1. Introduction

1.1. Surface active agents:

Surface active agents (surfactants), literally means active at a surface. In other words, a surfactant is characterized by its tendency to absorb at surfaces and interfaces.

The term interface denotes a boundar between any two immiscible phases, while the term surface indicates that one of the phases is gas, usually air.

There are five different interfaces exist:

Solid – Vapor , Solid – Liquid , Solid – Solid , Liquid – Vapor and Liquid – Liquid.

The driving force for a surfactant to adsorb at an interface is to lower the free energy of that phase boundary. The interfacial free energy per unit area represents the amount of work required to expand the interface.

The term interfacial tension is often used instead of interfacial free energy per unit area. Thus, the surface tension of water is equivalent to the interfacial free energy per unit area of the boundary between water and the air above it. When that boundary is covered by surfactant molecules, the surface tension (or the amount of work required to expand the interface) is reduced.

The tendency to accumulate at interfaces is a fundamental property of a surfactant. In principle, the stronger the tendency, the better is the surfactant.

The degree of surfactant concentration at a boundary depends on surfactant structure and also on the nature of the two phases that meet at the interface.

Therefore, there is no universally good surfactant suitable for all uses. The choice will depend on the application.

A good surfactant should have low solubility in the bulk phases. Some surfactants are only soluble at the oil-water interface. Such compounds are difficult to handle but are very efficient in reducing the interfacial tension.

There is of course a limit to the surface and interfacial tension lowering effect by the surfactant. In the normal case that limit is reached when micelles start to form in bulk solution [1].

The many guises of surfactants functional names:

Wetting Agents
Emulsifiers
Demulsifiers
Dispersants
Corrosion Inhibitors
Foam Boosters
Defoamers
Soaps
Detergents
Sanitizers
Tensides
Solubilizers
Antistatic Agents
Plasticizers

1.2. Surfactants are Amphiphilic:

The name amphiphile is sometimes used synonymously with surfactant. The word derived from the Greek word amphi, meaning both, and the term relates to the fact that all surfactants molecules consist of at least two parts, one which is soluble in a specific fluid (the Lyophilic part) and one which is insoluble (the Lyophobic part).

When the fluid is water one usually talks about the Hydrophilic and Hydrophobic parts, respectively. The Hydrophilic part is referred to as the head group and the hydrophobic part as the tail (c.f. fig. 1)

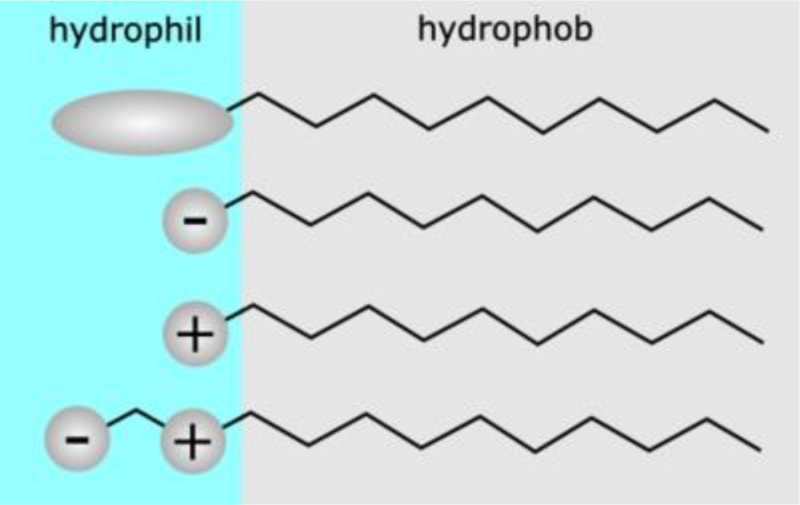


Fig. (1): Surfactant classification according to the composition of their head: nonionic, anionic, cationic and amphoteric.

When a surfactant adsorbs from aqueous solution at a hydrophobic surface, it normally orients its hydrophobic group towards the surface and exposes its polar group to the water. The surface has become hydrophilic and as a result the interfacial tension between the surface and water has been reduced.

Adsorption at hydrophilic surfaces often results in more complicated surfactant assemblies.

The hydrophobic part of a surfactant may be branched or linear. The polar head group is usually but not always attached at one end of the alkyl chain. The length of the chain is in the range of 8-18 carbon atoms.

The hydrophobic group is normally hydrocarbon (alkyl or alkyl aryl) but may also be polydimethylsiloxane or fluorocarbon. The two latter types of surfactants are particularly effective in non-aqueous systems.

The polar part of the surfactant may be ionic or non-ionic and the choice of polar group determines the properties to a large extent.

A surfactant usually has one polar group. Recently, there has been valuable research in certain dimeric surfactants, containing two hydrophobic tails and two head groups linked together with a short spacer. These species, generally known under the name Gemini surfactants, are not yet of commercial importance.

Weakly surface active compounds which accumulate at interfaces but which don't readily form micelles are of interest as additives in many surfactant formulations. They are referred to as hydrotropes. Addition of hydrotropes is a way to prevent the formation of highly viscous liquid crystalline phases which constitutes a well known problem in surfactant formulation. Xylene sulfonate and cumene sulfonate are typical examples of hydrotropes used.

- Effects of nature of Hydrophobic Group

A. Length of hydrophobe:

Increase in the length of the hydrophobic group:

1. Decreases water solubility and increases solubility in organic solvents.
2. Increase surface activity.
3. Causes closer packing of the surfactant tails at an interface.
4. Increase sensitivity of surfactant to electrolyte, pH or Temperature.

