁴⁾.





Some of physical properties of the sodium salt of N,N-hexane-bis (1-dodecen-1-ylsuccinamic acid) were reported lowered of the interfacial tension between n-heptane and water by ring tensiometry measurements⁽¹⁴⁵⁾. The surface properties and micellar effect on oxidation of reducing sugars by hexacyanoferrate(III) were studied, the foaming power and contact angle have also been determined⁽¹⁴⁶⁾.

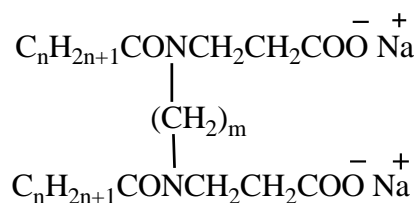
Another anionic Gemini surfactant **66** have two amide groups with two hydrocarbon chains, two carboxylate groups, were synthesized by three-step reactions and their physicochemical properties were investigated.



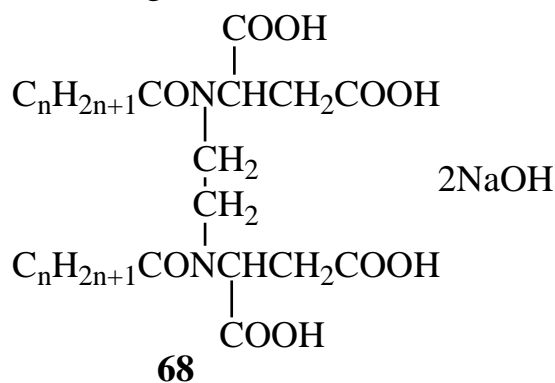
Where $n = 6, 8, 10, 12$ and 14 .

The novel gemini surfactants (1,2-bis(N- β -carboxypropanoyl-N-alkylamino)ethane) possess amide groups between the hydrocarbon chain and the carboxylate headgroup. It is expected that the presence of amide groups in surfactant make it more easily hydrolyzable. The results obtained show that the anionic gemini surfactants give unusual properties at the air/water interface and in bulk solution and show fairly low critical micelle concentration and high efficiency in lowering surface tension⁽¹⁴⁷⁾.

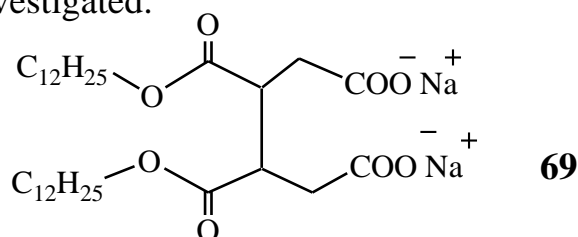
A novel series of anionic gemini surfactants, alkanediyl- α,ω -bis(sodium N-acyl- β -alaninates) **67**, were prepared. The anionic geminis is differing in the lengths of the polymethylene spacer (m : 2, 4) and the acyl chain ($n + 1 = 10, 12, 14, 16$).

**67**Where $n+1 = 10, 12, 14, 16$ and $m = 2$, and 4

Also, the surface active properties of these compounds were determined and the effect of the spacer chain length, head groups, and main hydrophilic chain length of the gemini surfactant on the solution and surface properties has been studied ⁽¹⁴⁸⁾. Another series of anionic gemini surfactants **68** was synthesized. The responses of humans to closed patch tests with these anionic gemini surfactants were also investigated ⁽¹⁴⁹⁾.

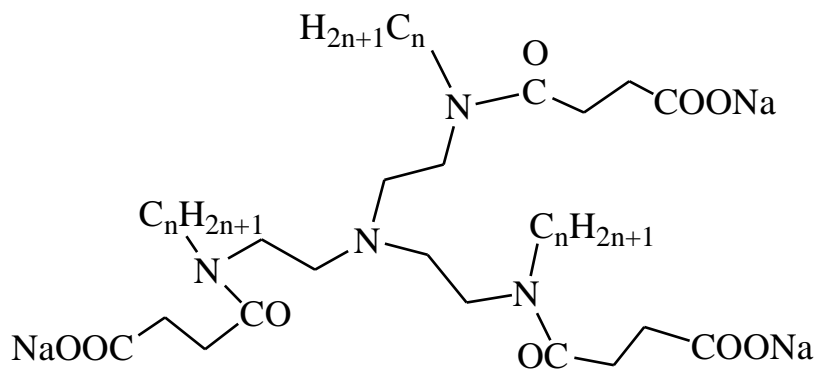
**68**Where $n+1 = 10, 12, 14, 16$

Most of the gemini surfactants studied so far have a spacer chain between two hydrophilic groups in the molecule, usually represented by $m-s-m$, where m and s are the carbon number in the alkyl chains and of the alkanediyl spacer. It is known that the spacer chain largely influences the physicochemical properties of the surfactants. However, a novel anionic gemini-type surfactant without a spacer group is known. Thus, sodium 2,3-didodecyl-1,2,3,4-butane tetracarboxylate **69** was prepared and its surface active properties were investigated.



