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Chapter

Structure and Applications of Surfactants

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Abstract

Surfactant molecules have two parts, a lipophilic (apolar) part that retains fat and a hydrophilic (polar) part that is miscible with water. The lipophilic portion consists of one or more aliphatic, straight or branched or aromatic or even alkylaromatic hydro- or fluorocarbon chains. The hydrophilic portion or polar head consists of one or more polar groups, ionic or nonionic. Surfactants have a wide variety of applications that include membrane permeabilization and dissolution, inclusion body solubilization, as well as membrane protein solubilization, biochemistry, crystallization, and manipulation. The behavior of these molecules is directly related to the aversion to water of the nonpolar groups, whereas the polar moieties tend to be highly hydrated. Their surfactant properties are therefore essentially based on the balance between the hydrophilic and hydrophobic parts of the molecule, called HLB (Hydrophile-Lipophile Balance).

Keywords: surfactant, structures, applications, monotailed, bitailed, bolaphiles, hydro-fluorocarbon, chains

1. Introduction

1.1 General

Surfactant molecules are amphiphilic compounds. These molecules have two parts with different affinities with water. One part is polar and soluble in water, commonly called "hydrophilic head", while the other part is apolar, presenting rather an affinity for fatty substances and commonly called "hydrophobic chain." This feature gives surfactant molecules the property of adsorbing preferentially at interfaces and thus reducing the interfacial tension to improve the dispersion or solubilization of one phase in another immiscible one.

1.2 Properties of surfactants

The amphiphilic nature of surfactant molecules induces a very strong tendency to migrate at the interfaces [1], which allows them to improve the wettability of a liquid, to stabilize a foam or an emulsion, to promote the dispersion of a solid in a liquid [2, 3].

The physico-chemical properties of surfactants, which determine their potential applications, depend on several physical quantities [4].

1.2.1 Hydrophilic/lipophilic balance

To determine the hydrophilic power of a surfactant, the HLB (Hydrophilic Lipophilic Balance) defined by Griffin [5] can be used. The HLB of a surfactant is related to its solubility. It extends on a scale from 0 to 20, and the higher the value, the more the surfactant is soluble in water (more hydrophilic, **Table 1**).

The HLB value of surfactants can be calculated by the empirical method of Griffin (Eq. 1) [5], with H and L the respective molar masses of the hydrophilic part and the lipophilic part. However, this relationship is not suitable for other surfactants, since it does not take into account counterions in the case of ionic surfactants, nor the existence of establishments or functional groups on the hydrophobic chain.

$$HLB = \left(\frac{H}{H + L} \right) + 20 \tag{1}$$

1.2.2 Surface tension

Surface tension is the tension that exists at the interface between a gas and a liquid. This tension accounts for the force exerted by the molecules which are on the surface separating two media. In the presence of surfactants on the surface, this force decreases.

1.2.3 Critical micellar concentration

The Critical micellar concentration (CMC) is the concentration above which the interface is saturated and part of the surfactant molecules come together in the form of aggregates called micelles. Beyond that, the surface tension is no longer modified, even at concentrations clearly above the CMC

1.3 Classification of surfactants

There are different possible classifications of surfactants. They can be classified according to:

Surfactant properties	HLB value	Solubility
Defoamer	1-3	↑ Lipophilic
Water-in-oil emulsifier	3-6	
Wetting	7-9	
Oil in water emulsifier	8-18	↓ Hydrophilic
Detergent	13-15	
Peptizer-solubilizer	15-18	

Table 1. Classification of surfactants according to value by HLB [6].

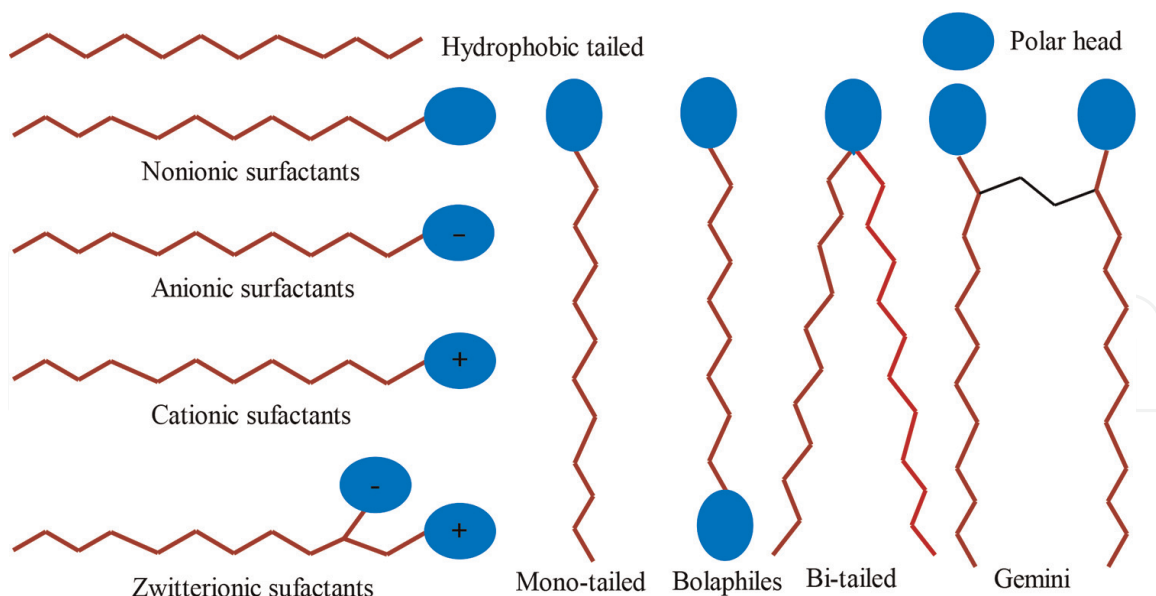


Figure 1.
 Schematic representations of surfactants according to their polar heads and hydrophobic chain.

- the nature of their polar head (nonionic, anionic, cationic or amphoteric) (**Figure 1**).
- number of polar head and hydrophobic chain which makes it possible to classify surfactants as mono-chain, bi-chain, ... , bolaphiles, gémini, ... (**Figure 1**).
- the length of the lipophilic part which makes it possible to classify surfactants as wetting agents (C8–C10), detergents (C12–C16), emulsifiers or softeners (C18–C22).
- their origin, natural or synthetic.

2. Anionic surfactants

2.1 Preparation and applications

These molecules have one or more functional groups that ionize in the aqueous phase to give negatively charged surfactant ions to which are associated cations such as alkali metals (Na, K) or quaternary ammoniums (NR_4). They have detergent, wetting and foaming properties and are therefore present in most hygiene and cleaning products. More rarely, they are used as emulsifiers. Among the anionic surfactants, we can count:

2.1.1 Carboxylate derivatives

Carboxylate-based surfactants are mainly used as soaps [7]. These are the salts of carboxylic acids, resulting from the saponification of triglycerides of vegetable (palm oil, olive oil, etc.) or animal (tallow) origin. The part hydrophilic consists of a saponified carboxylic group. These are products detergents, wetting agents and foamers. The saponification reaction leads to very alkaline solutions, a pH 10 can then be reached, resulting in irritant reactions which can appear on certain fragile skins following soaping.

Among the Carboxylate-based, we can count:

- **Sodium stearate** or sodium octadecanoate (**Figure 2**) prepared by saponification of triglycerides from vegetal or animal source. This sodium salt of stearic acid has many applications in scientific world as well as in daily use. This white solid is the most common soap. It is found in many types of solid deodorants, rubbers, latex paints, and inks.
- **Sodium laurate** or sodium dodecanoate (**Figure 3**) prepared by saponification of coconut oil or palm oil. In addition to its use in bar soaps and liquids, sodium laurate as a strong surfactant can be used at high concentrations to extract and solubilize the membrane proteins particularly integral membrane proteins.