B. Branching and unsaturation:

1. Increases solubility in water or organic solvents relative to straight chain.
2. Causes looser packing at interfaces and inhibits precipitation and liquid crystal formation.
3. May result in oxidation or colour formation in unsaturated compounds.
4. May decrease biodegradability for branched chain compounds.

C. Aromatic group:

1. Can cause an increase in adsorption on polar surfaces.
2. Decreases biodegradability relative to a straight chain.
3. Causes looser packing at interfaces.

D. Polyoxypropylene chain:

1. Increases adsorption on polar surfaces via the hydrophobe.
2. Increases solubility in organic solvents.

E. Perfluoroalkyl or Polysiloxene groups:

1. Permit lower surface tensions than hydrocarbon surfactants.
2. Permit better wetting than hydrocarbon surfactant.
3. Can make surfaces both water repellant and oil repellant.

1.3. Classification of surfactants:

The primary classification of surfactants is made on the basis of the charge of the polar head group.

Surfactants divide into the classes Anionics, Cationics, Non-ionics and Zwitter-ionics. The latter class contains both an anionic and a cationic charge under normal condition.

An amphoteric surfactant is one that depending on pH can be either cationics, zwitterionics or anionics. Simple aminoacids are well-known examples of amphoteric compounds.

A surfactant that contains a carboxylate group and a quaternary ammonium group is zwitterionics, unless the pH is very low, but is not an amphoteric surfactant.

For the ionic surfactants the choice of counterion plays a role for the physico-chemical properties. Most anionic surfactant have Sodium as counterion but other cations, such as Lithium, Potassium, Calcium and protonated amines are used as surfactant counterions for speciality purposes.

The counterion of cationic surfactants is usually a halide or methyl sulfate.

1.3.1. Anionic Surfactants

Carboxylate, sulfate, sulfonate and phosphate are the polar groups found in anionic surfactants. Figure (2) shows structures of the more common surfactant types belonging to this class.

Sodium and Potassium as a counterions impart water solubility, whereas Calcium and Magnesium promote oil solubility.

Important facts about anionic surfactants

1. They are the largest surfactant class
2. They are not compatible with cationics
3. They are sensitive to hard water
4. A short polyoxypropylene chain between the anionic group and the hydrocarbon improves solubility in organic solvents but may decrease the rate of biodegradation.

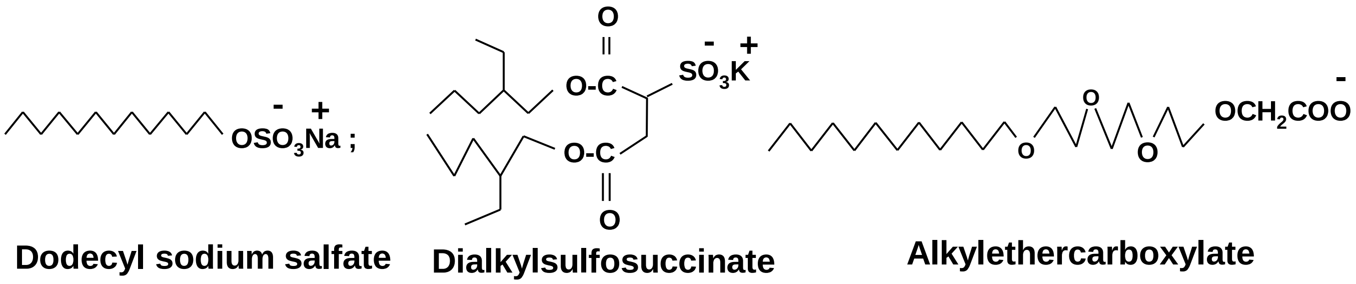


Fig. (2): Structure of some anionic surfactants.

1.3.2. <u>Cationic Surfactants:</u>

The vast majority of cationic surfactants are based on the nitrogen atom carrying the cationic charge. Both Amine and Quaternary ammonium based products are common. The amines only function as a surfactant in the protonated state. Therefore, they can't be used at high pH. Quaternary ammonium compounds are not pH sensitive as shown in figure (3).

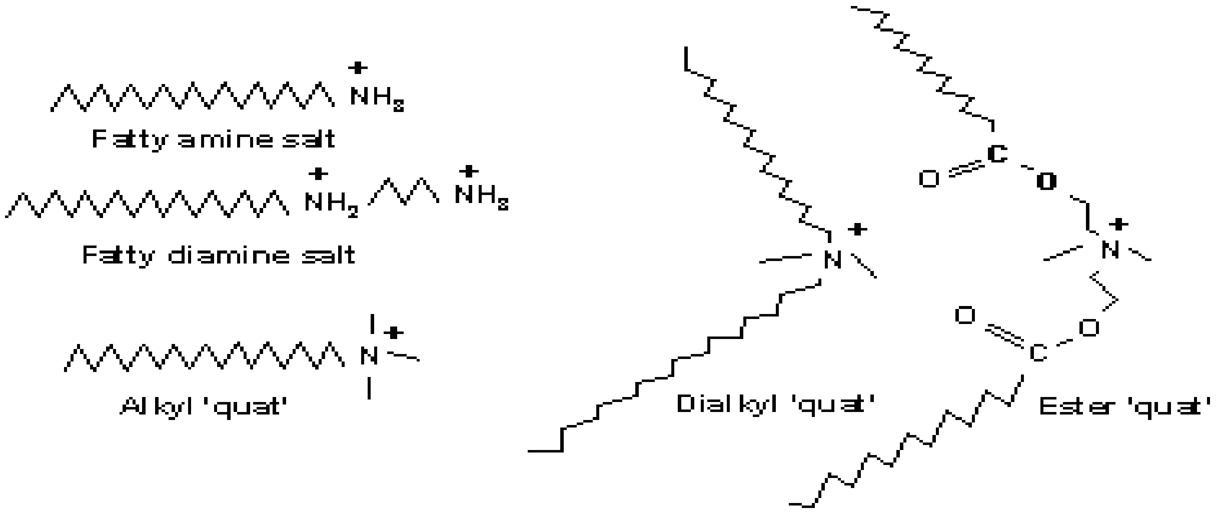


Fig. (3): Structure of some cationic surfactants.

