

INTRODUCTION

1-INTRODUCTION

1.1) Surface - Active Agents:

Surface active agents (usually referred to surfactants) are amphiphilic compounds, i.e., they have one part that has an affinity for non polar media and one part that has an affinity for polar media. Furthermore, it can be defined as molecules capable of associating to form micelles. These molecules oriented between phases lowering the surface or interfacial tension of the medium in which they are dissolved.

The unusual properties of aqueous surfactant solutions can be ascribed to the presence of hydrophilic head group and a hydrophobic chain (or tail) in the molecule where the polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole – dipole or ion – dipole interactions (Schramm, 2000).

1.2) Classification of Surfactants:

Surfactants are classified according to their polar head group into four main types; i.e., surfactants with a positively charged head group are referred to as cationic surfactants, whereas anionic surfactants contain polar head groups with a negative charge. Uncharged surfactants are generally referred to as non-ionic, whereas zwitterionic surfactants contain both a negatively charged and a positively charged group Fig. (1) (Malmsten, 2002).

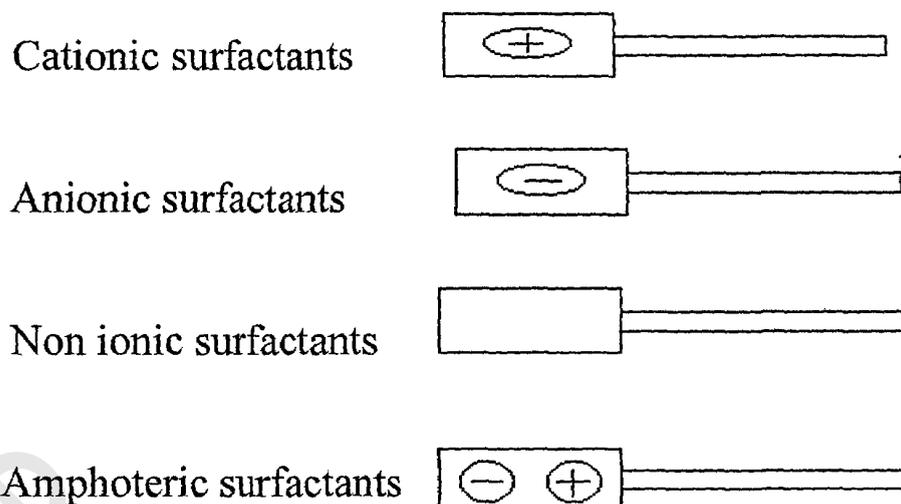


Fig.(1): Schematic illustration of various types of surfactants.

1 .2.1) Cationic Surfactants:

Cationic surfactants are frequently based on amine-containing polar head groups. Due to their charged nature, the properties of cationic surfactants, e.g; surface activity and structure formation, are generally strongly dependent on the salt concentration, and on the valency of anions present. Cationic surfactants are generally water soluble when there is only one long alkyl group (Husain, 1993). They are generally compatible with most inorganic ions and hard water, but they are incompatible with metasilicates and highly condensed phosphates. They are also incompatible with protein-like materials. Cationic surfactants are generally stable to pH changes, both acid and alkaline. They are incompatible with most anionic surfactants, but they are compatible with non-ionics. These cationic surfactants are insoluble in hydrocarbon oils. In contrast, cationic surfactants with two or more long alkyl chains are soluble in hydrocarbon solvents, but they become only dispersible in water (sometimes forming bi layer vesicle type structures).

The critical micelle concentration (CMC) of cationic surfactants is close to that of anionics with the same alkyl

chain length (Tadro, 2005). Cationic surfactants are frequently used as antibacterial agents, which may be advantageous also in certain drug delivery applications, such as delivery systems to the oral cavity. However, cationic surfactants are frequently also irritant and some times even toxic, and therefore their use in drug delivery is significantly more limited than that of non-ionic, zwitterionic, and anionic surfactants (Kwon *et al.*, 1995).

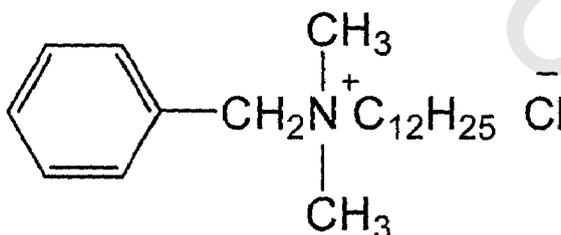
Some Examples of Cationic Surfactants:

1) Alkyl Quaternary Ammonium Salts such as:



N-Hexadecyltrimethylammonium chloride

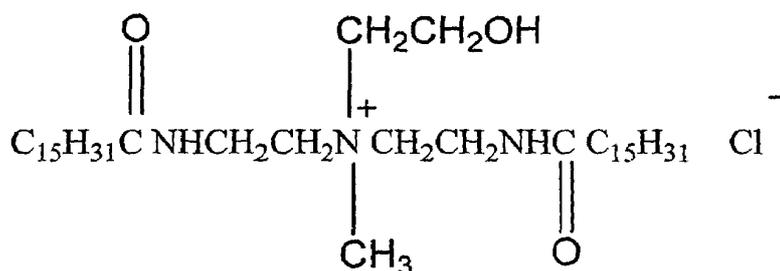
2) Benzyl Alkyl Dimethyl Ammonium Salts such as:



Benzyl dodecyl dimethyl ammonium chloride.

benzalkonium salts are widely used in pharmaceuticals. (Schmitt, 2001).

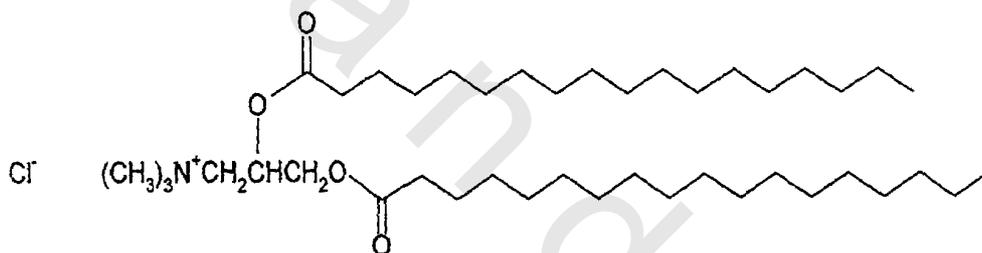
3) Amidoamine Quaternaries such as:



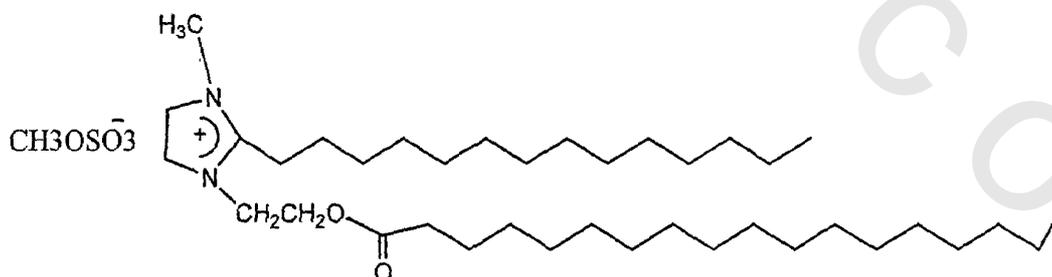
Methyl-bis(hexadecylamidoethyl)-2-hydroxyethyl ammonium chloride.