The anionic gemini surfactant without a spacer chain, shows significantly low values for both critical micelle concentration and surface tensions ⁽¹⁵⁰⁾.

Another interesting class of geminis is trimeric-type anionic surfactants **70** with three hydrocarbon chains and three carboxylate head groups. They were synthesized from tris(2-aminoethyl)amine, and their properties were investigated by surface tension, electrical conductivity, dynamic and static light-scattering, and emulsification power techniques. The degree of emulsification remained at 69% after 24 h of standing. This trimeric-type anionic surfactants exhibited unique properties superior to monomeric or dimeric surfactants that were significantly influenced by their hydrocarbon chain lengths ⁽¹⁵¹⁾.



70

Where n = 8,10 and 12

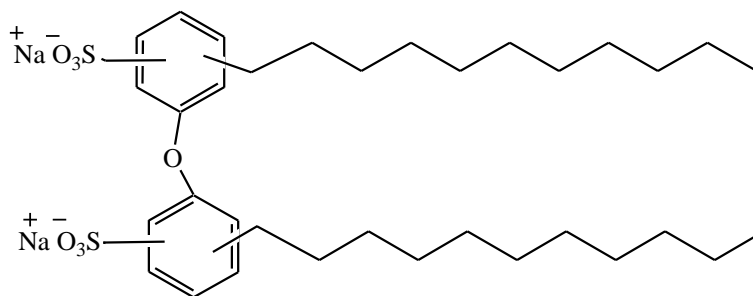
The trimeric surfactant was shown to have much lower critical micelle concentration than the corresponding dimeric surfactants.

- Sulfonated gemini surfactants:

Bis (sulfonate) types of gemini surfactants with three long chain alkyl groups were prepared by the reaction of N-(long chain acyl) diethanolamine diglycidyl ethers with long chain fatty alcohols, followed by the reaction with propanesultone. The surface tension and the critical micelle concentration of these compounds are much smaller than general types of single chain surfactants with one sulfonate group ⁽¹⁵²⁾.

A series of new dimeric anionic surfactants contains both carboxylate and sulfonate head groups as the hydrophilic part were prepared and their surface-active properties in water were studied. These compounds contain a flexible hydrophilic linkage of two different lengths between the hydrophilic groups and all the synthesized gemini compounds were readily soluble in water. Results of these Gemini surfactants were compared to those obtained with the corresponding monomeric surfactants, their critical micelle concentration values were much smaller than that of the corresponding monomeric surfactants and it was found the increasing the length of the connecting group between the two lipophilic chains decreases the critical micelle concentration ⁽¹⁵³⁾.

Didodecyldiphenylether disulfonate gemini-type surfactant **71** is a Friedel–Craft reaction product of an olefin (6–16 carbons) and diphenyl oxide using chlorosulfonic acid (AlCl_3 as a catalyst), followed by sulfonation with SO_3 in methylene chloride.

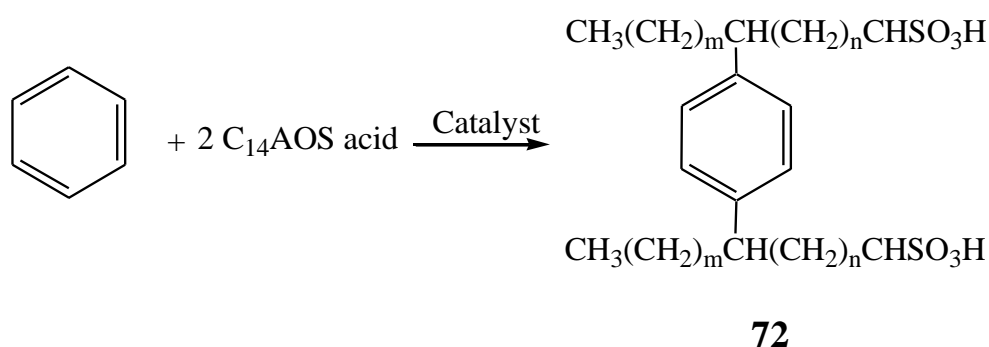
**71**

Also, the surface activity of the dialkyldiphenyl ether disulfonate, gemini-type surfactants was studied, and compared it to the monoalkylated and monosulfonated analogues and to the conventional sodium dodecyl benzene sulfonate ⁽¹⁵⁴⁾. The didodecyldiphenylether disulfonate gemini-type surfactant used for the preparation of microemulsions which are used for preparation of ink-jet inks ^(155, 156).

