CHAPTER 1

GENERAL INTRODUCTION

1.1 Amphiphiles and Classical Surfactants:

The word amphiphilie was coined by Paul Winsor and it comes from two Greek words, prefix amphi means “double”, “from both sides”, “around” and then root philos, which expresses friendship or affinity. Therefore an amphiphilic structure exhibits a double affinity, which can be defined from the physico-chemical point of view as a polar-dipolar duality. A typical amphiphilic molecule consists of two parts: on the one hand a polar group which consists heteroatoms such as O, S, P or N, as included in various functional groups such as alcohol, ether, thiol, ester, acid, sulfate, sulfonate, phosphate, amine, amide, etc. On the other hand, a nonpolar or apolar group, which is in general an hydrocarbon chain of the alkyl or alkylbenzene types, some times with halogen atoms and even a few nonionized oxygen atoms. The polar portion exhibits a strong affinity for polar solvents, particularly water and it is called hydrophilic part or hydrophile. The apolar part is called hydrophobic or lipophile.

Because of the dual affinity, an amphiphilic molecule exhibits a very strong tendency to migrate to interfaces or surfaces or orientate so that the polar groups lies in water and the apolar group is placed out of it. It is worth mentioning or remarking that all amphiphiles do not display such activity and only amphiphiles with more or less equilibrated or balanced hydrophilic and lipophilic tendencies are likely to adsorb on to the surface or interface. Since amphiphiles are surface or interfacially active, they are also referred as surfactants. Surface activity is strictly equivalent to the lowering of surface tension. Amphiphiles exhibit other properties than just lowering of surface tension and thus are labeled according to their main uses such as soaps,
detergents, wetting agents, dispersants, emulsifiers, foaming agents, bactercides, corrosion inhibitors, antistatic agents etc. In some cases, they are known by the type of structures they are able to build, i.e. membrane, microemulsion, liquid crystal, liposome, vesicle or gel etc. In following sections, a brief account of various types of surfactants or amphiphiles that are available in the market is given along with their uses and limitations.

1. 2 Hydrogenated or Hydrocarbon Based Surfactants (HS):

Several classes of HS are reported and are widely used [1-18]. Their classification of HS is based on their dissociation in water. Table 1.1 lists few typical examples of each class of HS. The polar or ionic head group usually interacts strongly with aqueous environment, in which case it is solvated via dipole-dipole or ion-dipole interactions. It is in fact the nature of the polar head group, which is used to classify the surfactants or amphiphiles into different categories:

Anionic surfactants are dissociated in water in an amphiphilic anion and a cation, which in general an alkaline metal (Na⁺, K⁺) or a quaternary ammonium species. These are the most commonly used surfactants and include alkyl benzene sulfonates (detergents), fatty acids (soaps), lauryl sulfate (foaming agent), dialkyl sulfosuccinates (wetting agents), lignosulfonates (dispersants) etc. Anionic surfactants account for 50% of the world production.

Cationic surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammonium, with one or several long chains of the alkyl type. As compared to anionic surfactants, cationics are more expensive and therefore are used only when there is no cheaper substitute i.e. as bactericide or adsorbing agent on negatively charged
substrates to produce antistatic and hydrophobant effects useful in corrosion inhibition.

Nonionic surfactants do not ionize in aqueous solution, because their hydrophilic group is of a non dissociable type, such as alcohol, phenol, ether, ester or amide. A large proportion of nonionic surfactants are called polyethoxylated nonionics, because they are made hydrophilic by the presence of polyethylene glycol chain. The lipophilic group of a nonionic surfactant is often comes from the alkyl or alkylbenzene type obtained from fatty acids of natural origin. Nonionic surfactants come as a close second with about 45 % of the overall industrial production.

In aqueous solution, dilute concentrations of surfactants act much as normal electrolytes, but at high concentrations, they self associate into organized aggregates of large number of molecules called micelles, in which lipophilic parts of surfactants associate in the interior of the aggregate, leaving hydrophilic parts to face the aqueous medium. A wide range of applications are established for HS [19-24]. Some of them are: wetting agents – ability to reduce the surface tension of aqueous solutions below \(~40 \text{ mN m}^{-1}\), so that a drop of the solution, when applied on a solid surface spread and form a film – even distribution of textile dyes among fabric surfaces, facilitation of satisfactory surface coverage of pesticide or herbicide on to an hydrophilic surface are some examples.

Ore flotation – the flotation of solid particles on a liquid medium can be facilitated by altering the contact angle of solid particles by surfactant addition. Crude mineral ores are treated by flotation method using collector oils based on ionic or nonionic surfactants.
**Table 1.1 List of Hydrocarbon Surfactants**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Name</th>
<th>Structure</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dodecylbenzene sulfonic acid</td>
<td><img src="image1" alt="Structure Image" /></td>
<td>It is a colorless salt with useful properties as surfactants. It is usually produced as a mixture of related sulfonates. It is a major component of laundry.</td>
</tr>
<tr>
<td>2.</td>
<td>Sodium dodecylbenzene sulfonate</td>
<td><img src="image2" alt="Structure Image" /></td>
<td></td>
</tr>
</tbody>
</table>
3. Calcium dodecylbenzene sulfonate

It can be used to formulate pesticide, fungicide and herbicide, agrochemical emulsifiers. It is widely used to formulate pesticide emulsifier for organic phosphorus and organochlorine products.