The most common products are prepared from tallow fatty acids and diethylenetriamine. These are widely used as fabric softeners and antistatic agents (**Richmond, 1990**).

4) Ester Quaternaries such as:



Ditallow ester of 2,3-dihydroxypropanetrimethylammonium chloride.



Ditallow imidazolium ester

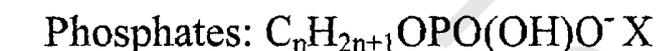
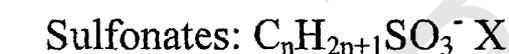
These are analogs of previously described quaternaries that contain ester linkages to speed biodegradation. The most common are fatty acid esters of triethanolamine, quaternized with dimethyl sulfate or methyl chloride. They

are mixtures of quaternized mono-, di-, and triesters. The prime use of cationic surfactants is their tendency to adsorb at negatively charged surfaces, e.g. anti corrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, anti static agents for plastics, other anti static agents, fabric softeners, hair conditioners, anti caking agent for fertilizers and as bactericides (**Osvan, 1993**).

They are not used in general purpose detergents because they do not provide effective cleaning at neutral pH. They are adsorbed rapidly to textiles so that their solution concentration drops very quickly to low levels, making them unsuitable for industrial processing baths (**Wilkes, 1996**).

1.2.2) Anionic Surfactants:

They are the most widely used class of surfactants in industrial applications due to their relatively low cost of manufacture, and they are used in practically every type of detergent. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 carbon atoms. Linear chains are preferred since they are more effective and more degradable than branched ones. The most commonly used hydrophilic groups are carboxylates, sulfates, sulfonates and phosphates. A general formula may be ascribed to anionic surfactants as follows:



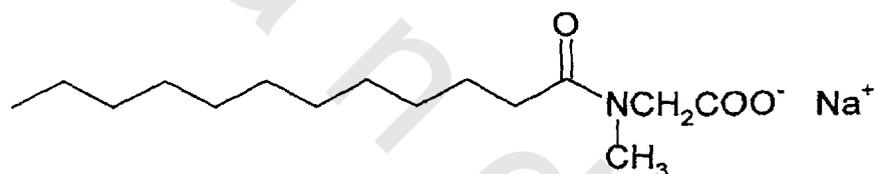
Where $n = 8-16$ atoms and the counter ion X is usually Na^+ .

Several other anionic surfactants are commercially available such as sulfosuccinates, isethionates and taurates and these are sometimes used for special applications (Tavernier, 1981).

1.2.2.1) Carboxylates:

These are perhaps the earliest known surfactants, since they constitute the earliest soaps, e.g. sodium or potassium stearate, $C_{17}H_{35}COONa$, sodium myristate, $C_{13}H_{27}COONa$. The alkyl group may contain unsaturated portions, e.g. sodium oleate, which contains one double bond in the C_{17} alkyl chain (Majcherczyk, 1997). Most commercial soaps

are a mixture of fatty acids obtained from tallow, coconut oil, palm oil, etc. The main attraction of these simple soaps is their low cost, their ready biodegradability and low toxicity. Their main disadvantages are their ready precipitation in water containing bivalent ions such as Ca^{+2} and Mg^{+2} . To avoid such precipitation in hard water, the carboxylates are modified by introducing some hydrophilic chains, e.g. ethoxy carboxylates with the structure $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{COO}^-$, ester carboxylates containing hydroxyl or multi COOH groups, sarcosinates which contain an amide group with the general structure $\text{RCON}(\text{R}')\text{COO}^-$ like Sodium lauryl sarcosinate.



These sarcosinates have been used in toothpaste, shampoo, and hand cleaners as lather boosters. Unlike most anionics, they are compatible with cationic surfactants. Sarcosinates are not very soluble in acid or neutral solutions, but are quite soluble in alkaline media. They are compatible with other anionics, non-ionics and cationics. The addition of the ethoxylated groups increases water solubility and enhances chemical stability (no hydrolysis). The modified ether carboxylates are also more compatible both with electrolytes and with other non-ionic, amphoteric and sometimes even cationic surfactants. The ester carboxylates are very soluble in water, but undergo hydrolysis (Reynders, 1981).

1.2.2.2) Sulfates:

They are the largest and most important class of synthetic surfactants, which were produced by reaction of an alcohol with sulphuric acid, i.e. they are esters of sulphuric acid. In practice, sulphuric acid is seldom used and chlorosulfonic or sulphur dioxide/air mixtures are the most common methods of sulfating the alcohol. However, due to their chemical instability (hydrolyzing to the alcohol, particularly in acid solutions), they are now overtaken by the chemically stable sulfonates. The properties of sulfate surfactants depend on the nature of the alkyl chain and the sulfate group. The alkali metal salts show good solubility in water, but tend to be affected by the presence of electrolytes. The most common sulfate surfactant is sodium dodecyl sulfate (abbreviated as SDS and sometimes referred to as sodium lauryl sulfate), which is extensively used both for fundamental studies as well as in many industrial applications (Czichocki, 1981).

As with the carboxylates, the sulfate surfactants are also chemically modified to change their properties. The most common modification is to introduce some ethylene oxide units in the chain, usually referred to as alcohol ether sulfates, e.g. sodium dodecyl 3-mole ether sulfate, which is essentially dodecyl alcohol, reacted with 3 moles EO (ethylene oxide) then sulfated and neutralized by NaOH. The presence of PEO (polyethylene oxide) confers improved solubility than for straight alcohol sulfates. In addition, the surfactant becomes more compatible with electrolytes in aqueous solution. Ether sulfates are also

more chemically stable than the alcohol sulfates (Yamaguchi, 1978).

Some Examples of Anionic Sulfates:

1) Alkyl Sulfates such as:



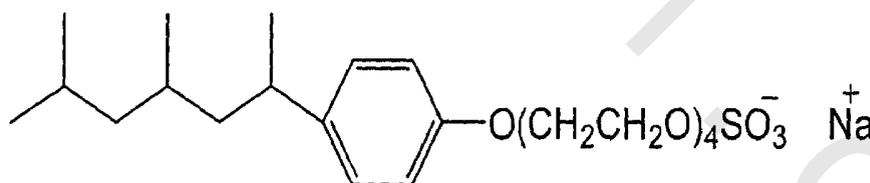
Sodium n-dodecyl sulfate

Alkyl sulfates, also called alcohol sulfates, are formed by making the sulfuric acid esters of linear alcohols. Alkyl chain lengths range from C10 to C18. The properties of the alkyl sulfates vary with the alkyl chain length distribution.