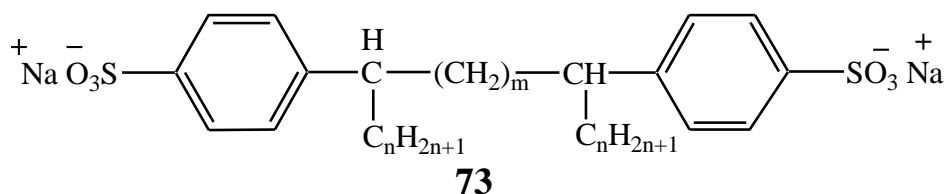
Furthermore, a new family of sulfonate surfactants, in which the sulfonyl group is attached to one of the alkyl chains, has gained interest owing

to their biodegradability, low sensitivity to water hardness, foaming ability, and lower skin irritability than the conventional alkylbenzene sulfonate. In single-step route was developed for synthesizing a dialkylaryl disulfonate gemini surfactant using α -olefin sulfonic acid (AOS acid).

The new process is very simple and effective, requiring neither the conventional alkylation, and the resulting dialkylaryl disulfonic acids differ from existing products by having the sulfonyl group attached to the alkyl chain rather than the aromatic ring. Ditetradecylmethyl-naphthalene disulfonate and ditetradecylbenzene disulfonate **72** were prepared by this method. In addition, the surface active properties of the two anionic geminis had higher surface activities than the conventional dodecylbenzene sulfonate⁽¹⁵⁷⁾.



Also, dialkyldibenzene disulfonate gemini surfactants **73** with different spacer length have been synthesised. The physicochemical properties such as their surface tensions, krafft temperatures and melting temperatures have been measured. It was found that the anionic gemini surfactants showed some aberrant properties.

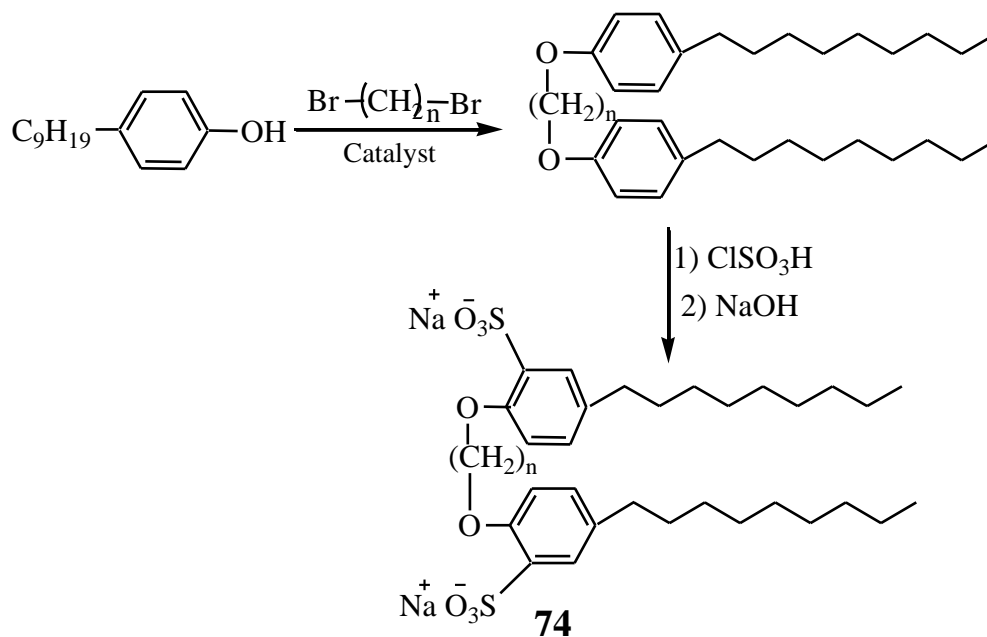


Where $n = 5, 7, 9, 11, 13$ and $m = 4, 6$

The surfactant with two longer chains had a higher critical micelle concentration than that for shorter chain surfactant, the spacer carbon number

had more important effects than the alkyl chain carbon number on their krafft temperatures and melting temperatures⁽¹⁵⁸⁾.