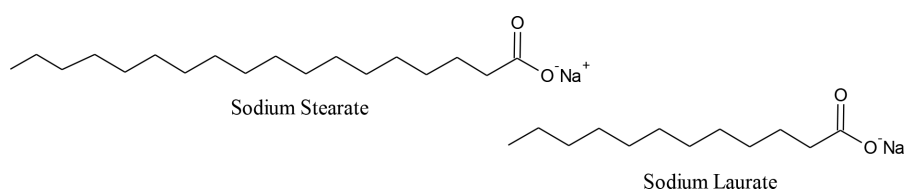


Figure 2.
Examples of carboxylate derivatives surfactants.

2.1.2 Amino acid carboxylate derivatives

Amino acid surfactants (AAS) are biocompatible and biodegradable surfactants obtained by condensation of natural amino acids with fatty acids (or their derivatives) of oleochemical source [8–10]. Moreover, AAS can be produced in large scale by green chemistry approaches, including enzyme-catalyzed synthesis using immobilized lipases and proteases, although chemical processes still prevail due to high yields and low production costs [11–16].

Among the Amino acid carboxylate -based, we can count:

- **Sodium lauroyl glycinate** (**Figure 3**) was used as the main surfactant in a body wash product for its mildness and lather properties [17].
- **Sodium lauroyl sarcosinate** (**Figure 4**), was widely used in personal care products and has immense biological and industrial significance. It is used in a number of cosmetic formulations and in soaps [18, 19].

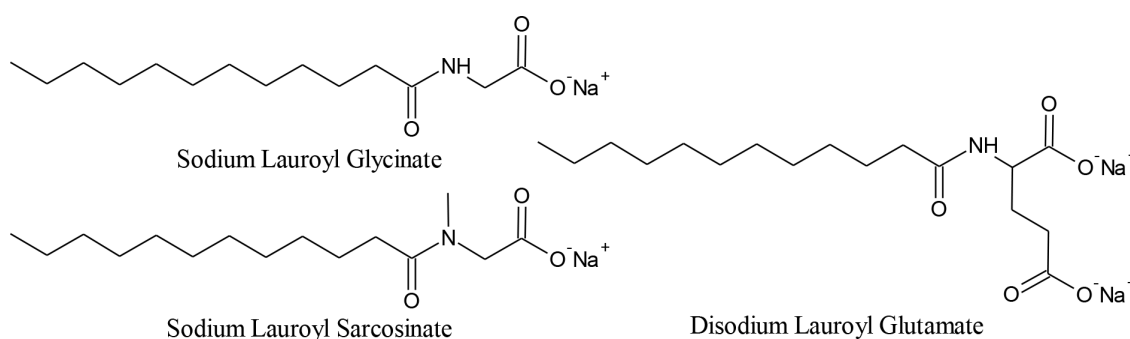


Figure 3.
Examples of amino acid carboxylate derivatives surfactants.

- **Disodium lauroyl glutamate (Figure 3)** have also been used in transparent soap bars [20] and this has been attributed to the presence of a unique cubic phase in between the micellar phase and the anisotropic hexagonal liquid crystalline phase in their phase behavior [21].

2.1.3 Sulphate derivatives

They are composed of a hydrophilic part consisting of a sulfate group ($-\text{O}-\text{SO}_3^-$) and a lipophilic alkyl chain, most often C12 and usually saturated (C12:0). They have the advantages of being good detergents, good foaming and wetting properties. Among them, we can count:

- Alkyl sulphates: sodium lauryl sulphate (SLS) or SDS (dodecyl sulphate of sodium) (**Figure 4**) are prepared by neutralization of the alkyl-ester-sulfuric acid by the appropriate base.
- Alkyl ether sulfates, (ex: Sodium Lauryl Ether Sulfate) (**Figure 4**) which are less irritating than SDS while having the same properties. For these surfactants, the ether group is a poly (ethylene oxide) chain (POE).

Same results obtained with sulfated alkanonamides prepared by sulfating of the alkanol amides, in particular those in C12–C14 (cocoamide). Neutralization of alkylamide sulfuric acid with monoethanolamine in the following example (**Figure 4**), resulting in a foam booster used in shampoos and bubble baths. These surfactants have a large hydrophilic group and do not irritate the skin. They are used as LSDA and foam stabilizers in soap bars and shampoos.

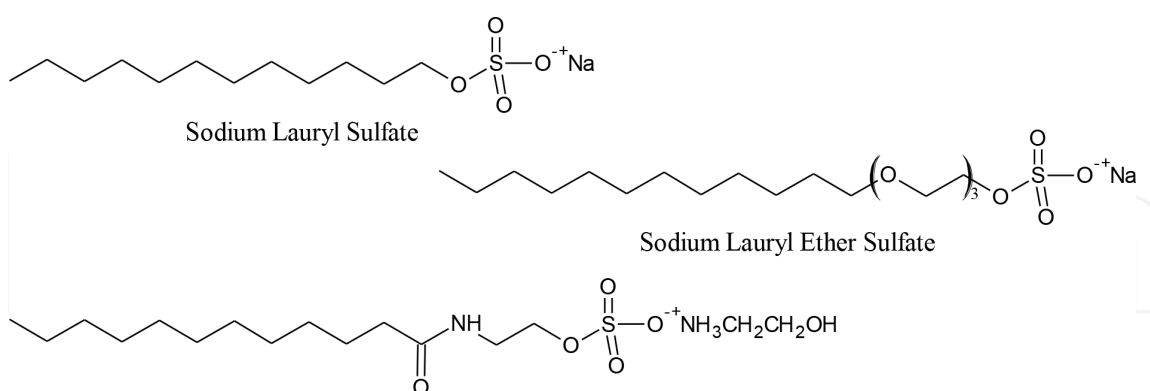


Figure 4.
Examples of Sulphate derivatives surfactants.

Petroleum sulfonates are sulfonates produced when an intermediate-molecular-weight refinery stream is sulfonated (**Figure 5**). These acids were then transformed into the corresponding surfactant and removed from the oil by liquid-liquid extraction with an alkaline solution (**Figure 5**). These surfactants have been widely used because they are effective at attaining low Interfacial tension, are relatively inexpensive, and have been reported to be chemically stable [22].

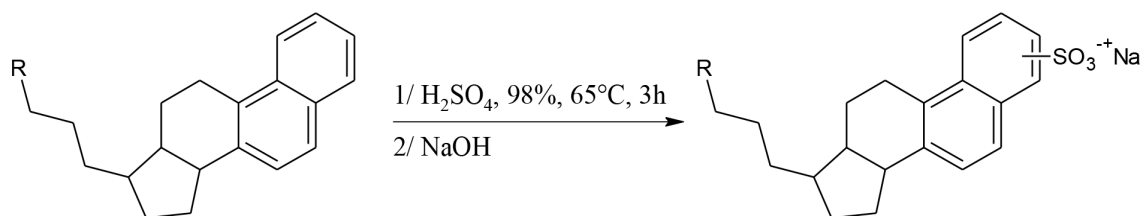


Figure 5.
General chemical reaction taking place in the preparation of petroleum sulfonates.

2.2 Phosphate ester surfactants

Alkyl phosphates are the organic esters of ortho-phosphoric acid. These ingredients are mixtures of esters and salts wherein a phosphate may have one to three alkylations and one to two potassium or sodium cations (**Figure 6**). Phosphate esters are anionic surfactants which are produced by phosphorylation of aliphatic or aromatic (ethoxylated) alcohols [23]. The properties of phosphate esters can be altered by the type of alcohol used as raw material and degree of ethoxylation of the alcohol [24]. Phosphate esters are known for exhibiting mild and nonirritating properties [25]. Phosphate esters are widely used as lubricants and hydraulic fluids because of high performance and safety advantage over others due to their high thermal stability [26].