- Tetra alkyl ammonium salts widely used for textile softening.
- N-alkyl trimethyl ammonium chlorides are used as emulsifying agents for acidic emulsions or where adsorption of emulsifying agent is desirable (as in insecticide or herbicide formulations).
- Effective Germicides especially the monoalkyls
- Used as hair conditioners and as oral antiseptics as in mouthwashes.

Important facts about cationic surfactants:

1. They are the third largest surfactant class.
2. Good compatibility with nonionics and zwitterionics.
3. Poor compatibility with anionics.
4. Adsorbs strongly on most solid surfaces.
5. Many are biocides.
6. Generally more expensive than anionics or nonionics.
7. Show poor detergency.

1.3.2. A. Biological properties:

One of the most important uses for quaternary ammonium compounds depends on their biological activity [2]. Generally, optimum activity of completely aliphatic compound is achieved if the higher aliphatic group contains a normal chain of 16-18 carbon atoms. The bactericidal activity of benzyl quaternary compounds is optimum if the higher aliphatic chain contains 14 carbon atoms. The anion has little influence except on solubility.

The mechanism of the bactericidal action is closely related to the surface activity of the quaternary ammonium compound. Undoubtedly, interaction of the bactericidal agent with the cell wall interferes with the metabolic process of the organism, and this causes the inhibiting or killing action. Results from pharmacological and toxicological studies of certain higher aliphatic quaternary ammonium compounds indicate that these compounds are innocuous in concentrations required for germicidal effectiveness.

1.3.2. B. Toxicity

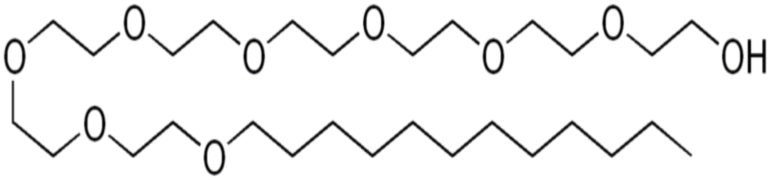
Because of their biocidal, algicidal and fungicidal properties, Quaternary ammonium compounds are toxic to some sewage systems [3]. However, the organisms in the sewage systems develop so that, unless the quaternary ammonium concentrations are too high, they can biodegradable most compounds.

1.3.3. Non ionic Surfactants:

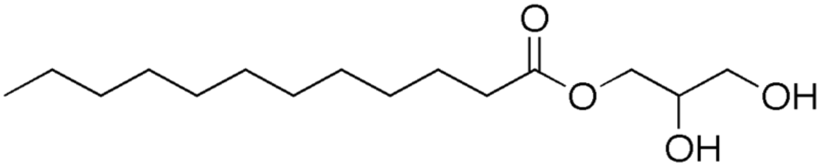
Non ionic surfactants have either polyether or polyhydroxyl (polyol-) as the polar group as shown in figure (4). The polar group is polyether consisting of oxyethylene units, made by polymerization of ethylene oxide. The typical number of oxyethylene units in the polar chain is five to ten. Ethoxylation is usually carried out under alkaline conditions. Any material has an active hydrogen can be ethoxylated.

Important facts about Non ionic surfactants:

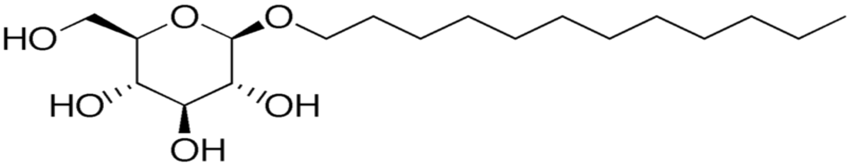
1. They are the second largest surfactant class.
2. Good compatibility with other surfactant types.
3. Soluble in both water and organic solvents.
4. Poor foams and good dispersants.
5. Solubility decreases with increasing temperature.
6. Good performance with high electrolyte concentrations.