4. Sodium lauryl sulphate

SDS is mainly used in detergents for laundry with many cleaning applications. SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues. For example, it is found in higher concentrations with industrial products including engine degreasers, floor cleaners, and car wash soaps. It is found in toothpastes, shampoos, shaving creams and bubble bath formulations in part for its thickening
<p>| | | | | |</p>
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<tbody>
<tr>
<td>5.</td>
<td>Sodium lauryl-2 sulphate</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Effect and its ability to create lather. It is an anionic detergent and surfactant found in many personal care products such as soaps, shampoos, toothpaste etc. It is an inexpensive and very effective foaming agent.</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Sodium dioctyl sulphosuccinate</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Effect and its ability to create lather. It is a common ingredient in consumer products. It is also used as an emulsifying, wetting, dispersing agent, as a pesticide, as well as a component of the oil dispersant.</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Poly(ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>Cutting fluids, leather, household,</td>
<td></td>
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<tr>
<td>8.</td>
<td>Poly aryl ether</td>
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<tr>
<td>Cationic type</td>
<td>Cationic detergent, Cell lysis reagent, precipitates nucleic acids.</td>
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<tr>
<td>--------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td><strong>1. Cetyl trimethylammonium bromide (CTAB)</strong></td>
<td><strong>Cationic detergent</strong>, <strong>Cell lysis reagent</strong>, precipitates nucleic acids.</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><img src="image" alt="CTAB" /></td>
<td><strong>Cationic detergent</strong>, <strong>Cell lysis reagent</strong>, precipitates nucleic acids.</td>
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<td></td>
</tr>
<tr>
<td>CH₃(CH₂)₁₅N⁺-CH₃⁻Br⁻</td>
<td><strong>Cationic detergent</strong>, <strong>Cell lysis reagent</strong>, precipitates nucleic acids.</td>
<td></td>
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<tr>
<td>H₃C(H₂C)₁₅⁻N⁺-CH₃⁻Br⁻</td>
<td><strong>Cationic detergent</strong>, <strong>Cell lysis reagent</strong>, precipitates nucleic acids.</td>
<td></td>
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<tr>
<td></td>
<td><strong>Cationic detergent</strong>, <strong>Cell lysis reagent</strong>, precipitates nucleic acids.</td>
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</tr>
<tr>
<td><strong>2. Methyltrialkyl (C₈-C₁₀) ammonium chloride</strong></td>
<td><strong>Common phase transfer catalyst. Used to extract metal ions for spectrophotometric determinations.</strong></td>
<td></td>
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<tr>
<td><img src="image" alt="Methyltrialkyl" /></td>
<td><strong>Common phase transfer catalyst. Used to extract metal ions for spectrophotometric determinations.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂(CH₂)nCH₃⁺N⁻-CH₂(CH₂)nCH₃⁻Cl⁻</td>
<td><strong>Common phase transfer catalyst. Used to extract metal ions for spectrophotometric determinations.</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂C⁺N⁻-CH₂(CH₂)nCH₃⁻Cl⁻</td>
<td><strong>Common phase transfer catalyst. Used to extract metal ions for spectrophotometric determinations.</strong></td>
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<td><strong>Common phase transfer catalyst. Used to extract metal ions for spectrophotometric determinations.</strong></td>
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</tr>
<tr>
<td><strong>3. Benzyldecyltrimethyl ammonium bromide</strong></td>
<td><strong>It has been used studies to assess the relation between chemical structure and germicidal efficacy in surface-active cations. It has also been used in studies to investigate pore size control during the synthesis of macroporous thermosensitive poly(N-isopropylacrylamide)</strong></td>
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<tr>
<td><img src="image" alt="Benzyldecyltrimethyl" /></td>
<td><strong>It has been used studies to assess the relation between chemical structure and germicidal efficacy in surface-active cations. It has also been used in studies to investigate pore size control during the synthesis of macroporous thermosensitive poly(N-isopropylacrylamide)</strong></td>
<td></td>
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</tr>
<tr>
<td>CH₃(CH₂)₁₀CH₂⁻N⁺-CH₃⁻Br⁻</td>
<td><strong>It has been used studies to assess the relation between chemical structure and germicidal efficacy in surface-active cations. It has also been used in studies to investigate pore size control during the synthesis of macroporous thermosensitive poly(N-isopropylacrylamide)</strong></td>
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</tr>
</tbody>
</table>

**phosphate agrochemicals, emulsion polymerization and pigment dispersion.**
<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical Name</th>
<th>Chemical Structure</th>
<th>Properties and Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Polyoxyethylene alcohol</td>
<td>$\text{C}<em>n\text{H}</em>{2n+1}(\text{OCH}_2\text{CH}_2)_m\text{OH}$</td>
<td>Used as emulsifiers, wetting agents, antistatics, solubilizers, defoamers, detergents, lubricants in pharmaceutical, cosmetics.</td>
</tr>
<tr>
<td>2.</td>
<td>Alkylphenol ethoxylate</td>
<td>$\text{C}<em>9\text{H}</em>{17-}\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_n\text{OH}$</td>
<td>Used in manufacturing antioxidants, lubricating oil additives, laundry and dish detergents, emulsifiers, and solubilizers.</td>
</tr>
<tr>
<td>3.</td>
<td>Polysorbate 80</td>
<td><img src="image" alt="Diagram" /></td>
<td>It is used as an emulsifier in foods, as surfactant in soaps and cosmetics or a solubilizer in a mouthwash. It is an excipient that is used to stabilize aqueous hydrogels.</td>
</tr>
<tr>
<td>4.</td>
<td>Laurylamine hydrochloride</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{11}\text{NH}_3^+\text{Cl}^-$</td>
<td>Excellent antistatic, dispersing, emulsifying, anticorrosive, lubricating, antirust abilities.</td>
</tr>
</tbody>
</table>