2) Ether Sulfates such as:



Sodium n-dodecyltetraethoxy sulfate



Sodium nonylphenoltetraethoxy sulfate

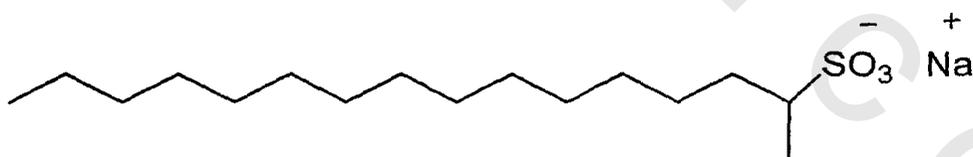
Alkyl ether sulfates, also called alcohol ethoxysulfates, are prepared by addition of one to four oxyethylene groups to an alcohol which is then sulfated. Oxyethylation enhances water solubility and foaming over the analogous alcohol sulfate, giving a product useful in shampoos and in liquid and powdered detergents.

1.2.2.3) Sulfonates:

With sulfonates, the sulphur atom is directly attached to the carbon atom of the alkyl group, giving the molecule stability against hydrolysis, when compared with the sulfates (whereby the sulphur atom is indirectly linked to the carbon of the hydrophobe via an oxygen atom). Alkyl aryl sulfonates are the most common type of these surfactants (e.g. sodium alkyl benzene sulfonate) and these are usually prepared by reaction of sulphuric acid with alkyl aryl hydrocarbons, e.g. dodecyl benzene. A special class of sulfonate surfactants is the naphthalene and alkyl naphthalene sulfonates, which are commonly used as dispersants. As with the sulfates, some chemical modification is used by introducing ethylene oxide units, e.g. sodium nonyl phenol 2-moles ethoxylate sulfonates $C_9H_{19}C_6H_4(OCH_2CH_2)_2SO_3^-Na^+$.

Some Examples of Sulfonate Surfactants:

1) Alkane Sulfonates such as:

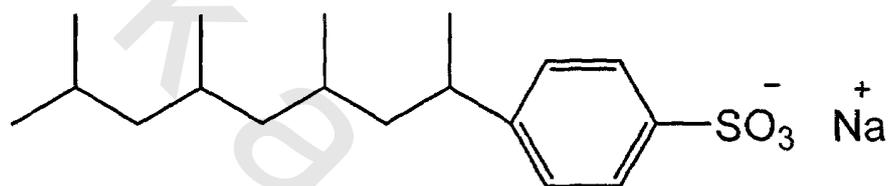


Sodium 2-hexadecanesulfonate

These are commonly called paraffin sulfonates or secondary alkane sulfonates and are used extensively, especially in Europe. Their commercial synthesis requires a relatively high capital investment, so they do not find worldwide application in household detergents. They have high biodegradability, low toxicity and depending on chain length and degree of sulfonation, reasonably good water

solubility. Paraffin sulfonates are made by sulfoxidation or sulfochlorination of n-paraffins in the C14-C17 range. About 90% of the product of sulfoxidation consists of monosulfonates, with the balance being di- and polysulfonates. Eighty to ninety percent of sulfonation occurs at the internal carbon atoms, rather than at the ends of the chain, with the sulfonate group substituted almost uniformly on secondary carbons throughout the chain (Senden, 1990).

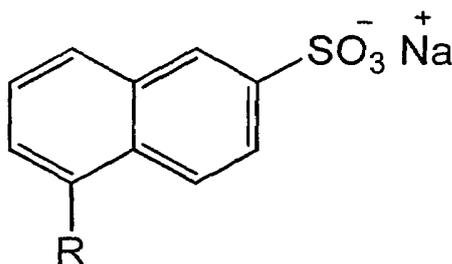
2) Alkyl Benzene Sulfonates such as:



Sodium tetrapropylenebenzenesulfonate

3) Petroleum Sulfonates:

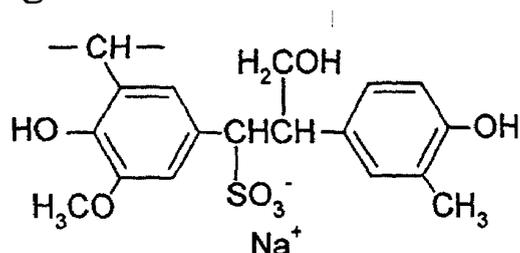
Petroleum sulfonates are prepared by sulfonation of hydrocarbons; most commercial products are actually by products of petroleum refining (alkyl naphthalene where alkyl group mainly butyl or isopropyl).



Petroleum sulfonates are oil-soluble compounds that find use as emulsifiers in lubricating oil and other functional fluids and in secondary oil recovery. They are usually supplied as sodium salts in mixtures with oil. They may contain unsulfonated oil or be diluted in a light

petroleum distillate. "Overbased" products contain high alkalinity additives, such as colloidal calcium carbonate.

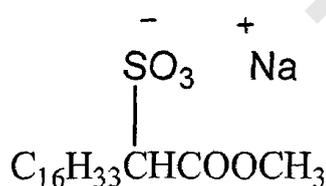
4) Lignin Sulfonate:



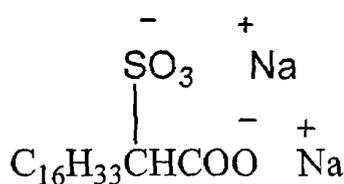
A lignin sulfonate fragment

Lignin is a complex polymer found in wood which is separated from cellulose during manufacture of paper and other products by various means, including sulfonation. Lignin sulfonates are obtained as a by products of the sulfite process. These are widely dispersed, water-soluble lignosulfonic acids. They find a variety of uses as low cost emulsifiers in areas such as ore processing and oilfield chemicals.

5) Ester Sulfonates such as:



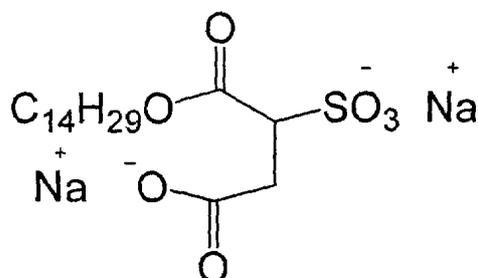
Sodium α -sulfooctadecanoic acid methyl ester



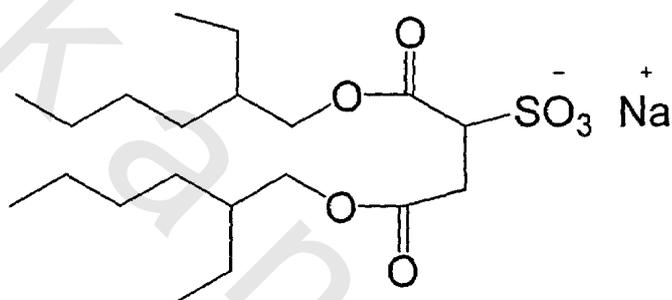
Disodium α -sulfooctadecanoate

Furthermore, called α -sulfo fatty acid esters. They possess good biodegradability and excellent hard-water detergency.