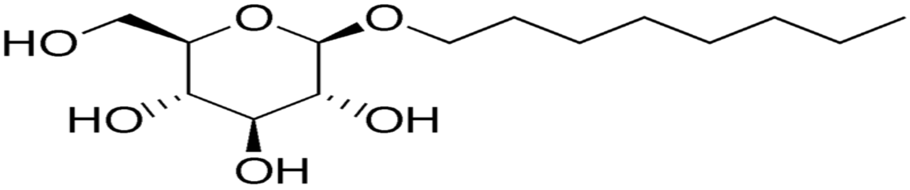
Octaethylene glycol monododecyl ether



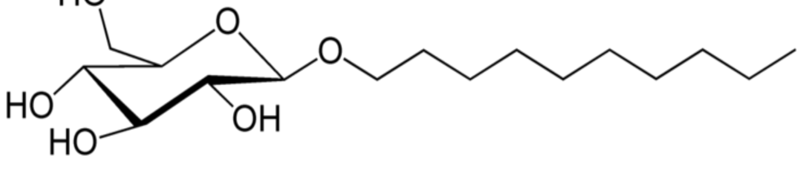
Glyceryl laurate



Lauryl glucoside



Octyl glucoside



Decyl glucoside

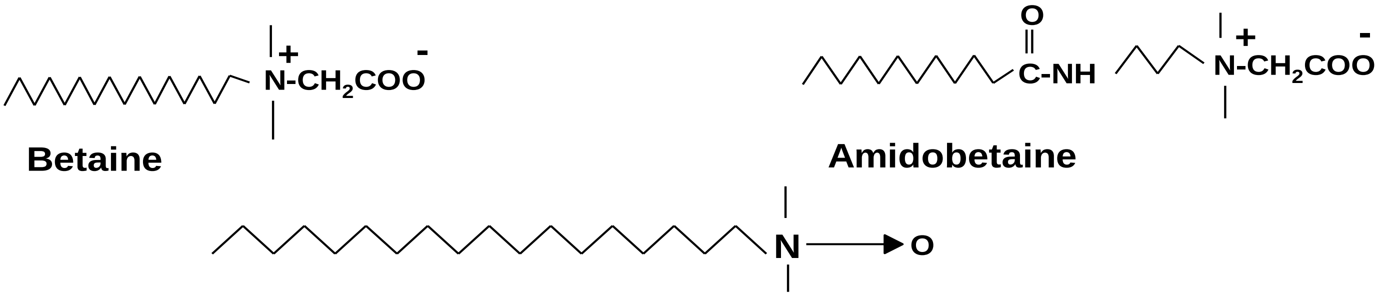
Fig. (4): Structure of some non ionic surfactants.

1.3.4. Zwitterionic surfactants:

Zwitterionic surfactants contain two charged groups of different sign. Whereas the positive charge is almost invariably ammonium, the source of negative charge may vary, although carboxylate is by far the most common as shown in figure (5). Zwitterionics are often referred to as amphoteric, but An amophoteric surfactant is one that changes from net cationic via zwitterionics to net anionic on going from low to high pH. The compound is only zwitterionic over a certain pH range. Zwitterionics exhibit low eye irritation and frequently used in Shampoos and other Cosmetic products.

Important facts about Non ionic surfactants:

1. They are the smallest surfactant class.
2. They are compatible with all other classes of surfactants.
3. They are generally stable in acids and bases.
4. Most types show very low eye and skin irritation.



Betaine

Amidobetaine

Amino oxide

Fig. (5): Structure of some Zwitterionic surfactants.

1.4. Adsorption of Surfactants:

Surfactants are characterized by their activity at the different interfaces (air / liquid, liquid / liquid or solid / liquid).

Since, the surface activity depends mainly on the influence of both hydrophobic and hydrophilic moieties towards the environments, solvent, temperature and other conditions of uses, which affect the adsorption of surfactant molecules at various interfaces. The measurements of adsorption at the interfaces are clarifying several variables [4].

1. Surfactant concentrations at the interface since measure how much of the interface has been covered.
2. The orientations of the surfactant molecules at the interface, this determine how the interface will be affected by the adsorption.
3. The energy change in the system ΔG, ΔS and ΔH resulting from adsorption, since these quantities provide information on the type and mechanism of any interaction involving the surfactant at the interface and the efficiency of its operation as surface active agent.

1.4.1. Mechanism of adsorption:

There are several suggestions of adsorption mechanisms as the following

1. Ion exchange, involving replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions [5].
2. Ion pairing, adsorption of surfactant ions from the solution onto oppositely charged sites unoccupied by counter ions [6].
3. Hydrogen bonding, adsorption of surfactant molecules at the interface through hydrogen bond formation [7].
4. Adsorption by polarization of Bi- electrons, occurred when the surfactant

molecules contain Bi-electrons rich moieties as in case of unsaturated hydrocarbons, benzene ring or unsaturated hetero rings [8].

5. Adsorption by dispersion forces occurred via Van-der-waals dispersion forces acting between surfactant molecules and the surface. This type increase by increasing the molecular weight of surfactant molecules [9].

1.4.2. Micelle formation (Micellization):

At sufficiently high concentration in solution, surfactant molecules will nucleate to form aggregates called micelles. The concentration at which this occurs is characteristic of each surfactant and is called critical micelle concentration (CMC) [10-14]. On other words, the CMC is the lowest total surfactant concentration at which micelles are present. There are key factors in micellization like hydrophobic group, hydrophilic moiety, charge-charge repulsion, counter ion binding, steric interactions, dispersion forces and hydrogen bonding. The lower the CMC, the easier the micelle forms [15-19].

Micelles are thermodynamically and geometrically stable phase [20].occurred in the bulk of the solution. Which is formed to decrease the polar / nonpolar interaction occurred between the surfactant and aqueous phase molecules.

1.4.3. Characteristics features of CMC:

All of the effects just described help determine the value of the lowest concentrations of surfactants at which micelles can form.

1. The CMC decreases strongly with increasing alkyl chain length of the surfactant. As a general rule the CMC decreases by a factor ca. 2 for ionic surfactants (without added salt) and by a factor of ca. 3 for non-ionic surfactants on adding one methylene group to the alkyl chain. Comparison between

different classes of surfactants is best made at a fixed number of carbons in the alkyl chain.