Non-ionic type
\[ w + x + y + z = 20 \]
\[ R = (C_{17}H_{33})\text{COO} \]

4. Polypylene oxide - modified polymethyl siloxane \((\text{EO} = \text{ethyleneoxy}, \text{PO} = \text{propyleneoxy})\):

\[
\text{CH}_2\text{CH}_2\text{CH}_2\text{O}(\text{EO})_m(\text{PO})_n\text{I}
\]

Textile and fiber industry, polyurethane foam manufacture, personal care and cosmetic applications, paints and coatings.

5. T-octyl phenoxy polyethoxy ethanol (TX-100)

It is a commonly used detergent in laboratories. Some of its applications are in conjunction with zwitterionic detergents for dispersion of carbon materials for soft composite materials, decellularization of animal-derived tissues. Used as cleaning formulations of medications for parenteral administration and used as an emulsifier in the manufacture of the popular anti-arrhythmic amiodarone.
compound, ranging from heavy-duty industrial products to gentle detergents. It is also a popular ingredient in home made vinyl record cleaning fluids together with distilled water and isopropyl alcohol. It is a good micellar catalyst.

6. Polyethylene glycol oleyl ether (Brij® 93)

7. Ethylenediamine tetrakis (ethoxylate-block-propoxylate) tetrol (Tetronic 90R4)

Hard and soft surface cleaners, defoamers in coatings and water treatment. Lubricant in metal working, anti-foaming aid and extender for linear and cross-linked polyesters and polyurethanes.
8. Polyoxyethylene-2-isooctylphenyl ether (IGEPAL® CA-210)

9. Sorbitan monopalmitate (Span® 40)

10. 2,4,7,9-Tetramethyl-5-decyne-4,7-diol ethoxylate

- Used as emulsifier for cosmetic formulations, household products and textile chemicals.
- Reduces surface tension, wetting agent, defoamer and emulsifier for emulsion polymerization.
11. Polyethylene glycol sorbitan monolaurate (TWEEN® 20)

It is used as a wetting agent in flavored mouth drops such as ice drops and as a washing agent in immunoassays. It helps to prevent non-specific antibody binding. Used to saturate binding sites on surfaces, to stabilize proteins purified protein derivative (PPD) solution used in skin testing for tuberculosis exposure, as a solubilizing agent of membrane proteins, as an excipient in pharmaceutical applications to stabilize emulsions and suspensions.
Detergency – it is a property caused by addition or action of surfactants that causes or aids in the removal of foreign material (or soil) from the solid surfaces and reducing energy needed to effect the removal. Soaps are used as detergents but they suffer from their sensitivity to acid p\textsuperscript{H} and presence of hardness in the water. For any surfactant to be considered a good detergent, it must be a good wetting agent, possess the ability to displace the soil materials into the washing fluid, be a good stabilizing agent, and be a reasonable anti-redeposition agent. The most successful detergents are those forming surfactant micelles, which provide a reservoir for replacing unassociated surfactant adsorbed from solution and for solubilizing greases and oils.

Oil recovery – The capillary forces are responsible for retaining much of the oil (residual oil) in parts of the pore structure in the rock or sand. These forces can be overcome by decreasing the interfacial tension between oil/rock or sand interface by addition of suitable surfactants. In oil recovery, one attempts to reduce the capillary forces restraining the oil and / or alter viscosity of the displacing fluid in order to modify the viscous forces being applied to drive oil out of the pores.

Soil remediation – The contamination of ground water by nonaqueous phase liquids like trichloroethylene, tetrachloroethylene is a serious and long term threat to ground water quality. These liquids can persist in soil for many decades as they have low biodegradability. Surfactant based enhanced oil recovery technology has been adapted to achieve the displacement, solubilization and flusing of the nonaqueous phase liquids.

Surfactant stabilized dispersions – An emulsion, foam or suspension can be made by mixing oil, gas or solids into another phase under mechanical shearing, to create additional interfacial area. Surfactant chemistry is used to lower the interfacial free
energy or interfacial tension and hence makes the dispersion easier to form and prevent the system from breaking or separating. This particular feature of surfactants resulted into various industrial applications that include wettability alteration, enhanced microdisplacement of oil, stabilizing foams for mobility control, stabilizing emulsions, breaking of oil spill emulsions etc. Other applications of HS include surfactant replacement therapy in treating the lung disease such as meconium aspiration syndrome, neonatal pneumonia, congenital diaphragmatic hernia; germicides, fabric softeners and antistatic agents, extraction of cholesterol, solubilization of oils and essential nutrients, ice cream stabilization, pesticides, fungicides, herbicides and insecticides etc.