6) Sulfosuccinate Esters such as:

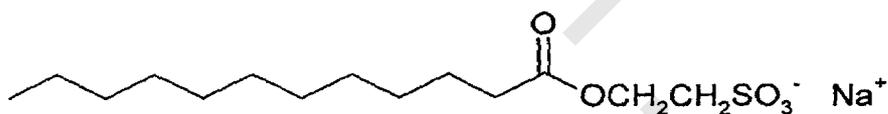


Disodium tetradecyl sulfosuccinate



Sodium bis(2-ethylhexyl)sulfosuccinate

7) Isethionate Esters such as:



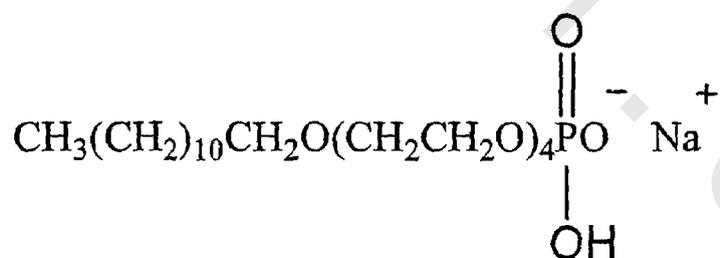
Sodium dodecyl isethionate

This class of specialty surfactants consists of the fatty acid esters of isethionic acid (2-hydroxyethane sulfonic acid). They have been good foaming and dispersing properties and are suitable for synthetic bar "soap" and cosmetic applications.

1.2.2.4) Phosphates:

Both alkyl phosphates and alkyl ether phosphates are made by treating the fatty alcohol or alcohol ethoxylates with a phosphorylating agent, usually phosphorous pentoxide, P_4O_{10} . The reaction yields a mixture of mono- and di-esters of phosphoric acid. The ratio of the two esters is determined by the ratio of the reactants and the amount of water present in the reaction mixture. The physicochemical properties of the alkyl phosphate surfactants depend on the ratio of the esters. Phosphate surfactants are used in the metal working industry due to their anticorrosive properties.

Example for Phosphates Ester such as:



Sodium dodecyltetraethoxy phosphate

Many members of this class have excellent skin compatibility, and are used in cosmetics as emulsifiers.

1.2.3) Non-ionic Surfactants:

The most common non-ionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide-propylene oxide copolymers (sometimes referred to as polymeric surfactants). Another important class of non-ionics is the multihydroxy products such as glycol esters, glycerol (& polyglycerol) esters, glucosides (& polyglucosides) and sucrose esters. Amine oxides and sulphinyl surfactants represent non-ionics with a small head group (Zeman, 1990).

They tend to be more effective than other surfactants for removal of oily soil from synthetic fabrics. Most non-ionics are considered low-foaming products, have good cold water solubility, and have a low critical micelle concentration, making them effective at low concentration. Their compatibility with cationic fabric softeners makes them preferable to anionics in certain formulations. They are more common in industrial applications than are anionics.

The CMC of non-ionic surfactants is about two orders of magnitude lower than the corresponding anionics with the same alkyl chain length.

Examples for Non-ionic Surfactants:

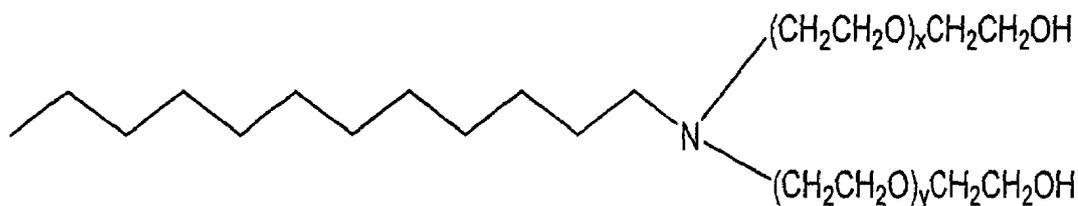
1) Alcohol Ethoxylates such as:



Dodecanol 9-moles ethoxylate

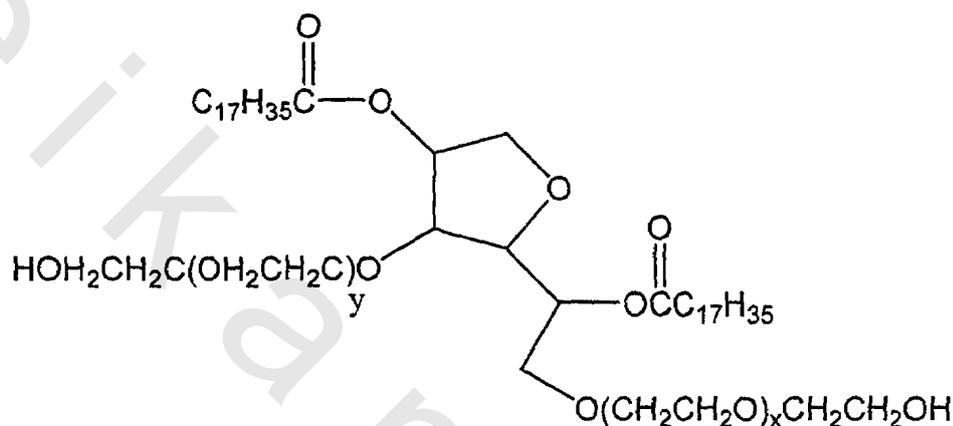
The solubility of the alcohol ethoxylates depends both on the alkyl chain length and the number of ethylene oxide (EO) units in the molecule. Molecules with an average alkyl chain length of C12 atoms and containing more than 5 EO units are usually soluble in water at room temperature. However, as the temperature of the solution is gradually raised the solution becomes cloudy due to dehydration of the polyethylene oxide (PEO) chain and the temperature at which this occurs is referred to as the cloud point (C.P.) of the surfactant. At a given alkyl chain length, C.P. increases with increasing EO chain of the molecule. C.P. changes with changing concentration of the surfactant solution and the trade literature usually quotes the C.P. of a 1% solution. The C.P. is also affected by the presence of electrolyte in the aqueous solution. Most electrolytes lower the C.P. of a non-ionic surfactant solution. Non-ionics tend to have maximum surface activity near to the cloud point. The C.P. of most non-ionics increases markedly on the addition of small quantities of anionic surfactants. The surface tension of alcohol ethoxylate solutions decreases with a decrease in the EO units of the chain. The viscosity of a non-ionic surfactant solution increase gradually with an increase in its concentration, but at a critical concentration (which

6) Ethoxylated Amines such as:



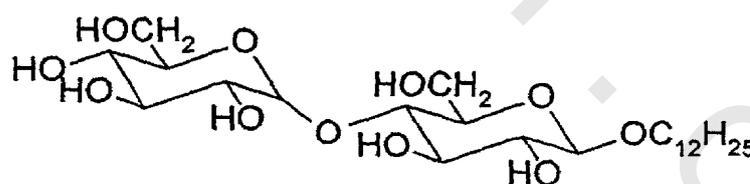
Ethoxylated dodecylamine

7) Ethoxylated Esters such as:



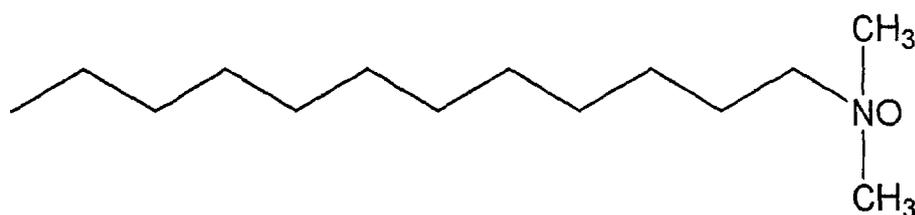
Ethoxylated sorbitan distearate

8) Alkyl Polyglycosides such as:



Lauryl diglucoside

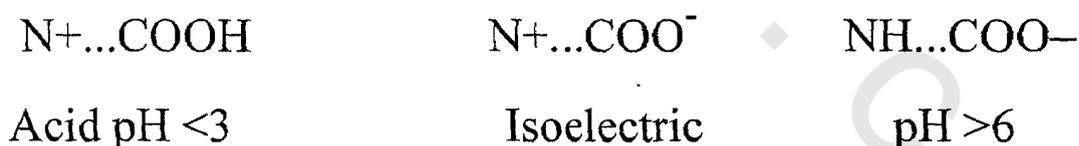
9) Amine Oxides such as:



Lauryl dimethylamine oxide

1.2.4) Amphoteric (Zwitterionic) Surfactants:

These are surfactants containing both cationic and anionic groups. The most common amphoteric surfactants are the N-alkyl betaines, which are derivatives of trimethyl glycine $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-$ (described as betaine). An example of betaine surfactant is lauryl amido propyl dimethyl betaine $\text{C}_{11}\text{H}_{23}\text{CONH}(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$. These alkyl betaines are sometimes described as alkyl dimethyl glycinates. The main characteristic of amphoteric surfactants is their dependence on the pH of the solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic surfactant (Zhao, 1987). A specific pH can be defined at which both ionic groups show equal ionization (the isoelectric point of the molecule) (Scheme 1).



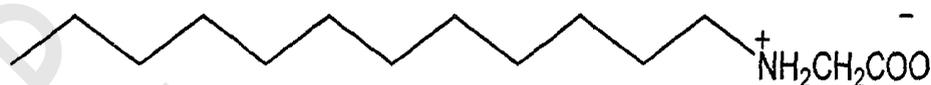
Scheme 1

Amphoteric surfactants are sometimes referred to as zwitterionic molecules. They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoteric surfactants show excellent compatibility with other surfactants, forming mixed micelles. They are chemically stable both in acids and alkalis. The surface activity of amphoteric surfactants varies widely and depends on the distance

between the charged groups, showing maximum activity at the isoelectric point (Schmitt, 2001).

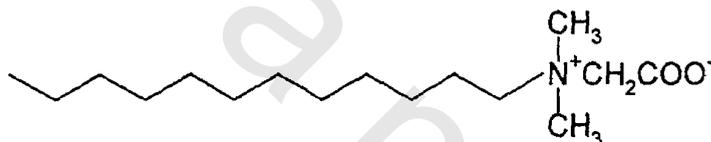
Some Examples of Amphoteric Surfactants:

1) Alkyl Amino Acids such as:



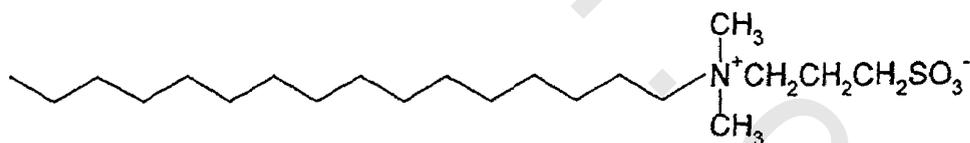
N-Dodecylaminoacetic acid

2) Alkyl Betaines such as:



Dodecyldimethylammoniummethane carboxylate

3) Sulfur-Containing Amphoterics such as:



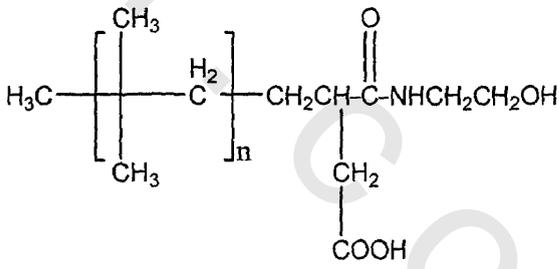
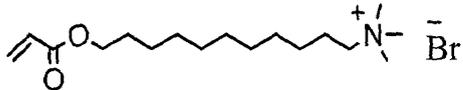
N-Cetyl-N,N-dimethylammoniumpropanesulfate

Amphoteric surfactants used in personal care products like, e.g. hair shampoos, liquid soaps, and cleansing lotions. Other applications include all purpose cleaning agents, hand dishwashing agents, and special textile detergents and shower gels.

With the continuous search for improving surfactant properties, new structures have recently emerged that

exhibit interesting synergistic interactions or enhanced surface and aggregation properties. These novel surfactants have attracted much interest, and include the catanionics, bolaforms, gemini (or dimeric) surfactants, polymeric and polymerisable surfactants as shown in table (1) (Robb, 1997).

Table (1): Structural features and examples of new surfactant classes.

Class	Structural characteristics	Example
Cationic	Equimolar mixture of cationic and anionic surfactants (no inorganic counter ion)	n-Dodecyltrimethylammonium n-dodecylsulfate (DTADS) $C_{12}H_{25} (CH_3)_3 N^+ O_3SO C_{12}H_{25}$
Bolaform	Two charged head groups connected by a long linear polymethylene chain	Hexadecanedi-yl-1,16-bis(trimethyl ammonium bromide) $Br^- (CH_3)_3 N^+ -(CH_2)_{16} - N^+ (CH_3)_3 Br^-$
Dimeric or trimeric	Two identical surfactants connected by a spacer close to or at the level of the head group	Propane-1,3-bis(dodecyl dimethyl ammonium bromide) $C_3H_6 - 1,3-bis[(CH_3)_2 N^+ C_{12}H_{25} Br^-]$
Polymeric	Polymer with surface active properties	Copolymer of isobutylene and succinic anhydride 
Polymerisable	Surfactant that can undergo homo-polymerisation or copolymerisation with other components of the system	11-(acryloyloxy)undecyltrimethyl ammonium bromide 

1.3) Hydrophobic Effect and Micelle Formation:

In diluted concentrations of aqueous solution of surfactant, the surfactant acts as normal electrolyte, but at higher concentrations different behavior result. This behavior is explained in terms of the formation of organized aggregation (self-assembly) of large number of molecules called micelles, in which the lipophilic parts of the surfactants associate in the interior of the aggregate leaving the hydrophilic parts to face the aqueous medium. The formation of micelle is due to the tendency of alkyl chain (non polar part) to avoid energetically unfavorable contact with water, and desire of the polar part to contact with aqueous media (Schramm, 2000).

The surfactants decrease the surface tension by value equal to surface pressure

$$\gamma = \gamma_0 - \Pi$$

Where

γ is the surface or interfacial tension in the presence of surfactant.

γ_0 is the surface or interfacial tension in the absence of surfactant.