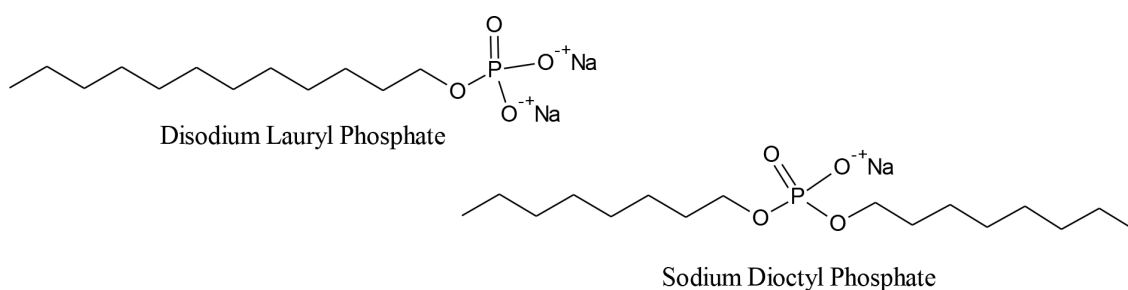


Figure 6.
Examples of alkyl and dialkyl phosphate esters.

3. Cationic surfactants

They contain a positively charged ionic group in aqueous solution. Their part hydrophilic positively charged allows them to adsorb very easily on substrates negatively charged. Thus, this positive charge gives them in particular affinities with the keratin, protein which mainly constitutes the hair (95%). On the other hand, many of them possess bactericidal properties. Indeed, they have the ability to destroy (lyse) the membrane of microorganisms when the fatty chain is short. From Cationic surfactants, the most used are quaternary ammonium and pyridinium derivatives.

3.1 Alkyl-ammonium surfactants

Alkyl-ammonium ions are produced in acid medium by the reaction of a proton with the amine (**Figure 7**). The resulting salt (in general chloride or bromide) is soluble in water thanks to the cation solvation. Fatty amines come from fatty acids, hence their chain is linear with an even number of carbon atoms. These surfactants are used as antistatic agent, emulsifying agent, and dispersing agent and corrosion inhibitor [27–29].

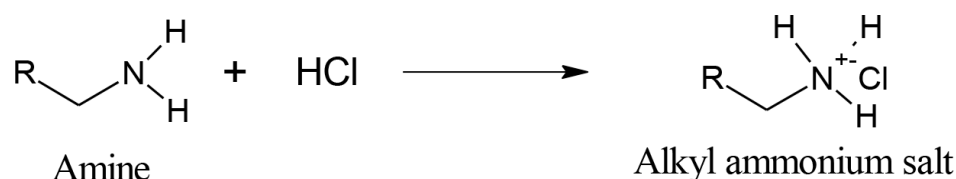


Figure 7.
General chemical reaction of preparation of ammonium salts.

3.1.1 Surfactants with one quaternary ammonium head

3.1.1.1 Quaternary ammonium salts

Quaternary ammonium salts also called Quats: are organic ammonium compounds to which the fourth valences of a nitrogen molecule are organically bound (**Figure 8**). In the general formula of quaternary ammonium salts, at least one of the radicals is formed by a long aliphatic chain of more than eight carbon atoms [30].

These products are stable in acidic and basic medium and are usually soluble in water and alcohols. They adsorb strongly on different materials, which can decrease the concentration of their solutions. Quaternary ammonium derivatives are bactericidal on a wide variety of germs, especially on Gram positive ones. They often have fungicidal, virucidal and algicidal properties. The pH, the presence of proteins, the hardness of the water influence their activities. Finally, the presence of carbon and nitrogen atoms in their molecules promotes the multiplication of resistant strains. Contamination of dilute solutions must therefore be avoided [31].

Quaternary ammonium salts are soluble both in aqueous medium because it is polar but also in organic medium since it has aliphatic chains: $(R_4N^+, ^-X)$. They are used as phase transfer catalysis in a two-phase organic/aqueous medium [32–35].

3.1.1.2 Alkyls quaternary ammonium salts

Alkyl trimethylammonium is produced by the reaction of a fat-rich amine and chloromethane in the presence of sodium hydroxide. In the case of dialkyl dimethyl ammonium, the amine used is dialkylated. Alkyl-dimethyl benzyl quaternary ammonium is produced by the reaction of alkyl dimethylamine with benzyl chloride or epichlorohydrin. The number of carbons in the long alkyl chains in these surfactants is usually 8 to 22, while that of the short chains is 1 to 7 (**Figure 9**).

The most common quaternary ammonium disinfectants are probably benzalkonium chloride (BAC), and didodecyldimethylammonium chloride/bromide [36]. BAC is utilized in hand sanitizers, soaps, cleaning wipes, hospital sanitation kits, surface disinfectants [37, 38], etc. Quaternary ammonium compounds, with double-chain called dialkyl (e.g., didodecyldimethylammonium bromide (C12-C12DMA)), are used for emulsion stabilization [39].

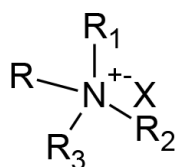


Figure 8.
Structure of an ammonium salt.

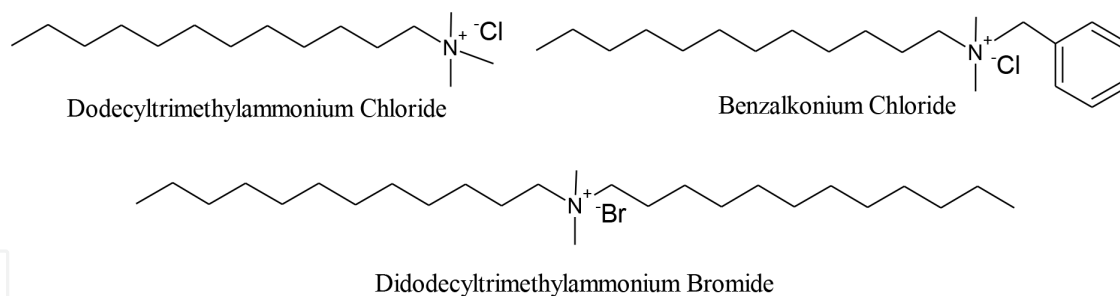


Figure 9.
Examples of alkyl trimethylammonium surfactants.

3.1.1.3 Alkylcyclic quaternary ammonium salts

Another important cationic surfactants class contains aromatic or saturated heterocycles including one or more nitrogen atoms. This is the case of a well used n-alkylpyridinium chloride, which is prepared by reacting alkylchlorure on pyridine. Pyridinium compounds (**Figure 10**) have been also used to achieve asymmetric and regioselective synthesis by additions of Grignard reagent [40]. Pyridinium cationic surfactants (**Figure 10**) have applications in the synthesis of TiO₂ nanoparticles [41], in the synthesis of ionic liquids [42] or as electrolytes for dye-sensitized solar cells [42]. Some of the pyridinium salts (C12 and C16) have been used as agents for solubilizing compounds in water in analytical chemistry applications [41].

Piperidinium compounds find application in hair conditioning formulations as anti-static agents. Piperidinium surfactants, including those functionalized with OH groups, show a high antimicrobial effect at concentrations lower than critical micelle concentration for both bacteria and fungi, with the low hemolytic activity revealed [43].