Limitations of HS: Surfactants are so common in every day household use and they are considered to be quite safe. But it is reported that commercial surfactants can pose serious toxic problems especially to aquatic organisms, when they enter surface waters. The toxicity and persistence of surfactants is now fairly predictable for a wide variety of environmental situations [25-31]. Under aerobic conditions, many surfactants are biodegraded, while anaerobic biodegradation generally proceeds more slowly [25]. The toxicity of surfactants naturally depends greatly upon their structure. Increasing alkyl chain length in the hydrophobic group will generally increase toxicity, where as increasing ethylene oxide numbers with the same hydrophobic group decreases the toxicity. In fact the membrane disruption and protein denaturation is found to be a function of their surface active properties [25].

Surfactant micelles are capable of performing number of different functions and can act as primary carriers of drugs to the body, solubilize drugs into hydrophobic core and protect them from hydrophilic surroundings. These functions ensure increased
absorption of drug into cell membrane, enhanced solubility of drug into carrier, and increased stability of drug into delivery system. However, several other undesired effects have been highlighted. These include i) disruption of biological membrane due to interaction of surfactants with membranes, ii) dissolution of many body substances and disturb the body processes, iii) it is difficult to disturb the equilibrium between the dissolved drug and micelles surrounding.

The bulk of surfactant applications have been limited to the domains of single headed, single tailed surfactants. Alternate structures have also been receiving interest because the limitations of conventional HS based on sulfate or sulphonate head groups, related to their hard water tolerance or their cold water solubility. A series of sulphonate surfactants in which the point of substitution of the sulfate group was varied and tunable surfactants based on disodium α–sulfocarboxylates, with excellent properties in terms of hard water tolerance, foam stability and detergency, when compared with single headed counter parts are some examples with different structures. But they suffered from the draw back of causing skin irritation. One of the most exciting developments in the surfactant chemistry is the emergence of Gemini surfactants, the word coined by Menger [32,33]. These surfactants have two hydrophilic (chiefly ionic) groups and two tails per surfactants molecule (dimeric surfactants). The two parts of the surfactants are linked by spacer group of varying length (methylene or oxyethylene spacer). Some of the representative examples of Gemini surfactants are listed in Table 1.2. The architecture of the Gemini surfactants offer a great deal of variation in the nature of the spacer (short, 2-methylene groups to long C₁₂ units; rigid (stilbene) or flexible (methylene) and polar (polyether) or nonpolar (aliphatic, aromatic), the polar group can be positive
(ammonium), negative (phosphate, sulfate, carboxylate or nonionic polyether, sugar etc). Unsymmetric gemins i.e. different polar groups or different nonpolar chains are also reported. Even geminis with three or more polar groups have also been synthesized [34].

The gemini surfactants are reported to possess a number of superior properties such as lower CMCs, increased surface activity (C\textsubscript{20}), lower surface tension at the CMC, enhanced solutions properties such as hard water tolerance, superior wetting times and lower kraft points. These properties may lead to performance advantages in a variety surfactant applications e.g. soil remediation, oil recovery and detergents.

Gemini surfactants are of interest for cosmetics and toiletries, in particular shampoo and personal care products because of their midness, soft feeling and low skin irritation. However, the cost/performance ratio needs to be worked out. Like single chain HS, gemini surfactants also have poor biodegradability and hence cause environment problem. So Tatsumi et al have prepared a new type of hydrolyzable cationic gemini surfactants containing oxycarbonyl groups in the lipophile, or having butylenes or butylylene spacer and an oxycarboxylic group in lipophilic part.

Amphoteric surfactants – they are also known as zwitter ionic surfactants, have two functional groups, one anionic, and one cationic. In most cases, it is the p\textsubscript{H} of the medium, that determines which of the groups dominates by favoring one or the other ionization: anionic at alkaline p\textsubscript{H}, and cationic at acid p\textsubscript{H}. Near the so called isoelectric point, these surfactants display both the charges and posses minimum of interfacial activity and maximum of solubility. The type of amphoteric surfactants and their properties are listed in Table 1.3.
Table 1.2 List of Gemini surfactants