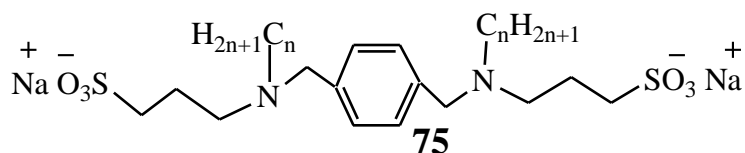
On the other hand, a series of anionic gemini surfactants with the same structure except the spacer length of the polyethylene chain like **74** have been synthesized based on nonylphenol.



Where n = 2, 3, 4 and 6

The critical micelle concentration of the studied surfactants in aqueous solutions has been investigated and surface tension at critical micelle concentration was also obtained. It was found that the critical micelle concentration of gemini surfactants has much lower values compared with those conventional monomeric ones and the value of critical micelle concentration decreases with the increase of carbon atom numbers of the spacer⁽¹⁵⁹⁾. This kind of gemini surfactant was used successfully in synthesized of polyaniline salts via the micellar polymerization⁽¹⁶⁰⁾.

Another type of anionic sulfonate gemini surfactants **75** with low critical micelle concentration has been synthesized. Also these surfactants have higher surface activities values than the corresponding single-chain surfactants.



Where R, R' = C₈H₁₇, C₁₀H₂₁ and C₁₂H₂₅, R ≠ or = R'

The critical micelle concentrations of the gemini surfactants decrease with the increase of the hydrophobic chain length. The aggregation behaviors of the surfactants have been investigated and compared with monomeric surfactant⁽¹⁶¹⁾.

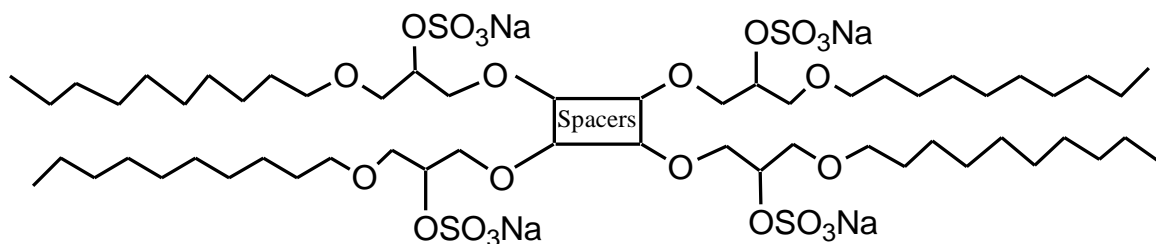
- Sulfated gemini surfactants:

A series of sulfated gemini surfactants were prepared by the reaction of glycol diglycidyl ethers with long chain alcohols followed by sulfation with chlorosulfonic acid in the presence of glacial acetic acid. And the product was neutralized with alcoholic sodium hydroxide⁽¹⁶²⁾.

A series of glycerol-based double- or triple-chain surfactants with two sulfonate, two sulfate or two carboxylate groups was conveniently prepared by reactions of 1-*O*-alkylglycerol diglycidyl ethers with long-chain fatty alcohols followed by reactions with propanesultone, chlorosulfonic acid or bromoacetic acid, respectively. Both sulfate and carboxylate types of compounds have higher water solubilities than the corresponding sulfonate type of compound bearing the same lipophilic group. The triple-chain surfactants show excellent surface-active properties, such as micelle forming and ability to lower surface tension, compared not only with the corresponding single-chain anionic surfactants, but also with the corresponding double-chain surfactants⁽¹⁶³⁾.

New anionic oligomeric surfactants with different spacing architecture based on dioxane rings were synthesized, and their surface-active properties were studied. The synthesis of these compounds e.g. **76** involves a three-step procedure comprising tetraglycidyl ethers as key intermediates for connecting four amphiphilic moieties. The ability of these compounds to lower

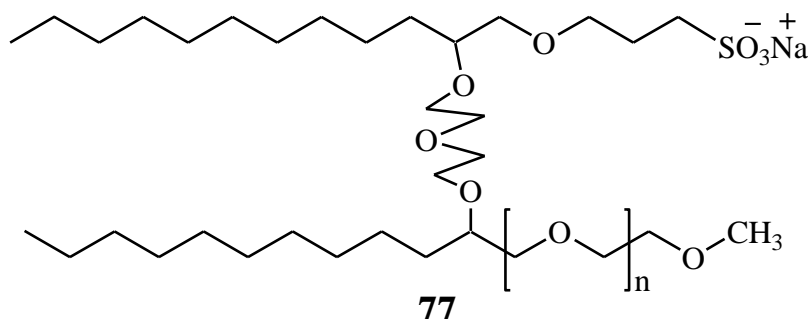
surface tension is good, but the high relative propensity to form aggregates (164).