Piperidinium salts attract considerable interest due to their superior performance in terms of high ionic conductivity, wide electrochemical window, low volatility and low flammability. One of the most important applications of piperidinium salts is its application in electrolyte systems. They are used in battery systems [44, 45].

A cyclic compound with two nitrogen atoms, so-called imidazole is prepared from ethylene diamine [46]. Due to their low toxicity [47], these compounds are widely used as precursors in the synthesis of cationic surfactants called imidazolium salts (**Figure 10**). Cationic imidazolines or imidazolium salts derive from N-alkylation which results in the attachment of an alkyl or aryl to the ring of the imidazoline.

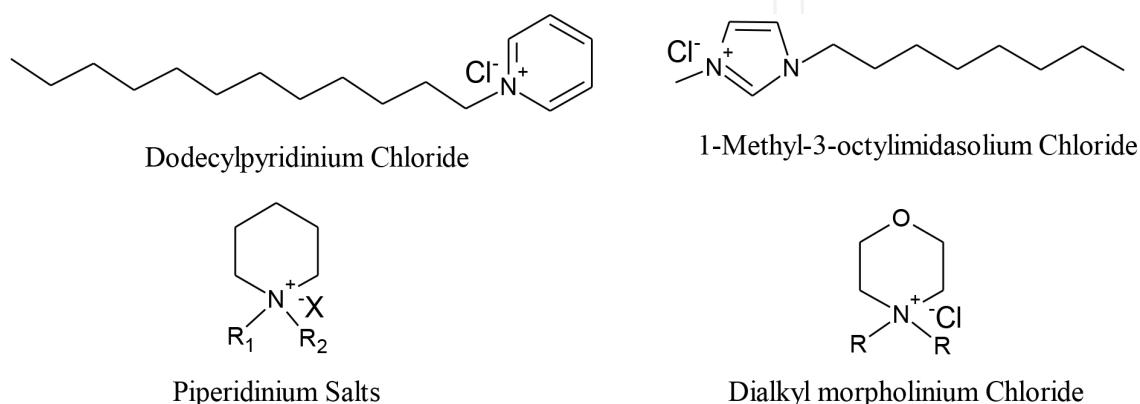


Figure 10.
Examples of alkylcyclic quaternary ammonium surfactants.

Imidazolium salts are much more hydrophilic than their bases and therefore function as stable acid detergents with good wetting agents [48]. They also show good lubricating power to form complexes with bentonites. They are also compatible with aqueous systems. The oleic acid salt of imidazolium is a good lubricant, it is widely used in various industrial applications [48].

Morpholine is a saturated cycle containing both an oxygen and a nitrogen atom. The dialkylation of the nitrogen atom results in a salt called *N,N*-dialkyl-morpholinium. These dialkylation were observed when morpholine carried out with alkylhalogenur (**Figure 10**). Morpholinium cationic liquids are less toxic than other cationic groups of ionic liquids such as imidazolium, pyridinium, piperidinium, pyrrolidinium, etc. [49]. They were shown to perform well in the electrolyte systems for lithium batteries, supercapacitors and solar cells [50]. Morpholine and its *N*-Alkyl derivatives are a class of important intermediates for many fine chemicals, which have been widely used in rubber, medicine, pesticide and other fields (**Figure 10**) [51].

3.1.2 Surfactants with two quaternary ammonium heads

3.1.2.1 Gemini quaternary ammonium surfactants

Gemini surfactants, or dimers, are organic compounds formed from two hydrophilic heads and two hydrophobic chains, separated by a covalently bonded spacer [52–58].

Most studies, however reported on the surface tension of the aqueous solutions of gemini cationic surfactants for CMC determination and assessment of their capacity in the reducing the surface tension of water [59–61]. The CMC values of piperidinium and morpholinium gemini surfactants (**Figure 11**) are lower or comparable to counterparts reported in the literature such as conventional quaternary ammonium gemini surfactants and heterocyclic gemini surfactants. Many results of physicochemical property studies of gemini surfactants show that these properties depend not only on changing the length of the hydrophobic alkyl or the length of the spacer, but also on varying the type of cationic head group. They have found broad utility ranging from industrial to personal care applications [62–64]. When these salts with two alkyl chains and two ammonio groups show good extractive abilities as phase transfer

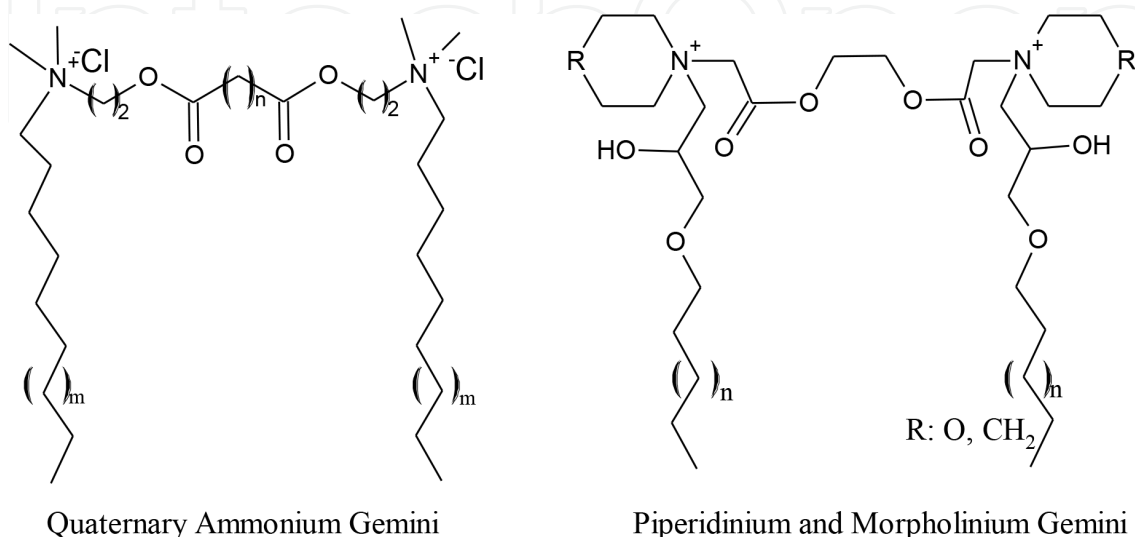


Figure 11.
Examples of gemini cationic surfactants.

catalyst [65]. These Cationic geminis surfactants were used to separate all members of a family ergot alkaloids by micellar electro kinetic capillary chromatography when the spacer is 1, 3-bis (dodecyl-*N,N*-dimethyl ammonium)-2-propanol dichloride [66].

3.1.2.2 Bolaamphiphils quaternary ammonium surfactants

Bolaamphiphiles are composed of two polar head groups separated by one, two or three long hydrophobic spacers that are mostly alkyl chains, and can even be steroids or porphyrins [67]. Bolaamphiphiles can be divided in two main categories (**Figure 12**): symmetric [68] (with same polar headgroups at both ends) and asymmetric [69] ones (possessing different polar headgroups at both ends), however both capable of self assembling to yield interesting nano-assemblies. Chemical structure of bolaamphiphiles can dictate their arrangement into parallel or antiparallel sheets resulting in formation of either unsymmetrical or symmetrical monolayer membranes [70–72]. Bolaamphiphiles have been used in formulating stable nanocarriers systems and have already demonstrated enough potential in effective drug as well as gene delivery [73, 74]. The self-assembly characteristics in aqueous solutions of cationic bolaamphiphiles with systematic changes in their chemical structure has been investigated [75]. Generally, it has been shown that symmetrical bolaphiles can self associate into mechanically very stable monolayer. Upon sonication, the single-chain bolaphile forms spherical aggregates [75].