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Structure</th>
<th>Applications</th>
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<tbody>
<tr>
<td></td>
<td>C_{12}H_{25}N^+(CH_3)<em>2-(CH_2)</em>{16}-N^+(CH_3)<em>2C</em>{12}H_{25} 2Br^-</td>
<td>Surfactants are used for wettability modification, detergency, and the displacement of liquid phases through porous media, mineral and petroleum processing, biological systems, health and personal care products, foods, and crop protection etc.</td>
</tr>
<tr>
<td>2.</td>
<td>C_8H_{17}N^+(CH_3)<em>2-(CH_2)</em>{17}-N^+(CH_3)<em>2C</em>{8}H_{17} 2Br^-</td>
<td>Petroleum industry, concrete additives, agro and food processing, cosmetics and pharmaceuticals.</td>
</tr>
<tr>
<td>3.</td>
<td>C_{12}H_{25}N^+(CH_3)<em>2-(CH_2)</em>{2}-O-(CH_2)<em>{2}-N^+(CH_3)<em>2C</em>{12}H</em>{25} 2Cl^-</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>C_{16}H_{33}N^+(CH_3)<em>2-(CH_2)</em>{5}-N^+(CH_3)<em>2C</em>{16}H_{33} 2Br^-</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>C_{16}H_{33}N^+(CH_3)<em>2-(CH_2)</em>{2}-O-(CH_2)<em>{2}-N^+(CH_3)<em>2C</em>{16}H</em>{33} 2Br^-</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>C_{16}H_{33}N^+(CH_3)<em>2-(CH_2)</em>{2}-O-(CH_2)<em>{3}-CH</em>{2}-N^+(CH_3)<em>2C</em>{16}H_{33} 2Br^-</td>
<td>Commercial interests in oil crisis, new methods of enhanced oil recovery, such as microemulsions were heavily investigated.</td>
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<tr>
<td>7.</td>
<td>C_{12}H_{25}N^+(CH_3)<em>2-CH_2-CH(OH)-CH_2-N^+(CH_3)<em>2C</em>{12}H</em>{25} 2Br^-</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>C_{12}H_{25}N^+(CH_3)<em>2-CH_2-C_6H_4-CH_2-N^+(CH_3)<em>2C</em>{12}H</em>{25}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chemical Formula</td>
<td>Description</td>
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<tr>
<td>9.</td>
<td>C₁₂H₂₅N⁺(CH₃)₂-CH₂-CH(OH)-CH(OH)-CH₂⁻ N⁺(CH₃)₂C₁₂H₂₅2Br⁻</td>
<td>Laundry detergents, household, and personal care products and account for over half of all use of surfactants.</td>
</tr>
<tr>
<td>11.</td>
<td>C₁₂H₂₅N⁺(CH₃)₂-CH₂-CH(OH)-CH₂⁻N⁺(CH₃)₂-CH₂-CH(OH)-CH₂⁻C₁₂H₂₅3Cl⁻</td>
<td>They possess special rheological and unusual aggregation properties, widely used as effective emulsifiers, bactericidal agents, dispersants, anti-foaming agents, detergents, etc. Recently these compounds were also applicable in the solubilization of dyes and pigments in the textile industry, gene therapy, the synthesis of highly mesoporous materials, etc.</td>
</tr>
<tr>
<td>12.</td>
<td><img src="image" alt="Anionic Types" /></td>
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</tbody>
</table>

### Anionic Types

<table>
<thead>
<tr>
<th></th>
<th>Chemical Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C₁₂H₂₅OPO₂⁻-O-(CH₂)₆-O-PO₂OC₁₂H₂₅ 2Na⁺</td>
<td>These surfactants have excellent solubilizing and foaming properties and depending on the nature of the spacer, may have very low Krafft temperatures.</td>
</tr>
<tr>
<td>2.</td>
<td>C₁₀H₂₁O-CH₂-CH(OSO₃⁻)-CH₂-O-(CH₂)₂-O-CH₂-CH(OSO₃⁻)-CH₂-OC₁₀H₂₁ 2Na⁺</td>
<td></td>
</tr>
</tbody>
</table>
Very attractive for catalysis and adsorption applications, new synthetic vectors for gene transfection, analytical separations, solubilization processes, nanoscale technology, biotechnology, enhanced oil recovery and as paint additives.
Greater efficiency in reducing surface tensions of water, better for wetting, solubilizing and foaming properties useful in many applications in soil remediation, enhanced oil recovery, drug entrapment and release.

They have better wetting, solubilizing and foaming properties, and good mildness to the skin, safe ecology, and environmental control. So potentially useful in soil remediation, enhanced oil recovery, drug entrapment and release and the construction of high-porosity materials.

The mixtures of polymers and surfactants are widely applied in a variety of fields, including enhanced oil recovery, bioscience and pharmaceuticals.
9. They are used for the manufacturer of shampoos, cosmetics, body lotions, and personal care products because of their pulpy effect, mildness, and absence of skin irritation.

10. Non ionic types

Food elaboration, polymer manufacture and solubilization of biological membranes are some of
The wide spectrum of application of glycosides.

2.

3.

4.

5.

6.
Surfactants for industrial applications including pharmaceuticals, material manufacture, and membrane protein isolation.

Potentially useful in many applications for soil remediation, enhanced oil recovery, drug entrapment and release and the construction of high-porosity materials.
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<th>Sr. No.</th>
<th>Name</th>
<th>Structure</th>
<th>Applications</th>
</tr>
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<tbody>
<tr>
<td>1.</td>
<td>Aminopropionic acid</td>
<td>$\text{RN}^+-(\text{CH}_2-\text{CH}_2)-\text{COO}^-$</td>
<td>Isoelectric point 4.0- soluble in acidic/alkaline solutions, adsorb on skin, hair and textile filters, used as wetting agents and bactericide in cosmetics, antistatic and lubricants for hair and fabrics.</td>
</tr>
<tr>
<td>2.</td>
<td>Imidopropionic acids</td>
<td>$\text{HOOC-CH}_2-\text{CH}_2-\text{RN}^+\text{H-CH}_2-\text{CH}_2-\text{COO}^-$</td>
<td>Isoelectric point around 2-3, more water soluble, used as textile softeners, cosmetics and soap bars.</td>
</tr>
<tr>
<td>3.</td>
<td>Quarternized Compounds</td>
<td>(a) Alkyl bataine $\text{R-N}^+(\text{CH}_3)_2-\text{CH-COO}^-$</td>
<td>Amphoteric, tolerance to high salinity especially to divalent Ca and Mg</td>
</tr>
<tr>
<td></td>
<td>(b) Alkylsulfo betaine</td>
<td></td>
<td>R-N(^+(\text{CH}_3)_2\text{-CH}_2\text{-SO}_3^-)</td>
</tr>
<tr>
<td>---</td>
<td>-------------------------</td>
<td>---</td>
<td>-----------------</td>
</tr>
<tr>
<td>4.</td>
<td>Dodecyl betaine</td>
<td></td>
<td>C(<em>{12})H(</em>{25})N(^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-)</td>
</tr>
<tr>
<td>5.</td>
<td>Lauramidopropyl betain</td>
<td></td>
<td>C(<em>{11})H(</em>{23})CONH(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-</td>
</tr>
<tr>
<td>6.</td>
<td>Cocoamido-2-hydroxypropyl sulfobetaine</td>
<td></td>
<td>C(<em>n)H(</em>{2n+1})CONH(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH(OH)}\text{CH}_2\text{SO}_3^-</td>
</tr>
</tbody>
</table>
7. Dodecyldimethyl (3-sulfopropyl) ammonium hydroxide