Π is the surface pressure

Micellisation is, therefore an alternative mechanism to adsorption by which the interfacial energy of a surfactant solution might decrease. When one considers the energetics of micellisation in terms of the hydrocarbon chains of the surfactant molecules,

the following factors are among those which must be taken into account:

- 1- The intermolecular attraction between the hydrocarbon chain in the interior of the micelle is energetically favorable more than that which result from alternative hydrocarbon-water attraction in case of single dissolved surfactant molecules.
- 2- Micellisation permit strong water-water interaction (hydrogen bond) which would otherwise be prevented if the surfactant was in solution as single molecules wedged between the solvent water molecules. This is a most important factor in micelle formation and also of course, in any adsorption process at an aqueous interface. It is often referred to as the hydrophobic effect.

The micelle existed in solution on different pictures as shown in Fig. (2) (Evans *et al.*, 1994).

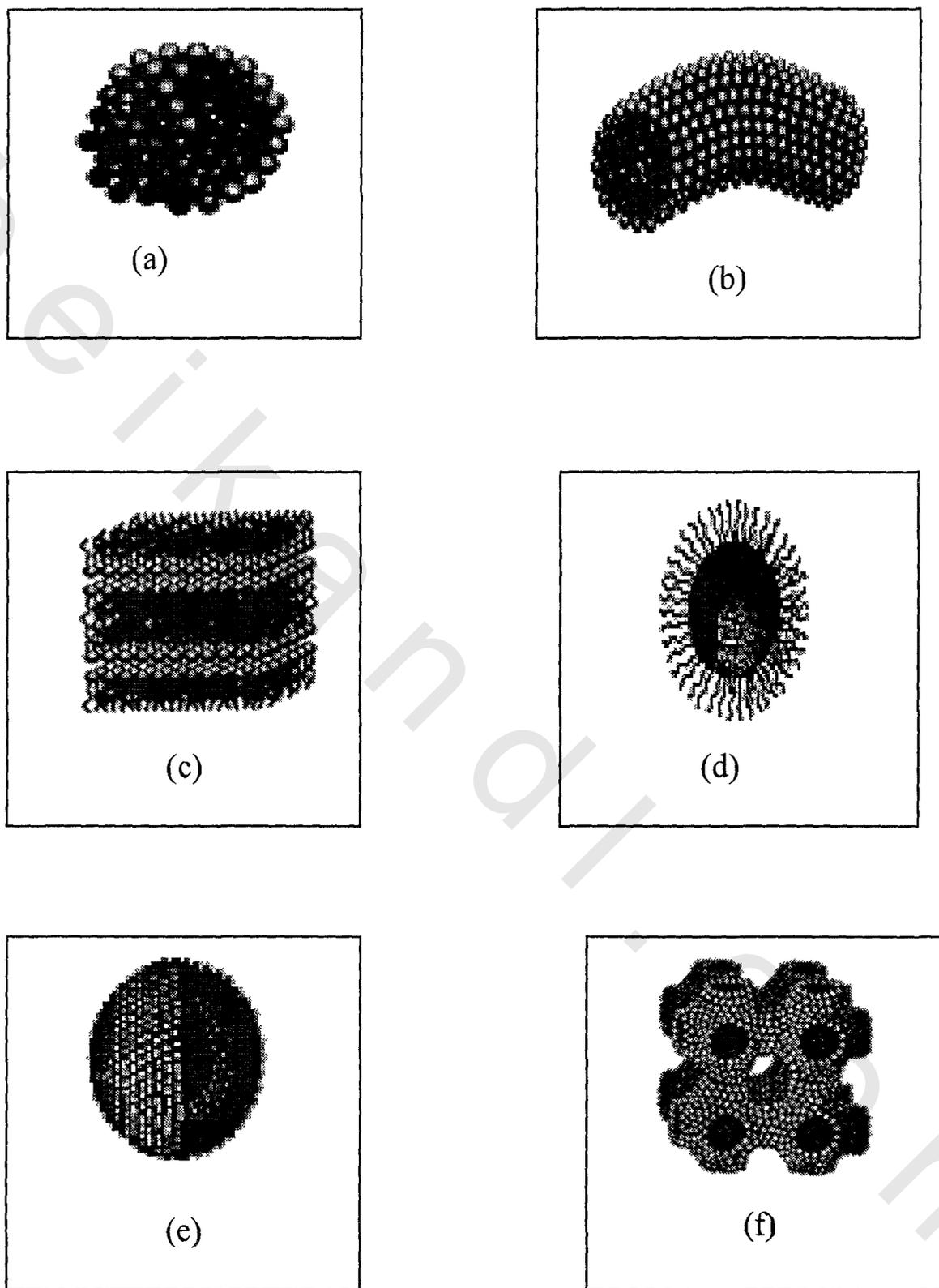


Fig. (2): Surfactant self-assembly leads to different structures.

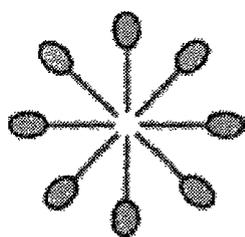
The previous pictures of micelle can be illustrated as follows:

- (a) Spherical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups (pictured as spheres) facing water. Spherical micelles are characterized by a low surfactants number, strongly positive spontaneous curvature and the hydrocarbon core has a radius close to the length of the extended alkyl chain.
- (b) Cylindrical micelles with an interior composed of the hydrocarbon chains and a surface of the polar head groups (pictured as spheres) facing water. The cross-section of the hydrocarbon core is similar to that of spherical micelles. The micelles length is highly variable so these micelles are poly disperse.
- (c) Surfactant bi layers which build up lamellar liquid crystals have for surfactant-water systems a hydrocarbon core with thickness of ca. 80% of the length of two the extended alkyl chains.
- (d) Reversed or inverted micelle has a water core surrounding surfactant polar head groups. The alkyl chains together with a non-polar solvent make up the continuous medium (Holmberg *et al.*, 2002).
- (e) 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 the other the external medium. Vesicles may have different shapes and there are reversed-type vesicles.

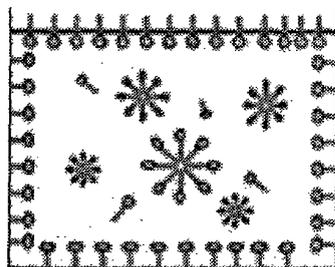
- (f) A bicontinuous structure with the surfactant molecules aggregated into connected films characterized by two curvatures of opposite sign. The mean curvature is small (zero for minimal surface structure) (Holmberg *et al.*, 2002).

1.4) Critical Micelle Concentration:

It is well known that the physico-chemical properties of surfactant vary markedly above and below a specific surfactant concentration as shown in the following Fig. (3). Below the CMC value, the physico-chemical properties of ionic surfactant (e.g., conductivities, electromotive force measurements) resemble those of strong electrolyte. Above the CMC value, these properties change dramatically, indicating a highly cooperative association process is taking place. The CMC is a property of the surfactant and several other factors, since micellisation is opposed by thermal motion and electrostatic force. A low CMC is favoured by increasing the molecular mass of lipophilic part of the molecule, lowering the temperature (usually), and adding electrolyte (Schramm, 2000).



A micelle



Critical micelle concentration

Structure of micelle and critical micelle concentration in solution.