Others formed a gelatinous network of fibers or multi-lamellar vesicles [76]. Vesicles made from cationic bolaamphiphiles (bolas), GLH-19 and GLH-20, (**Figure 13**) are used to investigate their ability to protect siRNAs from nuclease degradation while delivering them to target cells, including including brain cells are computational and experimental studies. These studies show that that GLH-19 vesicles have better delivery characteristics than do GLH-20 vesicles in terms of stability, binding affinity, protection against nucleases, and transfection efficiency, while GLH-20 vesicles contribute to efficient release of the delivered siRNAs, which become available for silencing [77–79]. Compared with vesicles prepared from phospholipids or double chain amphiphiles, the cationic vesicles can form spontaneously and remain stable for a longer time, which takes the big advantage in practical applications [80].

The vesicles formed from cationic bolaamphiphile synthesis from *N,N'*-alkylenebis (vernolamide) and the corresponding α,ω -alkylene vernoldiester with choline esters as cleavable head groups (**Figure 13**) can be use for targeted drug delivery as hydrolysis of the head group by specific enzyme, abundant in the target organ, will results in efficient decapsulation of the vesicles and the release of the encapsulated drug at the target site [81]. These bolaphiles have much weaker surface activity but stronger aggregation ability which is characterized by much higher surface tension but lower CMC (critical micelle concentration) than their conventional counterparts with the same hydrocarbon/head group ratio [82–84].

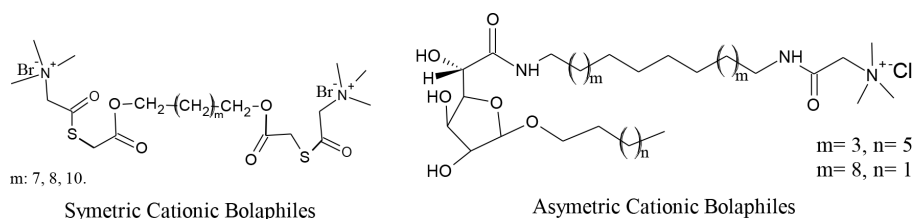


Figure 12.
Examples of symmetric and asymmetric cationic surfactants.

4. Nonionic surfactants

Nonionic surfactants contain an uncharged polar group with a high affinity to water. They consist of a saturated or slightly unsaturated hydrocarbon chain to which are attached several polar groups such as ether, alcohol, carbonyl, amine type or a polymeric chain, in particular a polyoxyethylene chain.

4.1 Ethoxylated nonionic surfactant

4.1.1 Alcohol ethoxylates

Alcohol ethoxylates (EAs) are a class of nonionic surfactants that contain a hydrophobic alkyl chain attached to a chain of hydrophilic ethylene oxide (EO) groups through an ether bond, and have a general structure $R(OCH_2CH_2)_nOH$ (**Figure 14**). These products are based on either synthetic or natural fatty alcohols [85]. Synthetic alcohol ethoxylates are produced by direct ethoxylation of alcohols, whereas natural fatty alcohols are first reduced to make them saturated before going for ethoxylation. Both synthetic and natural alcohol ethoxylates are used as nonionic surfactants in many industries. They are mainly used in industrial and consumer products, such as laundry detergents and multi-purpose cleaning products; to a lesser extent, they are also used by the agriculture, cosmetics, textiles, paper and petroleum products sectors [86, 87].

Lauryl alcohol ethoxylate, stearyl alcohol ethoxylate, behenyl alcohol ethoxylate, etc. are examples of fatty alcohol ethoxylates. All these ethoxylated products vary in physical appearance and have different properties like pour point, cloud point, density, viscosity, and flash point depending on the level of ethoxylation process from which they are formed [23].

4.1.2 Fatty acid ethoxylates

Fatty acid ethoxylates are produced by ethoxylation of fatty acids derived from saturated or unsaturated animal or vegetable fats like Coconut Fatty Acid, Lauric

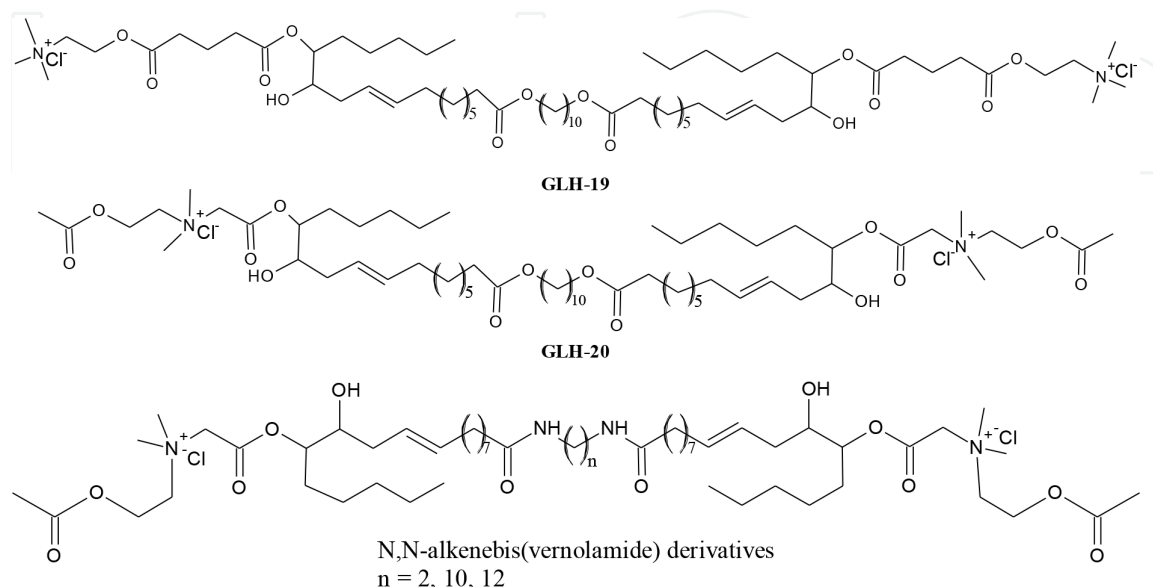


Figure 13.
Chemical structure of selected bolaamphiphiles GLH-19, 20, and N,N'-alkylenebis(vernolamide) derivatives.

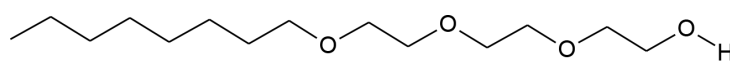
Acid, Oleic Acid and Stearic Acid. These nonionic surfactants manufactured by addition of ethylene oxide to fatty acids producing a range of ethoxylates having different moles of EO. These are extensively used in formulations of emulsifying softeners, wetting agents, cleansing agents and dispersants. The stearic acid ethoxylates (**Figure 15**) are applied in cosmetic industrial sectors as emulsifiers in oil-in-water type creams and lotions. Fatty acid ethoxylate includes; lauric acid ethoxylates and coco fatty acid ethoxylate. These products are used in textile and in the manufacture of spin finishes [23].

4.1.3 Alkyl phenol ethoxylates

The basic element of the alkylphenol molecule is a phenolic ring on which is substituted, generally in the para position, an octyl, nonyl, or dodecyl radical (**Figure 16**). This molecule comprises a variable number of ethoxylate groups ($-\text{CH}_2-\text{CH}_2-\text{O}-$) in the $-\text{OH}$ functional group of phenol. The number of ethoxylates determines the physico-chemical properties of the product and is fixed according to the uses for which it is intended. Most common commercially used products are octyl, nonyl, and dodecylphenol with a degree of ethoxylation ranging from 4 to 40. Octyl and nonylphenols with 8–12 ethylene oxide moles are used in detergents [23]. Ethoxylates with ethylene oxide moles ranging from 12 to 20, are wetting agents and O/W emulsifiers. More than 20 ethylene oxide moles exhibit detergents properties at high temperature and high salinity [23]. Compounds having ethylene oxide moles <5 are applied in antifoaming agents or detergent in non-aqueous media [23].