\[
\text{CH}_3^+ \text{CH}_3(\text{CH}_2)_11-N-(\text{CH}_2)_3\text{-SO}_3^- \quad \text{CH}_3
\]

8. Hexadecyldimethyl (3-sulfopropyl) ammonium hydroxide

\[
\text{CH}_3 \text{CH}_3(\text{CH}_2)_11-N-(\text{CH}_2)_3\text{-SO}_3^- \quad \text{CH}_3
\]

9. Coco(amidopropyl) hydroxyldimethylsulfobetaine

\[
\text{O} \text{R-C-NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}-\text{CH}_2\text{-CH-CH}_2\text{-SO}_3^- \quad \text{CH}_3 \text{OH}
\]
1.3 Fluorosurfactants:

Fluorosurfactants (FS) are also known as fluorinated surfactants. They can be polyfluorinated or fluorocarbon based (perfluorinated) synthetic organofluorine chemical compounds that have multiple fluorine atoms [35-37]. Fluorosurfactants have a fluorinated tail and hydrophilic head. Fluoronited surfactants have several advantages over their hydrogenated counter parts. FS, i) have very low critical micelle concentration, ii) are best known products for wetting, iii) have superior interfacial tension reduction which speeds up emulsion formation and iv) can perform vital surfactant functions. Therefore, FS are employed in various technical and industrial formulations, based on their vital characteristics such as wetting ability, dispersing ability, emulsification, foaming, corrosion inhibition, pore penetration, leveling and antiblocking etc. As per the estimates of 2009-2010, FS are found in more than two hundred applications [38], that includes soil and stain repellants, plane hydraulic fluids, fire fighting foams, paints, electroplating, coating for clothing fabrics, leather, carpets, paper coatings, photographic emulsifiers, pressure sensitive additives, waxes, polishes, pharmaceuticals, insecticides etc. Perfluorooctanoic acid is also used as surfactants in aqueous media for polymerization of hydrophobic monomers especially fluorinated monomers such as tetrafluoroethylene and other C₂-C₃ alkanes.

Some of the commonly used examples are listed in Table 1.4. Besides several unbeatable advantages and applications of FS, as mentioned above, FS suffer major disadvantages such as, PFOS based products are very stable and persistent i.e. they do not break down or degrade under enzymatic or metabolic decomposition in the environment, they are bioaccumulative i.e. they can build up over time and their half life in human body
may be about four years and PFOS based chemicals are reported to be toxic via acute oral exposure (for rats, LD$_{50}$ lethal dose for 50 percent of damaged cells) is 251 mg/kg. The systematic and reproductive toxicity studies, serious effects were reported: post natal deaths in rats at 3.2 and 1.6 mg/kg/day and in repeat-dose treated Rhesus monkeys, death was reported within 7 weeks at 4.5 mg/kg/day [39].

FS are found all over the planet (surface waters of Atlantic and Pacific oceans [40] coastal waters, rivers, drinking and rain waters fresh water ecosystems, urban centers, soils, sediments [41-43], high Arctic ice caps [44,45], in the blood of many animal species (fish and even livers of polar bears), and general human population world wide [46]. For the reasons, as mentioned above, during the period, 2002-2005, major manufacturers of PFSO (Asahi Glass, Atofina, Daikin and Dopont) have decided to decrease the production of PFOA and PFOS to 95 % by 2010 and their emissions and product contents completely by 2015. Attempts to degrade PFOA and PFOS were even through suggested [38], the results showed that the stability of C-F bond, hinders the mineralization.