2. The CMCs of non-ionic surfactants are much lower than for ionic surfactants. The relation depends on the alkyl chain length, but two orders of magnitude is a rough starting point.
3. Besides the major difference between ionic surfactants and non-ionic surfactants, the effects of the head group are moderate. Cationic surfactants typically have slightly higher CMCs than anionic surfactants. For non-ionic surfactants of the oxyethylene varity, there is moderate increase of the CMC as the polar head becomes larger.
4. Added salts will decrease the CMC of ionic surfactants, but have relatively little effect on nonionic surfactants.
5. The valency of the counterion is significant. While, simple monovalent inorganic counterions give roughly the same CMC, increasing the valency to two gives a reduction of the CMC by roughly a factor of four. Organic counter ions reduce the CMC compared to inorganic ones, the more so the larger the non-polar part.
6. While alkyl chain branching and double bond, aromatic groups or some other polar character in the hydrophobic part reduce produce sizeable changes in the CMC, a dramatic lowering of the CMC (one or two order of magnitude) results from perfluorination of the alkyl chain. Partial fluorination interestingly may increase the CMC.

1.4.4. Surfactants self-assembly:

1.4.4. A. Ordered structures of surfactant molecules:

By measuring different physicochemical properties of aqueous solution of a surfactant or liquid that is polar enough to be water soluble up to relatively high concentrations. At low concentrations, most properties are similar to

Those of a simple electrolyte. One notable exception is the surface tension which decreases rapidly with surfactant concentration.

At some higher concentrations, which are different for different surfactants, unusual changes are recorded. For example, the surface tension, as also the osmotic pressure, takes on an approximately constant value, while light scattering starts to increase and self diffusion starts to decrease.

All the observations suggest and are consistent with a change-over from a solution containing single molecules or ions, unimers to a situation where the surfactant occurs more and more in a self-assembled or self-associated state.

The concentration for the onset of self-assembly is quite well defined and becomes more so the longer the alkyl chain of the surfactant. The first formed aggregates are generally approximately spherical in shape. We call the aggregates micelles, and the concentration where they start to form is CMC. An illustration of a micelle's structure c.f Figure (6).

Spherical micelles

Cylindrical micelles

Lamellar micelles

Reversed or inverted micelles

Vesicles micelles

Bi continuous micelles

Fig. (6): Illustration of a micelles structure.

Surfactant self-assembly leads to a range of different structures of which a
few are shown:

1. Spherical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups (pictured as sphere) facing water. They are characterized by a low surface number (critical packing parameter) and a strongly positive spontaneous curvature. The hydrocarbon core has a radius close to the length of the extended alkyl chain.
2. Cylindrical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups facing water. The cross section of the hydrocarbon is similar to that of spherical micelles. The micellar length is highly variable to these micelles are polydisperse.
3. Surfactant bilayers which build up lamellar liquid crystals have for surfactant water systems a hydrocarbon core with a thickness of ca. 80% of the length of two extended alkyl chains.
4. Reversed or inverted micelles have a water core surrounded by the surfactant polar head groups, the alkyl chains together with a non-polar solvent make up the continuous medium. Like normal micelles they can grow into cylinders.
5. Bi-continuous structure with the surfactant molecules aggregated into connected film characterized by two curvature of opposite sign. The mean curvature is small (zero for a minimal surface structure).
6. Vesicles are built from bilayers similar to those of the lamellar phase and are characterized by two distinct water compartments, one forming the core and one the external medium. Vesicles may have different shapes and there are also reversed- type vesicles [21].

1.4.4. B. Critical Packing Factor (Φ):

$\Phi = V/a_0 I_c$	**Aggregate Structure**
< 0.33	Spherical, Ellipsoidal micelles
0.33 – 0.5	Rod –like Micelles
0.5 – 1.0	Vesicles, Bilayer Structure
1.0	Planar Bilayers
>1.0	Reverse Micelles

V: Volume occupied by hydrophobic groups in micellar core

a_0: across-sectional are occupied hydrophilic group at the micelle surface

I_c: length of hydrophobic groups.

1.5. Surface Tension:

Surface tension is due to asymmetric cohesive forces at a surface. The surface tension of liquids causes the formation of drops and is related to the attractive forces between molecules, these attractive forces are the source of condensation of vapors into liquids and they originate from dispersion, dipole- dipole and dipole-induced-dipole forces and hydrogen bonding. In the bulk liquid a molecule senses the same attractive forces in all directions, while for a molecule at the surface this attraction is lacking in one direction. This asymmetry is the origin of the surface energy and is manifested in the surface tension. Thus, the surface tension is a reflection of the cohesive forces in a liquid.

A second molecular explanation for the surface tension due to the molecules that close to the surface are at larger separations and hence they have a larger energy.

Surface tension represents the force resisting an increase in the surface area of a liquid. As the surface is extended, more molecules must come to the surface. As a molecule moves through the surface, we must pull to oppose the attractive forces between the emerging molecule and surrounding solvent molecules.

The surface tension is expressed in units of dynes/cm or mN/m. fortunately the conversion factor is unity in going from one unit to other and hence they can be used interchangeably. Since the surface tension is equivalent to a surface energy, or to be more correct a surface free energy, the surface tension can also be expressed in energy units, erg/cm^2 or mJ/m^2, here also with a conversion factor of unity.