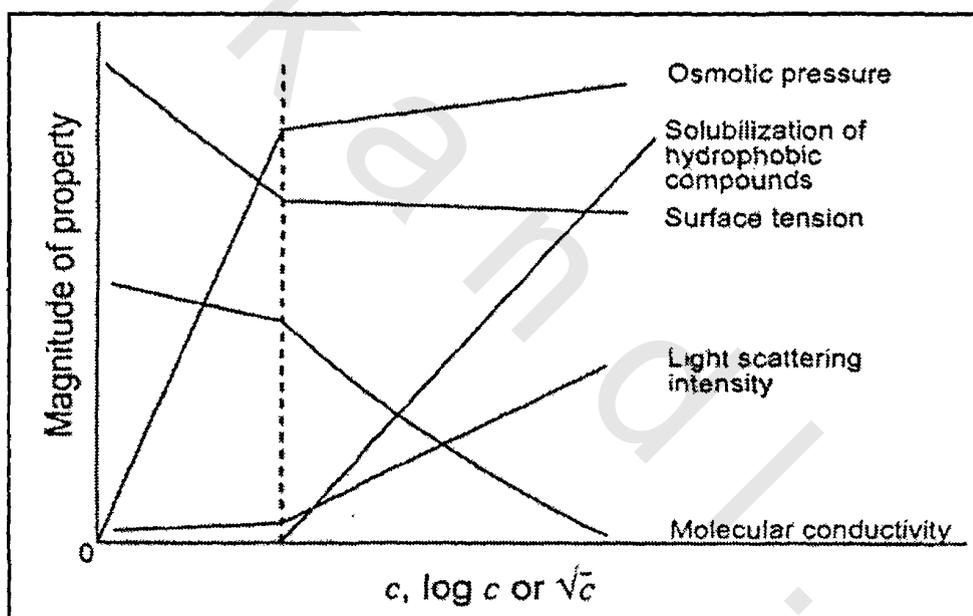


Fig. (3): Schematic representation of concentration dependence of some physical properties for solutions of micelle-forming surfactants.

1.5) Applications of Surfactants:

The surfactants are of widespread importance in personal care and cosmetics, pharmaceutical formulations, agrochemicals, food industry, emulsion polymerization, biochemistry and as corrosion inhibitors.

1.5.1) Surfactants in Personal Care and cosmetics:

Cosmetic and toiletry products are generally designed to deliver a function benefit and to enhance the psychological well-being of consumers by increasing their aesthetic appeal. Thus, many cosmetic formulations are used to clean hair, skin, etc. and impart a pleasant odour, make the skin feel smooth and provide moisturizing agents, provide protection against sunburn etc. In many cases, cosmetic formulations are designed to provide a protective, occlusive surface layer, which either prevents the penetration of unwanted foreign matter or moderates the loss of water from the skin (**Breuer 1985 and Friberg 1990**).

Since cosmetic products come in thorough contact with various organs and tissues of the human body, a most important consideration for choosing ingredients to be used in these formulations is their medical safety. Many cosmetic preparations are left on the skin after application for indefinite periods. Therefore, the ingredients used must not cause any allergy, sensitization or irritation, and they must be free of any impurities that have toxic effects (**Starch, 1984**).

1.5.2) Surfactants in Pharmaceutical Formulations:

Surfactants are used in all disperse systems employed in pharmaceutical formulations (Attwood, 1975). Several types of disperse systems can be identified Table (2).

Table 2: Types of disperse systems in pharmaceutical formulations.

Disperse phase	Dispersion medium	Class
Solid	Liquid	Suspensions
Liquid	Liquid	Emulsions
Liquid	Solid	Gels
Liquid	Air	aerosols
Gas	Liquid	Foams
Solid	Gas	Smokes
Solid	Solid	composites

1.5.3) Applications of Surfactants in Agrochemicals:

Agrochemical formulations cover a wide range of systems that are prepared to suit a specific application (Mukerjee, 1967). All these formulations require the use of a surfactant, which is not only essential for its preparation and maintenance of long-term physical stability, but also to enhance biological performance of the agrochemical. In some cases, an

agrochemical is a water-soluble compound, of which paraquat and glyphosate (both are herbicides) are probably the most familiar. Paraquat is a 2, 2'-bipyridium salt and the counter ions are normally chloride and glyphosate is (N-(phosphonomethyl) glycine). It is formulated as a 20% aqueous solution, which on application is simply diluted into water at various ratios (1:50 up to 1:200 depending on the application). To such an aqueous solution, surface active agents (sometimes referred to as wetters) are added, which are essential for several reasons. The most obvious reason for adding surfactants is to enable the spray solution to adhere to the target surface, and spread over it to cover a large area. In addition, the surface active agent plays a very important role in the optimization of the biological efficiency (Ogino, 1976).

1.5.4) Surfactants in the Food Industry:

Surfactants have been used in the food industry for many centuries. Naturally occurring surfactants such as lecithin from egg yolk and various proteins from milk are used for the preparation of many food products such as mayonnaise, salad creams, dressings, deserts, etc. Later, polar lipids such as monoglycerides were introduced as emulsifiers for food products. More recently, synthetic surfactants such as sorbitan esters and their ethoxylates and sucrose esters have been used in food emulsions (Larsson, 1980).

1.5.5) Surfactants in Emulsion Polymerization:

Surfactants used in emulsion polymerization, surfactants are involved in different steps of latex manufacturing and are essential for latex stabilization. Prior to the onset of polymerization, surfactants are used to reduce the interfacial tension between monomers and the aqueous phase. Surfactant selection is dependent upon the system to be emulsified. During nucleation, surfactant micelles help solubilize monomers and provide sites where polymerization occurs. Particle nucleation is controlled by the monomer/surfactant ratio. Due to their ability to stabilize small particles by electrostatic repulsion, anionic surfactants are generally used for nucleation. Blends of anionic and non-ionic surfactants are often used during polymerization to stabilize the formulation for a specific application and to ensure latex stability during storage and transport (**Lacks, 1979**).

1.5.6) Surfactants in Biochemistry:

In biochemistry, the practical as well as theoretical importance of surfactants may be illustrated with the following examples:

- 1- Surfactants have allowed the investigation of molecular properties of membrane proteins and lipoproteins, acting as solubilizing agents and as probes for hydrophobic binding sites (**Tanford *et al.*, 1976 and Fendler, 1982**). The properties of surfactants, as well as further facts relevant to the

particular experiments, must be carefully considered (**Helenius, 1979**). Surfactants have successfully contributed to the purification of receptors in their active forms such as the neuropeptide receptors and opiate receptors (**Venter *et al.*, 1984 and Perrin, 1986**). All holoreceptor- complex and reaction center isolations require the use of a surfactant in order to separate the integral protein systems from the rest of the membrane.

- 2- Surfactants have been used in the investigation of the denaturation of bacteriorhodopsin and in thermal stability experiments of rhodopsin (**de Grip, 1982**).
- 3- The operations of exchange and removal of surfactants bound to membrane proteins are crucial and have been successfully applied to a wide variety of these proteins (**Robinson, 1984; Laursen, 1986 and Kaplan *et al.*, 1987**).
- 4- The effects of surfactants on the function of membrane-bound enzymes such as cytochrome P-450 and (Na⁺ + K⁺)-ATPase (**Huang, 1985**) have also been determined (**Kaminsky, 1987**).
- 5- Integral membrane proteins can be separated from hydrophilic proteins and identified as such in crude surfactant extracts of membrane or cells (**Bordier, 1981**).
- 6- Methods for the solubilization of low-density lipoproteins have advanced the understanding of the assembly, interconversion and molecular

exchange processes with plasma lipoproteins (Walsh *et al.*, 1986).