Strategies have been worked out to synthesize non-bioaccumable alternatives to PFOA. Five main families are considered or recommended: (i) those bearing either a CF$_3$O or (CF$_3$)$_2$N end-groups, (ii) arising from oligo(hexafluoropropylene oxide), (iii) those produced from the telomerization of vinyledene fluoride with short perfluoroalkyliodides, (iv) 3,3,3-trifluoropropene telomers from either perfluoroalkyliodides or other chain transfer agents and (v) surfactants obtained from cotelomerization or by controlled polymerization of vinyledene fluoride and 3,3,3-trifluoropropene. Kostov et al have discussed the strategies for the synthesis of original fluorinated surfactants [38].
Table 1.4 Lists of Fluorosurfactants

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name</th>
<th>Structure</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anionic Fluorosurfactants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Alkyl sodium sulfonate</td>
<td>CF₃−[CH₂]ₙ−SO₃⁻⁺Na</td>
<td>Commercially available. Fluoro-surfactants provide exceptional wetting, levelling, emulsifying, foaming or repellency characteristics in a wide range of industrial and consumer products.</td>
</tr>
<tr>
<td>2.</td>
<td>Lithium 3-[2-(perfluoroalkyl) ethylthio] propionate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Lithium 3-[2-(perfluoroalkyl) ethylthio] propionate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Lithium 3-[2-(perfluoroalkyl) ethylthio] propionate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Cationic types**

1. TFP based fluorosurfactants

2. Nonionic ethoxylated fluorosurfactant

**Nonionic types**

2. Nonionic ethoxylated fluorosurfactant

3. Ammonium bis[2-(perfluoroalkyl)ethyl] phosphate

Surfactants are widely used in oil recovery for particle dispersion, emulsion stabilization, foam generation, reservoir wetting, and many other applications.
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4.</td>
<td>Triperfluoroalkyl citrate</td>
</tr>
</tbody>
</table>
|   | ![Triperfluoroalkyl citrate](image)
| 5. | 1H,1H,2H-Perfluoro-1-hexene, 3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexene |
|   | Effective in a variety of oil recovery (EOR) techniques including improving subterranean wetting, foam stability and modify surface properties. |
| 6. | 2-(Perfluoroalkyl)ethanol |
|   | ![2-(Perfluoroalkyl)ethanol](image)
| 7. | TFP based fluorosurfactant |
|   | ![TFP based fluorosurfactant](image)
<p>| 8. | Fluorinated xanthate |
|   | <img src="image" alt="Fluorinated xanthate" /> |</p>
<table>
<thead>
<tr>
<th>Amphoteric type</th>
<th>Soil and stain-repellents, plane hydraulic fluids, fire fighting foams, paints, coatings for clothing fabrics, leather, carpets, paper coatings, electroplating, photographic emulsifiers, pressure sensitive additives, waxes, polishes, pharmaceuticals, insecticides, etc. In addition, PFOA is also frequently used as surfactant in aqueous media of polymerization of hydrophobic monomers, especially fluorinated monomers such as tetrafluoroethylene and other C₂⁻C₃ alkenes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Perfluorooctanoic acid (PFOA) C₁₇F₃₅CO₂H</td>
<td></td>
</tr>
<tr>
<td>2. Ammoniumperfluorooctanoate (APFO)</td>
<td></td>
</tr>
<tr>
<td>3. Perfluorooctane sulfonate C₁₇F₃₇SO₃X where X = K, Na, H, PFOS</td>
<td></td>
</tr>
<tr>
<td>4. Perfluorooctylsulfonic acid C₁₇F₃₇SO₃H (PFOS)</td>
<td></td>
</tr>
</tbody>
</table>
1.4 Silicone Surfactants (SS):

They are a group of small molecule and polymeric surfactants that find a wide variety of applications due to their unusual properties [47-49]. Structurally, they consist of permethylated siloxane hydrophobic group (polydimethyl siloxane) coupled to one or more polar groups. Many types of polar groups have been described, but nonionic groups based on polyoxyethylene and polyoxypropylene are by far the most common. Silicone surfactants are highly surface active due to their low surface tension caused by the large number of methyl groups and small intramolecular interactions between the siloxane hydrophobes. The three most common molecular structures for silicone surfactants are rake type copolymers, ABA copolymers and trisiloxane surfactants, as illustrated below:

Molecular structure of a rake-type silicone surfactant

Molecular structure of an ABA-type siloxane surfactant
Molecular structure of a trisiloxane surfactant

\[
\begin{align*}
\text{CH}_3 & \\
\text{(CH}_3\text{)}_3\text{-Si-O-Si-O-Si-(CH}_3\text{)}_3 & \\
\text{(CH}_2\text{)}_3 & \\
\text{(OCH}_2\text{CH}_2\text{)}_n\text{OR} & \\
\end{align*}
\]

Polyether modified polydimethyl siloxane copolymer

\[
\begin{align*}
\text{CH}_3 & \\
\text{H}_3\text{C-Si-O} & \\
\text{A} & \\
\text{A} & \\
\text{Si-O-Si-O-Si-O-Si-Ch}_3 & \\
\text{CH}_3 & \\
\end{align*}
\]

\[A = (\text{CH}_2\text{)}_3\text{-O-(C}_2\text{H}_4\text{O)}_x\text{-C}_3\text{H}_6\text{O)}_y\text{-H}\]

Alkyl-polydimethylsiloxane copolymer

\[
\begin{align*}
\text{CH}_3 & \\
\text{H}_3\text{C-Si-O} & \\
\text{A} & \\
\text{A} & \\
\text{Si-O-Si-O-Si-O-Si-Ch}_3 & \\
\text{CH}_3 & \\
\end{align*}
\]

\[A = (\text{CH}_2\text{)}_n\text{-CH}_3\]

Diquaternary polydimethyl siloxane

\[
\begin{align*}
\text{R}^+\text{N}^+\text{-Z(SiO)}_n\text{Si-Z-N}^+\text{-R-CH}_3\text{COO}^- & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{OH} & \\
\text{Z = CH}_2\text{-CH-CH}_2\text{-O-(CH}_2\text{)}_3 & \\
\text{R = long hydrocarbon chain} & \\
\end{align*}
\]