76

Research on gemini surfactants expands rapidly. In technological and domestic applications surfactant mixtures are frequently used, either because commercial surfactants contain mixtures of different alkyl chain lengths and isomeric forms or because surfactants are mixed to optimize some aspect of performance. The heterodimeric surfactant has been designed so as to exhibit an original combination of the properties of non-ionic and anionic surfactants.

On the other hand, there are compounds have two identical hydrophobic chains but present two different hydrophilic head groups: one is a poly(oxyethylene) moiety and the second is sulfonic acid sodium salt. The two surfactant monomers are connected together by the mean of a flexible hydrophilic poly(oxyethylene) spacer compound **77** is an example of these derivatives.



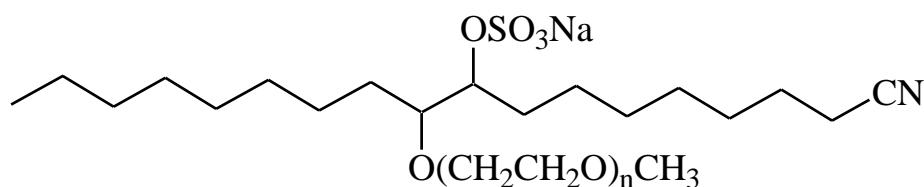
77

Where $n = 16-17$.

The new surface-active materials are different from those obtained by simply mixing the corresponding monomers. The values measured

for critical micelle concentration value far below that of the sulfonate and polyether monomers, and even below that of the symmetrical bis-sulfonate gemini⁽¹⁶⁵⁾.

Novel environmentally friendly gemini surfactants **78**, each with two hydrophilic and two hydrophobic groups, have been synthesized and their physicochemical properties were investigated. One of the hydrophilic groups is a methyl-capped polyoxyethylene chain with molecular weight 350, 550, and 750 g/mol, respectively, and the other are a sulfate group; the hydrophobic part of the surfactant is made from oleylnitrile⁽¹⁶⁶⁾.



78

Where n = 8,12 and 16

Application of surface active agents:

The applications of surfactants in science and industry are very widely distributed, such as detergents and cleaning products, personal care products applications as diverse as pharmaceuticals, purification of raw materials in the mining and petroleum industries, and to enhancing the quality of finished products such as paints, cosmetics, pharmaceuticals, and foods.

Also surfactants played an important role in the textile-and-fibers industry. The added surfactants serve to aid in the uniform dispersion of the dyes in the dyeing solution, the penetration of the dyeing solution into the fiber matrix.

The properties and applications of surfactants are determined by the balance between the lyophilic and lyophobic portions of the molecules. The desired properties such as solubility, surface tension reducing capability, critical micelle concentration, detergency power, wetting control, and foaming capacity may make a given surfactant perform well in some applications and less well in others.

Nonionic surfactants have a moderate foaming and good detergency make them very suitable for washing purposes. The good dispersion, emulsification of ethoxylated and propoxylated surfactants made them very useful in the formulation of cleaners for household and industrial uses.

Detergent composition contains C_{12} alcohol from tallow oil with 1-4 moles of propylene oxide are used as antifoaming agents⁽¹⁶⁷⁾. Also, alkyl or alkyl phenol with C_{8-18} carbon atoms with 1-10 moles of ethylene oxide was used as antifoaming cleaning composition for cleaning hard surface⁽¹⁶⁸⁾. The nonionic surfactant produced from ethoxylation of alcohols C_{6-22} ⁽¹⁶⁹⁾ or fatty alcohols with 15-40 moles of ethylene oxide⁽¹⁷⁰⁾ formulate with anionic surfactants are used as additives for improving the tolerance of skin, detergent cosmetics.

On the other hand, the nonionic polyoxyethylene alkyl ether surfactants can replace organic solvents in several liquid–liquid extraction processes and chromatographic separations of cholesterol. Their low toxicity compared with classical organic solvents is a great advantage. They are easier and safer to handle in chemical processes, producing less toxic wastes and saving the environment ⁽¹⁷¹⁾.