1.6. Surfactants for Germicidal and Fungicidal Applications:

The use of various surface active compositions for germicidal and disinfectant purposes was well established long before the synthetic surfactants were introduced to commerce. Soap –phenol compositions were among the most popular and versatile of these materials. Soap itself was also recognized as being lethal to some forms of microorganism, although, with regard to sanitation, the cleansing action of soap was held to be more important than its germicidal action. The recognition and study of the powerful germicidal action of certain cationic surfactants, which may be credited largely to the work of Valko and Domagk around 1935, stimulated widespread interest in the possible bactericidal potentials of the whole range of synthetic surfactants. Renewed interest was also aroused in studying the interactions between the well-recognized germicides such as phenols, halogens, heavy metal salts and the surfactants. These studies have led to notable advances in the cleaning, disinfecting and sanitation fields. Finally, the development of practical and commercially successful germicidal surfactants has stimulated a large amount of fundamental bacteriological work relating to the mechanisms by which surfactants exert their germicidal action [22]. At the present time, a survey of the germicidal surfactant field can be conveniently divided into the following broad sections:

1. Effects and utilization of the surfactants themselves. For this purpose, the surfactants can be considered according to their chemical classifications as cationic, anionic, nonionic and ampholytic.
2. Germicidal-cleansing compositions in which the surfactants (or at least one of the surfactants, if more than one is present) is the major germicidal agent.
3. Germicidal and germicidal-cleansing compositions in which the surfactant is primarily a cleanser or a carrier and the major germicidal ingredient is not surface active.

In the latter two categories the interaction of the ingredients with regard to bactericidal effect is of primary importance.

Fungicidal are conveniently classed as a separate and special subdivision of germicides. Many compounds which are germicidal are also fungicidal, as might be expected. There are few, if any, organic compounds (and none of the common surfactants) which are highly lethal to all microorganisms.

Each compound can be considered to have a characteristic germicidal spectrum, being highly toxic to some organisms and relatively innocuous to others, regardless of whether the organisms are bacteria, fungi, protozoa, or the tissue cells of higher plants and animals. The fungicidal are considered separately for the most part because their practical application often differ widely from the practical application of germicides. Thus, fungicides are most widely used in materials such as fabrics and plastics to prevent the growth and the deteriorating effect of fungi on the substrate. Germicides are usually applied not to prevent the deteriorating of an inanimate substrate but to protect human health directly or indirectly.

1.6.1. Cationic Germicidal Surfactants:

Among the various classes of surfactants the cationics, and more particularly the quaternary ammonium compounds, are by far the most effective all around germicides [23]. This series includes many compounds which kill or inhibit the growth of both Gram-positive and Gram-negative bacteria and which are effective over a rather wide pH range. The anionic surfactants, although frequently effective against Gram-positive bacteria, are very rarely effective against the Gram-negative group. Furthermore, their action tends to be much less rapid than that of cationics and is more susceptible to changes in the pH of the system [24]. The nonionic surfactants are not generally considered to be germicidal [25].

1.6.1. A. Organisms Susceptible to the action of Cationic Surfactants

The array of test organisms used by bacteriologists in studying the inhibitory or lethal effect of a germicide is sizable but not exceptionally large. The test organisms are usually selected from the more common and more virulent disease-producing strains. Frequently, however, special organisms are used, corresponding to some specific applications for which the germicide might be considered or proposed. There have been in recent years several reports of the effects of representative cationic surface active germicides on organisms other than those which are usually studied.

The growth of most strains of algae is said to be adequately inhibited by 5 to 15 p.p.m. of several of the better known quaternaries [26]. Certain strains of virus are also killed or inhibited by representative cationic surfactants [27].

Octimet, a brand of octadecyl dimethyl ethy lammonium bromide when used at 0.025% concentration is reported [28] to be effective against *Candida Albicans*, an organism found in the root canal of teeth. Against *Tubercle bacillus*, a relatively resistant organism which presents a serious disinfection problem in hospitals, relatively few of the cationics are markedly effective, and even these are mush less effective than mercury salts [29].

Considerable evidence has been gathered that certain strains of a single organism may be much more resistant than others to a cationic surfactant, and that these strains can be adapted to withstand as much as 1000 times the normal lethal concentration.

Chaplin [30], Fischer and Larose [31] have studied the adaptation of the organism *Serratia marcescens* to benzalkonium chloride. The technique was to expose a colony to a concentration of the germicide high enough to kill all but a few individuals. The rate of adaptation was found to depend on the pH, and the acquired resistance appeared to coincide with an increase lipid content of the cells. The widely studied organism *Escherichia coli* has also been selectively bred to show greatly increased resistance to quaternaries and the

Resistant strains differ markedly from the parent strains in their bacteriological reaction [32].

1.6.1. B. Mechanism of the Germicidal Action of cationic surfactants:

Although a relatively large amount of work has been done in studying the biochemical mechanism by which cationic surfactants exert their germicidal action, no complete theory of this subject has as yet been developed. It appears probably that the surfactant can attack the cell through many different routes and that the particular mechanism which is effective in any single case depends on the organism and the concentration of the surfactant. Simple adsorption, although it occurs in particularly all cases, may be not be sufficiently disturbing to kill unless it seriously upsets the osmotic balance between the organism and the medium[33]. Some remarkable parallels between the sorption of quaternaries on wool and their bactericidal action have been pointed out by Fischer and co-workers [34] .Some of the mechanism which have been suggested [35] and for which evidence has been brought fourth include:

1. Denaturation of the cell proteins.
2. Combination of the cationic surfactant with the cell lipids.
3. Interference with the enzyme balance within the organism.
4. Interference with the osmotic balance in such a manner as to release vital solute material outward through the cell wall.