4.1.4 Cyclic polyoxyethylene alkyl ethers

The attachment of lipophilic long-chain alkyl groups allows crown ethers to acquire some amphiphilic properties [88, 89]. When dispersed in an aqueous medium, these molecules self-organize upon sonication, often into monolayer vesicles [90].



Linear Alcohol Ethoxylate C_8EO_3

Figure 14.
Chemical structure of alcohol ethoxylates.

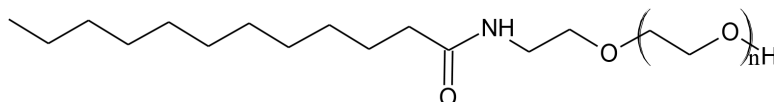


Figure 15.
Chemical structure of fatty acid ethoxylates.

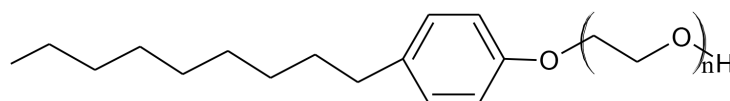


Figure 16.
Chemical structure of nonylphenol ethoxylates.

Nevertheless, the use of fluorocarbon chains instead of hydrocarbon analogues seems to constitute an efficient way to stabilize vesicular systems [91, 92] and to achieve their potential as drug delivery systems [93, 94].

Cyclic polyoxyethylene dialkyl ethers [95] are obtained by grafting two alkyl chains onto the crown head which is capable of organizing into membranes [90, 96]. These surfactants (**Figure 17**) may be inefficient in the formation of aggregates because of their low hydrophilicity. This problem is solved by the addition of a cap anion [97] or by the introduction of an oligooxyethylene group between the hydrophobic part and the ring of crown ethers [98–100] to reinforce the hydrophilicity.

4.1.5 Bolaphiles cyclic polyoxyethylene surfactants

Crown ether bolaphiles are molecules comprising two polar heads joined by one or more hydrophobic chains. Crown ethers based surfactant have been studied in various stages of drug delivery. The results of their studies showed that bolaform compounds BD-16 and BC-16 (**Figure 18**) are able to form niosomes, if prepared according to the thin-film hydration method, in which hydrophilic molecules can be entrapped [101]. They evaluated its ability to form vesicles and the influence of a membrane additive, such as cholesterol. Bola A-16 was used as the niosome carrier for 5-fluorouracil (5-FU).

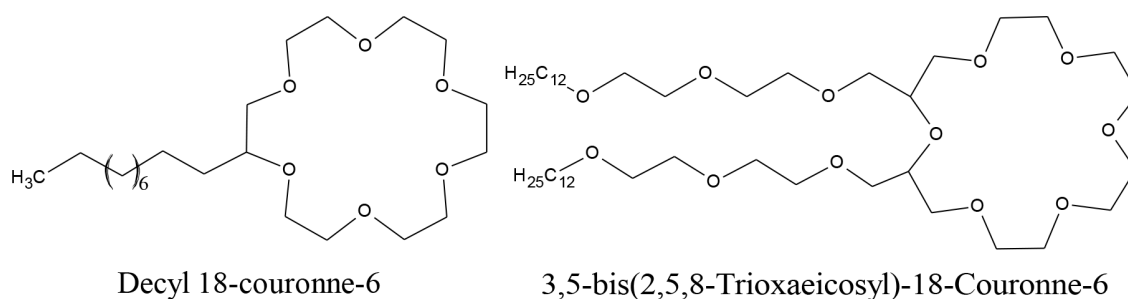


Figure 17.
Examples of Crown ethers surfactants.

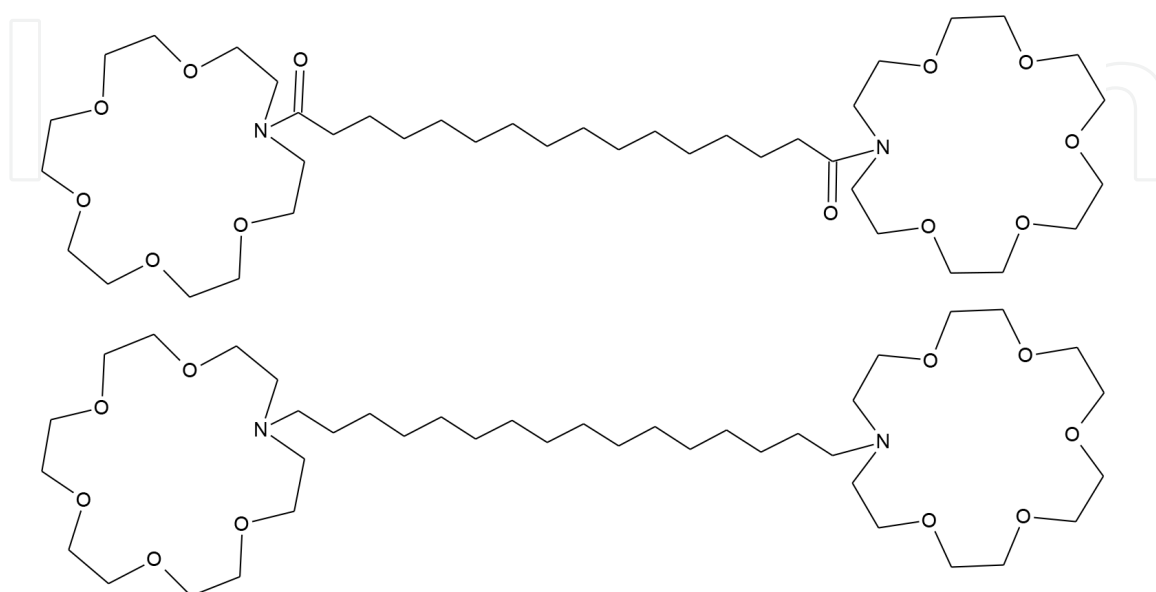


Figure 18.
Chemical structure of BD-16 and BC-16.

The results were very interesting and showed that the stability of the drug in encapsulated state in niosomes is more than a free solution [102].

4.2 Polyhydroxyl (polyol)-based surfactants

4.2.1 Sugar-based surfactants

Single-chain surfactants synthesized from sugars occur in large majority in the form of alkylpolyglycosides (APG) (**Figure 19**). They result from the fixation by O-glycosylation of an alkyl chain of variable length (8 to 18 carbons) on a unit carbohydrate in its pyranose or furanose form, usually glucose [103, 104], galactose [105] or more disaccharides.

The hydrophilic part of alkyl polyglucosides (APG) derives from sugars and the hydrophobic part comes from a natural or synthetic source, or from a mixture of fatty alcohols. Both monomeric and polymeric sugars can be used as feedstock [106]. The alkyl chain of APGs depends on the raw material used: coconut oil and palm kernel oil are used for the C12/C14 range, while tallow and rapeseed oil for the C16/C18 chains [107].

During the direct synthesis of APGs, glucose is suspended in an excess of fatty alcohol and the reaction takes place at 100–120°C, in the presence of an acid catalyst such as sulfonic acid. After removal of water, which is a by-product of the reaction, the final product is composed of a mixture of, alkyl oligoglucosides and alkyl polyglucosides. The average degree of polymerization for this type of APGs depends on the glucose/alcohol ratio [104].

The biodegradability study showed that APGs with the chain lengths of C8–C10, C10–C12, C12–C14 decompose from 95% to 100%. The toxicity study confirmed their compatibility with the environment and their less irritating nature than conventional surfactants [108].