1.5.7) Surfactants as Corrosion Inhibitor:

The corrosion is the degradation of a material's properties or mass over time due to the environmental effects. It is the natural tendency of a material's compositional elements to return to their most thermodynamically stable state. For most metallic materials, this means the formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores. Fortunately, the rate at which most of these processes progress is slow enough to provide useful building materials. Only inert atmospheres and vacuums can be considered free of corrosion for most metallic materials. Under normal circumstances, iron and steel corrode in the presence of both oxygen and water. If either of these materials is absent, corrosion usually will not take place. Rapid corrosion may take place in water, in which the rate of corrosion is increased by the acidity or velocity of the water, by the motion of the metal, by an increase in the temperature or aeration, by the presence of certain bacteria, or by other less prevalent factors. Conversely, corrosion is generally retarded by films (or protective layers) consisting of corrosion products or adsorbed oxygen; high alkalinity of the water also reduces the rate of corrosion on steel surfaces (Schweitzer, 2004). The amount of corrosion is controlled by either water or oxygen, which are essential for the process to take place. For example, steel will not corrode in dry air and corrosion is negligible when the relative humidity

of the air is below 30% at normal or reduced temperatures. Prevention of corrosion by dehumidification is based on this.

All structural metals corrode to some degree in natural environments. However, bronzes, brasses, zinc, stainless steels, and aluminum corrode so slowly under the condition in which they are placed that they are expected to survive for long periods of time without protection. These corrosion processes follow the basic laws of thermodynamics. Corrosion is an electrochemical process. Under controlled conditions it can be measured, repeated, and predicted. Since it is governed by reactions on an atomic level, corrosion processes can act on isolated regions, uniform surface areas, or result in subsurface microscopic damage. Complicate these forms of corrosion with further subdivisions; add just basic environmental variables such as pH, temperature, and stress, and the predictability of corrosion begin to suffer rapidly.

CORROSION INHIBITORS:

Corrosion inhibitors are chemicals usually added in a small amount to the environment, but are sometimes included in protective coatings or alloyed in metal to be protected. Their purpose is to interfere with corrosion reactions, the anode reaction, the cathode reaction, or both. The inhibitors may react with the metal surface as passivators and inorganic precipitation inhibitors do, or they may merely adsorb on the metal surface, as the organic filming inhibitors

and cathodic poisons do. Inhibitors prevent general corrosive attack; most are not effective in preventing localized attack such as pitting or in stopping cracking.

A different approach to corrosion control is chemical treatment to modify the environment, making it less corrosive by removing of the cathode reactant. If the dissolved oxygen or hydrogen ions are tied up, they will be unavailable to receive electrons from the metal anode, and corrosion practically decrease. Inhibitors reduce corrosion by altering the metal surface, either covering the metal surface completely so that the environment cannot contact the metal or affecting specific surface sites. These sites may be cathode sites where reactants would try to adsorb or anode sites where water molecules would try to attach to dissolving metal ions. Passivators react with the metal surface to form a complete, but thin layer of a reaction product, a passive film of hydrated oxide. Direct passivators are strong oxidizers that react with the metal surface to form a complete passive layer on the metal surface. They are anodic inhibitors: that is, the anodes react rapidly until they are covered with the passive film. That also means that the inhibitors must be maintained at a proper concentration and continually circulated to ensure that all anodes remain passivated. Insufficient passivators could leave the corrosion potential drop to an active peak and greatly increase corrosion.

The organic inhibitors consist mostly of straight hydrocarbon chains, typically about 18 carbon atoms long, with a polar end that will attach to the metal

surface. The polar end may be either positive or negative. Amines, with their slightly positive nitrogen, are favorites. Molecules with negative polar ends includes thio compounds ($-S^-$), aldehydes and alchole. Adsorption usually covers the entire metal surface, although a few inhibitors adsorb mainly at anode or at cathode sites on the metal. Addition of other organics to the blends may include molecules that are not polar but cling particularly well to polar molecules, thus building up a much more complete barrier layer. Also an organic inhibitor must be dispersed in an aqueous solution as an emulsion of extremely small micelles. Additive will be needed to aid in forming theses micelles and keeping them dispersed. Surfactants improve wettability and adherence to the metal surface. Adsorption inhibitors find their major use in protecting metals from strong acids, although some inhibitors are designed for neutral environments. One essential qualification must be made: the system must be clean no dirt, no deposits, and no corrosion products. These adsorption inhibitors adsorb on any surface (and porous rust has a tremendous surface area). A dirty system can soak up thousand of dollars of inhibitor with no effect on the corrosion whatever.

Forms of corrosion:

There are eight basic forms of corrosion that metallic materials may be subject to:

1. Uniform corrosion
2. Intergranular corrosion

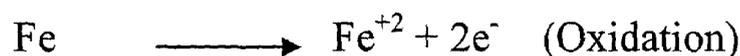
3. Galvanic corrosion
4. Crevice corrosion
5. Pitting
6. Erosion corrosion
7. Stress corrosion cracking
8. Microbial corrosion

In addition, there are other forms of corrosion that specific metals or alloys are subject to. Prevention or control of corrosion can usually be achieved by use of a suitable material of construction, use of proper design and installation techniques, and by following in-plant procedures, or a combination of these (Schweitzer, 2004).

Corrosion behaviour in acid media:

The open circuit corrosion of steel, which is contacting with acid media as electrolyte, will be a process involving at least two different phases on the same surface of a metal sample in electrochemical reaction. An active phase will react continuously with electrolyte but other phase, which is less in activity, will not react. If this process is not blocked with product formation then spontaneously reaction will proceed, where partial cathodic reaction will take place on a partial anode reaction, which brings the corrosion.

The corrosion of the carbon steel in aerated acidic solution is a result of partial anodic reaction, which involves the oxidation of metal atoms, and formation of Fe^{+2} ions in solution.



In addition, the partial cathodic reaction which involves evolution of hydrogen gas



Generally, the corrosion in acid media controlled by cathodic reduction of (H^+), the rate of corrosion varies by alternating the mechanism of discharge process or by changing the area of cathodic sites.

Efficiency of corrosion inhibitor:

The inhibition efficiency (P %) of an inhibitor calculated from the following equation:

$$P \% = ((W - W') / (W)) \times 100$$

Where W and W' are the corrosion rate of the carbon steel in absence and presence of inhibitors respectively at given inhibitor concentration and temperature.

Adsorption of surfactants at the solid-liquid interface governed not only by the solution properties of the surfactant but also by the properties of the solid-liquid interface and interactions among the various dissolved species.

Adsorption on the iron surface can explain by an electrostatic interaction between ammonium group and cathodic sites on the metallic surface (**Branzoi *et al.*, (1997).**