Also ethoxylated fatty acid esters have been used in combination with various types of builders, these surfactants are formulated for all types of household and industrial cleaning applications, and are excellent detergent when used with alkaline builders ⁽¹⁷²⁾.

Ethoxylated fatty acid amides are blended with other additive, forming detergent composition used in cosmetics and cleaning composition ⁽¹⁷³⁾. Also alkoxyated animal fatty acids diethanolamide with 5 moles of ethylene oxide was blended with C₁₂₋₁₆ fatty alcohol ethoxylated with 7-10 moles ethylene oxide, alkoxyated C₁₂₋₂₂ fatty alcohol with 3-7 moles ethylene oxide and 6-15 moles propylene oxide, nonyl phenol alkoxyated with 8 moles ethylene oxide and 7 moles propylene oxide to form nonionic surfactants with reduced foaming capacity ⁽¹⁷⁴⁾.

Nonionic surfactants derived from alkylglucoside are moderately foaming, highly soluble and suitable for use in variety of cleaning products. They are gradually replacing other known nonionic surfactants in industry, on account of their excellent biodegradability and the absence of toxic effects. Food elaboration, polymer manufacture, and solubilization of biological membranes are some of the wide spectrum of applications of alkyl glycosides.

Furthermore, alkylglucoside esters of fatty acids and ethoxylated fatty alcohols are used in all purposed cleaners, surfactants mixture comprising alkyl glucoside are used in low foaming cleaning for hard surface such as glass and plastic surfaces ⁽¹⁷⁵⁾. Polyoxyethylene methylglucoside, N-myristoyl-L-

glutamic acid and calcium salt, coconut oil fatty acid methyl laurate sodium salt, diglycerin, sorbitol was blended to form cream cleaning composition ⁽¹⁷⁶⁾.

The nonionic surfactant produced from addition of ethylene oxide and/or propylene oxide with fatty alcohols, fatty acids or fatty amines are used as laundry treatment compositions to reduce the drying time of laundered fabrics⁽¹⁷⁷⁾.

Anionic surfactants are very widely used in our life. They are used in laundering, dishwashing liquids and shampoos because of their excellent cleaning properties. The earliest anionic surfactants are soaps which are very desirable products. As already noted, soap is especially important in less industrialized countries because the sources are readily renewable, and the necessary production facilities and technology are relatively simple and inexpensive.

Also the application of sulfo fatty acids and sulfo fatty acid esters is known, the sulfonated methyl ester can be made from low cost vegetable and animal fat so it became a replacement for the traditional surfactants in consumer products ⁽¹⁷⁸⁾.

The linear alkylbenzene sulfonates family is probably the world's most important anionic surfactant family, taking into consideration their wide applicability, cost effectiveness, and overall consumption levels. The toxicity and foaming properties of alkylbenzenesulfonates were studied and it was found that they belong to low toxicity compounds and are recommended for applications in various washing compounds⁽¹⁷⁹⁾. A mixture of heavy alkylbenzene with molecular weight of 310-370 and C₈₋₂₆ linear alkylbenzene, followed by sulfonation with sulfuric acid, and the obtained sulfonate can be used as surfactant in tertiary petroleum recovery ⁽¹⁸⁰⁾.

A mixture of sulfated ethoxylated sorbitol and linear alkylbenzenesulfonate and C₁₂₋₁₅ ethoxy sulfated alcohol was used in laundry cleaning composition ⁽¹⁸¹⁾.

Polyethylene glycol 2-pentylnonyl ether sulfate sodium salt blended with other additive, forming detergent composition used in cosmetics, food and petroleum recovery⁽¹⁸²⁾.

Gemini surfactants are very interest in the academic and industrial communities working on surfactants. They are used in very different fields of application as conventional surfactants.

Gemini surfactants where chosen because of their low critical micelle concentration and enhanced surface activity⁽¹⁶⁶⁾. They are used is as detergents for industrial and household applications, stabilization of dispersed systems, also gemini surfactants are finding there way into skin care formulations, drug delivery systems, antipollution protocols, analytical separations, nanoscale technology, biotechnology, enhanced oil recovery and as paint additives.

Also, gemini nonionic surfactants derived from alkyl glucosides were used in personal care and household formulations, as they are nontoxic, biodegradable, and easily obtained from natural renewable resources. They can be used as minor additives to conventional surfactants, enhancing their properties and thus justifying the added cost⁽¹²⁸⁾.