4.2.2 Glycosides of fatty acids

The Simple glycolipids (**Figure 20**) are composed of a glycosyl group (one or more units) linked to a hydroxyl fatty acid or to a carboxyl group of a fatty acid (ester bond). These compound are found in bacteria, yeasts and lower marine invertebrates. They frequently possess interesting physical or biological properties [104, 107–111].

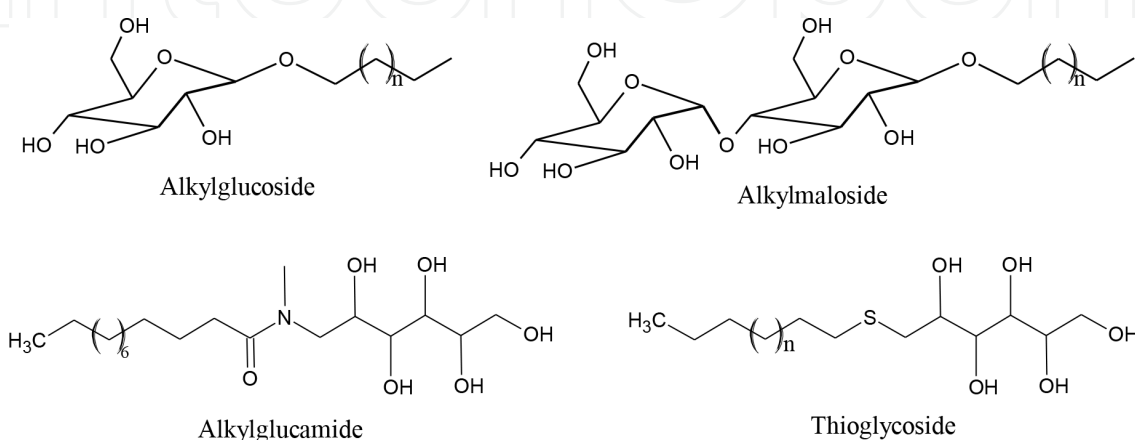


Figure 19.
Chemical structure of monotailed sugar-based surfactants.

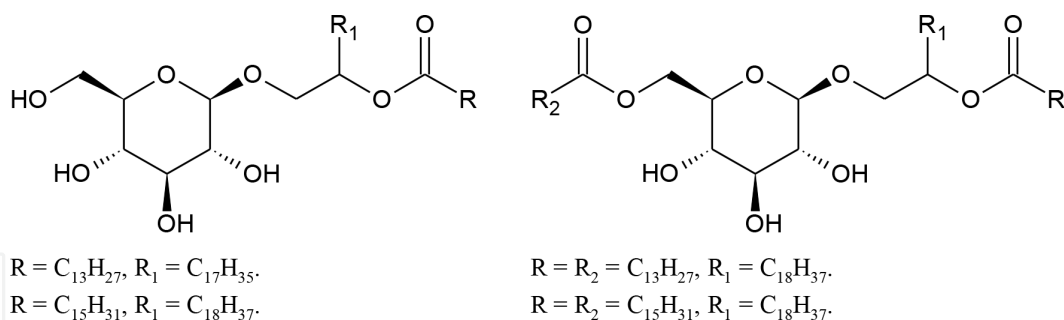


Figure 20.
 Examples of bi-tailed and tri-tailed glycosides based surfactants.

4.2.3 Sugar-based bolaamphiphiles

Sugar-based bolaamphiphiles [96, 112–114] are of special interest for pharmaceutical and other applications because of their natural origin, biocompatibility and biodegradability. A large variety of non-ionic [111, 112] sugar-based bolaamphiphiles (**Figure 21**) have been reported so far with wide variety of properties and applications, e.g., formulation of anti-HIV combination therapy [111], anticancer drug delivery [112], gene transfection [113], bacterial agglutination [114], etc.

4.2.4 Sorbitan esters of fatty acids

Sorbitan esters are nonionic surfactants that are commonly used as water-in-oil (w/o) emulsifiers and stabilizers. Sorbitan fatty acid esters are produced by esterification of dehydrated sorbitol (sorbitan) with a variety of fatty acids. There are many types of sorbitan esters with different kinds of fatty acids and varying degrees of esterification (**Figure 22**). Sorbitan esters are often used in the food industry, especially in chocolate and margarine production, where a high affinity for fats is desired. Polysorbates are also commonly used as emulsifiers in the food industry (salad dressing, ice cream) and in cosmetics, pharmaceuticals, detergents, paints, and plastic applications.

Polysorbate, a substance prepared by the reaction of sorbitan fatty acid ester (a nonionic surfactant) with ethylene oxide. Polysorbates ("tweens") are widely used in industry and medicine as antistatic agents, defoamers, emulsifiers and solubilizers, fiber softeners, dispersing agent and substance that contributes to the dissolution of both water-soluble in the fat phase and waxes in the pharmaceuticals, and fat-soluble in the aqueous phase, in animal feed and soil treatment [115–118].

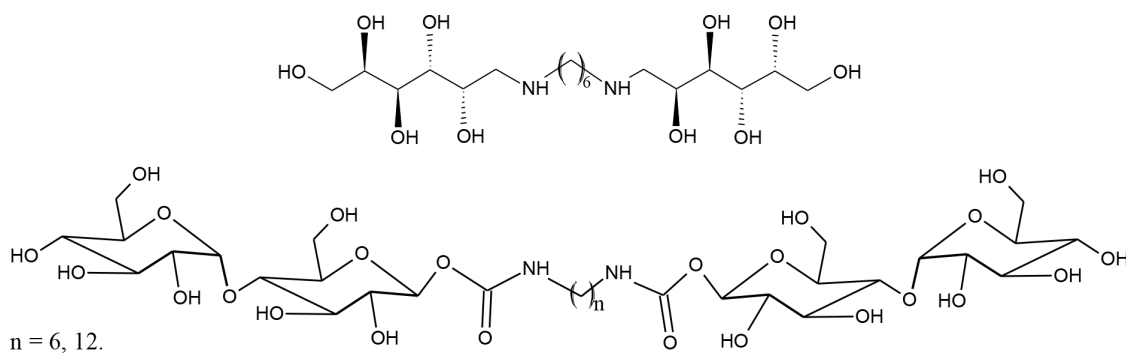


Figure 21.
 Examples of sugar-based bolaamphiphiles.

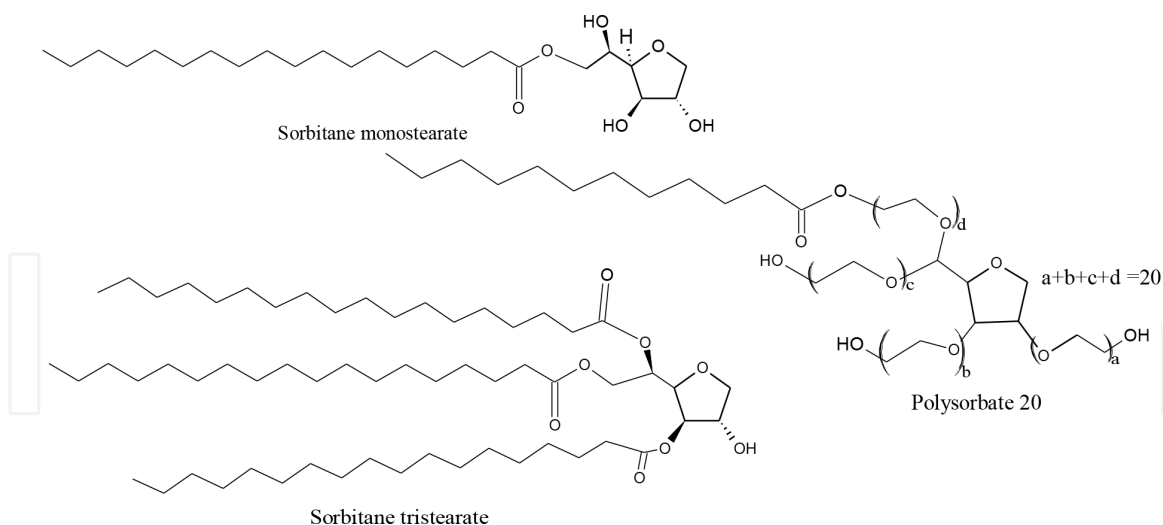


Figure 22.
Examples of Sorbitan based surfactants.