1.6.2. Fungicidal surfactant compositions:

With few exceptions the only surfactants which possess sufficient fungicidal activity to be used extensively in competition with other fungicides belong to the cationic class. Several members of this group appear to have pronounced activity against the fungi which invade the human skin. The heavy metal salts of carboxylic or sulfonic acid in the surfactant range, such as copper naphthalene and zinc petroleum sulfonated, largely depend for their action on the heavy metal component.

The anionic sulfate and sulfonated surfactants are frequently used as carriers and dispersing agents for water insoluble fungicides such as salicylanilide or the nitro phenols, but by themselves they are seldom sufficiently active to be of practical value [36].

Fungicidal activity, like bactericidal activity, tends to be specific with regard to the test organisms. In general, however, the quaternary cationic surfactants have a rather wide fungicidal spectrum, resembling in this respect the compounds of the heavy metals. Accordingly, the selection of a specific fungicidal compound usually depends on how well the other properties (such as solubility, stability, toxicity) fit in the field conditions. Thus, the simple long chain quaternary compounds which have good substantivity and low toxicity are used in mildew-proofing fabrics [37]. Among the more interesting cationic fungicides which can be applied to industrial fabrics is the product made by partial ammonolysis of chlorinated paraffin wax [38]. This material is stated to be resistant to leaching and to be effective against wide range of fungi and bacteria.

The long chain alkylolamines such as cetyl diethanol amine are effective fungicides[39] and the long chain quaternary compound which contain an alkyl sulfide group such as C_2H_5-S-C_2H_4- attached to the quaternary nitrogen are also stated to have high fungicidal activity[40] .

Aside from phenols and thiol salts, certain water insoluble carboxylic acid salts of the long chain cationic surfactants are said to be better fungicides than either of their components taken separately. Examples of such compounds are the dodecyl amine salt of o-chlorobenzoic acid and the hexadecyl amine salts of salicylic acid [41].

The cationic fungicides are frequently used in synergistic combinations with other fungicidal agents such as mercury compounds, the heavy metal soaps and lower halogenated fatty esters [42].

1.7. Literature Survey

A.M. Badawi,et al., [43], studied the surface and biocidal activity of some synthesized metallo azobenzene isothiouronium salts. A novel series of azobenzene isothiouronium salts of different alkyl chains (propyl, hexyl and dodecyl) were synthesized by reaction of 4-((4-methylphenyl)azo) phenol with 1,3-dibromopropane, 1,6-dibromohexane and 1,12-dibromododecane, respectively. These salts were reacted with copper (II) halide to give their corresponding metallo complexes. The surface tension measurements for the synthesized compounds show that the metallo complexes have adsorption and micellization better than that of the parent azobenzene isothiouronium salts. The pathogenic Gram-negative bacteria, Gram-positive bacteria, fungi and yeast were used to determine the biocidal activity of these compounds using gradient plate technique.

The results indicate that the copper complexes of the synthesized azobenzene isothiouronium salts have a relatively better biocidal activity than the parent salts.

Nabel A. Negm and Mohamed F. Zaki [44], studied the Structural and biological behaviors of some nonionic Schiff-base amphiphiles and their Cu (II) and Fe (III) metal complexes. Novel series of nonionic Schiff bases was synthesized and characterized using micro elemental analysis, FTIR and ^{1}H- NMR spectra. These Schiff bases and their complexes with Cu and Fe have been evaluated for their antibacterial activity against bacterial species such as *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida albicans*, *Bacillus subtilis* and *Escherichia coli* and their fungicidal activity against *Aspergillus niger* and *Aspergillus flavus*. The results of the biocidal activities showed high potent action of the synthesized Schiff bases towards both bacteria and fungi.

Furthermore, complexation of these Schiff bases by Cu (II) and Fe (III) show the metal complexes to be more antibacterial and antifungal than the Schiff bases. The results were correlated to the surface activity and the transition metal type. The mode of action of these complexes was discussed.

P.C. Griffiths, et al., [45], studied the Metallosurfactants: Interfaces and micelles. Incorporating a metal cation as an integral component of the head group of a surfactant – a metallosurfactant – offers a route to concentrate these ions and their associated functionality at interfaces. To reduce the lability of the metal, various chelating or macrocyclic ligands may be employed leading to a family of homologous series of related metallosurfactants with a structural diversity that is arguably broader than is inherently possible with conventional surfactants. This review discusses the small number of key papers that are quantifying the physico–chemical properties of metallosurfactants and highlights their "classical" as well as "non-classical" surfactant behavior, providing an insight into the structure of micelles and films formed from these novel materials.

N.A Negm, et al., [46], made a Synthesis, Characterization and Biological Activity of Sugar-Based Gemini Cationic Amphiphiles. Two series of Gemini cationic surfactants were synthesized based on glucose and fructose molecules. Their chemical structures were confirmed using micro-elemental analysis, mass spectral fragmentation and FTIR spectroscopic analysis. The surface activities of these Gemini amphiphiles were measured, including surface tension (γ), critical micelle concentration (CMC), effectiveness (π_{CMC}), efficiency (Pc_{20}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) at 25 ^{o}C. Adsorption and micellization free energies of these amphiphiles in their solutions showed a good tendency towards adsorption at the interfaces. The biological activity of the synthesized gemini amphiphiles showed good inhibition at concentrations of 1, 2.5 and 5 mg/mL. The synthesized amphiphiles showed antimicrobial activity on gram-positive and gram negative bacteria and antifungal activity equal to or comparable to commercially available controls. The discussion rationalized the antimicrobial activities of these amphiphiles with the surface activity and the adsorption parameters. In addition, the effect of sugar nuclei was discussed based on the chemical structure of the bacterial and fungal cell membranes.

A. M. Badawi, M. A. Mekawi, A. S. Mohamed, M. Z. Mohamed and M. M. Khowdairy [47], studied the Surface and Biological Activity of Some Novel Cationic Surfactants. In this study, steps were taken toward the development of bactericidal and fungicidal synthetic cationic surfactants by reacting decyl, dodecyl or tetradecyl amine with acetic or hydrochloric acid to produce a series of amine salts which consequently converted to copper or cobalt cationic complexes via complexing the first series compounds with copper (II) or cobalt (II) ions. Surface properties such as interfacial tension and emulsifying power of these surfactants were investigated. The surface parameters including critical micelle concentration (CMC), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) were studied. Free energy of micellization (ΔG^o_{mic}) and adsorption (ΔG^o_{ads}) were calculated. The antimicrobial activity was determined via the inhibition zone diameter of the prepared compounds, which measured against five strains of a representative group of microorganisms. FTIR spectra, elemental analysis and ^{1}H-NMR spectrum were performed to confirm compound structure and purity.

M.C. Murguı´a, et al., [48], Synthesized and studied the surface-active properties and antimicrobial activities of new neutral and cationic trimeric surfactants. Neutral and cationic series of new trimeric ß-hydroxy amino or ammonium surfactants were synthesized via a two-step process involving the Williamson etherification and regioselective oxirane ring opening with primary and tertiary amines, which afforded good to excellent yields.

The synthesized compounds were obtained in high purity by a simple purification procedure on column chromatography. The critical micelle concentration (CMC), effectiveness of surface tension reduction (γ_{CMC}), surface excess concentration (Γ_{max}), and area per molecule at the interface (A) were determined and values indicate that the cationic series is characterized by good surface-active and self-aggregation properties.

The antimicrobial activities are reported for the first time against representative bacteria and fungi for trimeric compounds. The antimicrobial potency was found to be dependent on the target microorganism (Gram-positive bacteria > fungi > Gram-negative bacteria), as well as both the neutral or ionic nature (cationic > neutral) and alkyl chain length (tri-C_{12} > tri-C_{18} > tri-C_8) of the compounds. The tri-C_8 and tri-C_{18} compounds were found to be almost inactive and the tri-C_{12} compounds, the most potent antimicrobial surface-active agents from the synthesized series. The trimeric C_{12} cationic compound was found to be comparable to benzalkonium chloride against Gram-positive bacteria and fungi, in vitro. The antimicrobial effectiveness of this new compound and the facile two step procedure for synthesizing it with an excellent overall yield (92%) provide a cost effective trimeric gemini surfactant.

R.Barney,et al., [49], carried out a Surfactant Studies of Quaternary Ammonium Compounds: Critical Surfactant Concentration. Quaternary ammonium salts (otherwise known as “quats”) commonly form the foundation of formulations in the antimicrobial industry. Although many studies have been conducted on the surfactant and biological aspects of single component systems, there are few studies concerning the surfactant or biological efficacy of these compounds in multiple component formulations. Preliminary data using simple emulsion studies with decane were determined to be inadequate. Several inexpensive ways to determine critical surfactant concentrations were developed with limited resources.

M.C. Murguı´a, Laura, et al. [50], Synthesized and studied the properties of novel antifungal gemini compounds derived from *N*-Acetyl Diethanolamines. A series of new N-acetylated non-ionic and cationic Gemini surfactants (3a–f) having dimeric structures derived from primary and tertiary amines with variably long tails (C_8 – C_{12} – C_{18}) were synthesized.

In addition, N-acetylated monomeric analogues 6a and 6b were prepared and their antifungal potency and surface properties were also determined. Critical micelle concentration (CMC), effectiveness of surface tension reduction (γ_{CMC}), surface excess concentration (Γ_{max}), and area per molecule at the interface (A) were also determined and the resulting values indicate that the cationic series is characterized by good surface-active and self-aggregation properties. For the first time, all surfactants were tested to valuate their antifungal properties using the method for the broth macrodilution test (M27-A2, NCCLS). Four microbial strains were used to perform the study: *Candida parapsilosis* (ATCC 22019), *Candida albicans* (ATCC 64548), and a wild-type strain of *C. parasilosis* and *Saccharomyces cerevisiae* (ATCC 9763). The antimicrobial activity was measured by yeast growth inhibition expressed as minimum inhibitory concentration (MIC) values. Results were compared to those obtained for their monomeric analogues and for a commercially available reference compound (Fluconazole). Gemini 3b, 3e and 3f were found to be the most potent compounds. The results show *S. cerevisiae* as the most sensitive strain. In contrast, the wild strain of *C. parapsilosis* was resistant.

T. Zhao and G.Sun [51], Synthesized and studied the properties of antimicrobial cationic surfactants: Aminopyridinium Salts. Three antimicrobial 4-aminopyridinium salts were synthesized using two different processes in an effort to develop antimicrobial surface treatment agents for wool fibers. The structures of the salts were fully characterized using FTIR, ^{1}H-NMR and ^{13}C- NMR analysis. In addition, their thermal stability was determined using differential scanning calorimetry and thermogravimetric analysis. The antimicrobial efficacy of these compounds was evaluated using minimum inhibitory concentration as an indicator. All of the synthesized aminopyridinium salts showed antimicrobial activity against gram-negative bacteria, but in different levels depending on their structures. The salts possessing longer alkyl chains demonstrated better antimicrobial function. The melting points of the salts decreases as the alkyl chain length increases.