5. Amphoteric or zwitterionic surfactants

Amphoteric surfactants have two functional groups, one anionic and the other cationic. In most cases, it is the pH that determines the dominant character. This dipolar structure is similar to that of natural phospholipids and leads to a family products that are generally non-irritating and not very aggressive on the biological level. They are compatible with both anionic surfactants and cationic surfactants and present the main properties of these two categories. Thus, they are detergents, wetting, foaming and slightly bactericidal. The main amphoteric surfactants are betaine derivatives (alkylbetaine) and imidazoline derivatives (amphoacetates).

5.1 Phospholipids

Phospholipids are esters of glycerol fatty acids with a phosphoester group linking the polar part to the hydrophobic composed of two aliphatic chains (**Figure 23**). According to the nature of the two pole parts and apolar, there is a wide variety of phospholipids, the most common of which are phosphatidylcholines, sphingomyelins and phosphatidylserines. Structurally, all phospholipids are amphiphilic molecules, serving as the molecular basis for their biological functions and as emulsifiers in food, cosmetic, or drug products.

Phospholipids are major membrane lipids that consist of lipid bilayers (**Figure 24**). This basic cellular structure acts as a barrier to protect the cell against various environmental insults and more importantly, enables multiple cellular processes to occur

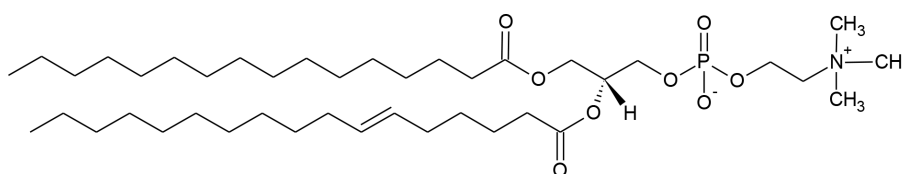


Figure 23.
Phosphatidylcholine.

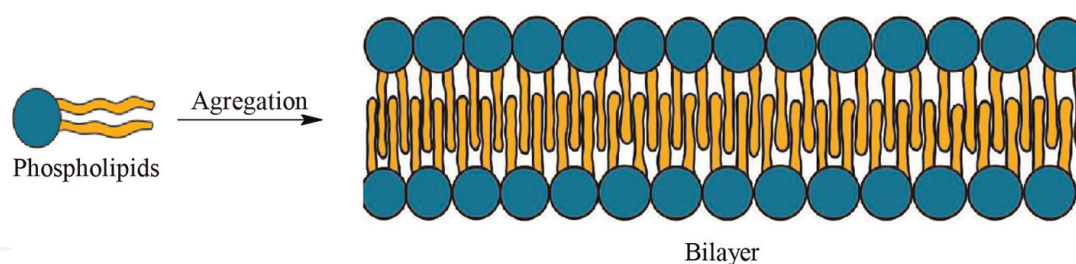


Figure 24.
Agregation of phospholipids to bilayer.

in subcellular compartments. PLs also function as precursors of second messengers such as diacylglycerol (DG) and inositol-1,4,5-P₃ (inositol trisphosphate). A third, and usually overlooked, function of PLs is the storage of energy in the form of fatty acyl components [119].

5.2 Alkyl betaines

Dodecylbetaine chloride (C₁₂Be) has been synthesized and purified by different methods. One method is to react sodium chloroacetate with *N,N*-dimethylamine-*N*-dodecylamine (molar ratio 1:1) in an aqueous solution of ethanol under reflux for 18 h [120, 121]. Alkyl betaine (**Figure 25**) is a very mild detergent that leads to a large amount of foam with good sensory properties. It is therefore logically used in a large number of hygiene formulations.

Lauryl betaine was reported to be used in hair sprays, body and hand products, non-coloring hair powders, and indoor tanning preparations that may be aerosolized or become airborne and could possibly be inhaled.

Zwitterionic surfactants based on 3-(1-alkyl-3-imidazolio) propane-sulfonate [ImS3-R] is an emerging and important class of amphiphile due to their relevance as nano reactors for the synthesis of metallic nanoparticles and accelerated acid hydrolysis [122]. The solubility of these surfactants is very low but increases when adding a salt which helps to stabilize the micellized surfactant, an increase in temperature increased the surface activity and decreased the CMC of both zwitterionic surfactants, although the changes were small [122].

Electrophoretic evidence and fluorescence inhibition for ImS3-14 (**Figure 26**) shows that the micellar aggregation number is only slightly sensitive to added salts, as is the critical micelle concentration, but NaClO₄ markedly increases zeta potentials of ImS3-14 in a similar way as in *N*-tetradecyl-*N,N*-dimethylammonio-1-propanesulfonate (SB3-14) micelles (**Figure 26**) [123].

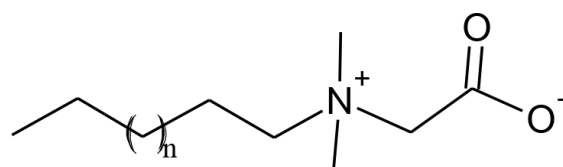


Figure 25.
Alkyl betaines.

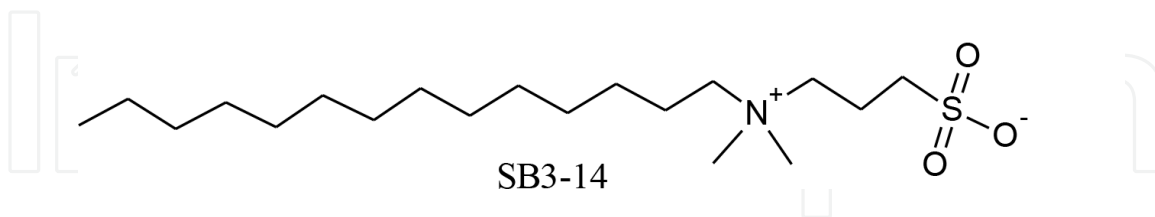
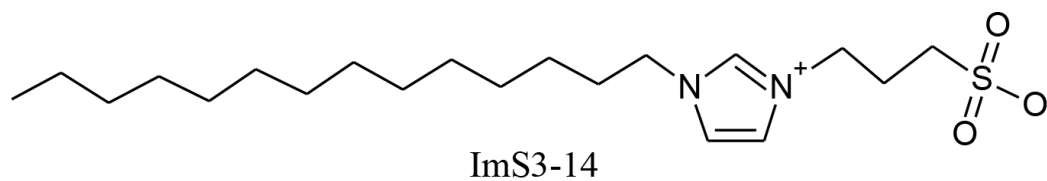


Figure 26.
Structure of *ImS3-14* and *SB3-14*.

6. Conclusion

In this study, we have shown that surfactants play an important role in various areas of daily life. Also that these have applications, depending on their structures and the conditions in which they are found. It is therefore possible to imagine that an ideal surfactant remains, in reality, inaccessible in any area whatsoever.

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