34
The hydrophilic part of the SS is invariably a low molar mass polymer based on ethylene oxide or propylene oxide or copolymer of both. The hydrophobic part is represented by permethylated siloxane moiety. The architectures, as mentioned above gives a great degree of flexibility in designing SS. A wide variety of copolymers is possible by varying molar mass, molecular structure (pendent/linear) and the compositions of polyether chain, ratio of siloxane to polyether etc. Other variables include absence or presence of functionality on end groups on the polyether fragments. Some of the largest applications of SS are in the manufacturing of plastic foams, as spreading and wetting agents and in personal care products. Foaming, wetting, emulsifications and phase behavior are basic properties relevant to these applications. SS are beginning to be used to prepare nanostructured materials including polymerizable vesicles. The trisiloxane structure of SS has been reported to give the best equilibrium surface tension reduction and excellent wetting to plastic surfaces and other low energy substrates. The high molecular weight siloxane surfactants with rake and linear structures gave moderate wetting.

1.5 Polymeric Surfactants or Surfactant-Like Polymers:

A polymer, properly designed obviously exhibit an amphiphilic structure. But such structures must have both polar and nonpolar groups. Asphatenes, which are natural compounds found in crude oil, have such polar and nonpolar groups. Infact, there are two main configurations, ‘block’ and ‘graft’ type copolymers that can have hydrophilic (H) and lipophilic monomer units respectively. The architecture of a typical di block hydrophilic-hydrophobic polyoxyethylene-polyoxypropylene copolymer is shown in Fig. 1.1. The triblock oxyethylene-oxypropylene-oxyethylene copolymers are commercially
available under the trade names of poloxamer or pluronic or reverse pluronic or tetronic. The molecular structure of such copolymers is shown in Fig 1.2. These copolymers are available in a wide range of molecular weights, % of oxyethylene moiety etc. Several of PEO-PPO copolymers were approved as thermo-viscositing materials and find applications as direct and indirect food additives, pharmaceutical ingredients and agricultural products [50-52,53,54]. Among the copolymers displaying the micelle formation ability, it is worth mentioning that, the copolymers with poly(oxyethylene) segments along with hydrophobic blocks of phospholipids [55-58], poly(l-amino acids) [59-62], poly esters [55,63,64], polyoxybutylene [65-67], polystyrene oxide [65-68] and phenylglycidyl ether [69,70] have also been reported to possess potential applications. Table 1.5 lists the structures of these copolymers based on polymeric surfactants. Among all of the above, PEO-PPO block copolymers have gained popularity over the decades due to a number of critical reasons: (i) a very broad range of compositions, (ii) commercial availability, (iii) proven biocompatibility for many of the derivatives and minor side effects in vivo, (iv) approval by regulatory institutions to be used in pharmaceutical formulations. However, inspite of above advantages, PEO-PPO block copolymers still present a number of limitations and the most important has to do with low stability of the self low assembled nanostructures upon dilution in the blood stream. Even through core and shell stabilized micelles have been produced, the modifications affected the release profile of the drugs. The concentrations needed for producing gels of high stability are high. The more hydrophilic representatives of pluronic copolymer family, display lower micellization ability and hence lower solubilization capacity.
Fig. 1.1 Sketch of an equilibrium between ABC and an ABC micelle

Fig. 1.2 Molecular structure of PEO-PPO block copolymers: (A) Linear bifunctional poloxamer, Pluronic F127 (MW = 12.6 kDa) and (B) branched 4-arm poloxamine, Tetronic 1107 (MW = 15 kDa), both polymers containing 70 wt % of PEO.
**Table 1.5 Hydrophobic-hydrophilic copolymer based polymeric surfactants**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Name</th>
<th>Structure</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PEO-PPO</td>
<td><img src="structure1.png" alt="Structure" /></td>
<td>Used for protection of cells from hydrodynamic damage, bioreagent, suitable for insect cell culture, controlled drug release and synthesis of nanoparticles.</td>
</tr>
<tr>
<td>2.</td>
<td>PEO-PPO-PEO (Pluronic)</td>
<td><img src="structure2.png" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>PPO-PEO-PPO (Pluronic R)</td>
<td><img src="structure3.png" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>PEO-PPO PPO-PEO PEO-PPO PPO-PEO Tetronic</td>
<td><img src="structure4.png" alt="Structure" /></td>
<td>Tetronic amphiphilic block copolymers display great potential as components of smart or biodistribution-modified drug delivery systems, tissue engineering scaffolds and synthesis of nanoparticles.</td>
</tr>
<tr>
<td>5.</td>
<td>PPO-PPO PEO-PPO PPO-PPO PEO-PPO Tetronic R</td>
<td><img src="structure5.png" alt="Structure" /></td>
<td></td>
</tr>
</tbody>
</table>
6. poly(ethylene oxide)-b-poly(aspartic acid)  

PEO-poly(l-amino acid)  

Used for controlled drug release systems and synthesis of nanoparticles.

7. PEO-PBO  

Controlled release of bioactive agents, sutures and bioabsorbable implantable devices, medical, pharmaceutical, cosmetic, agricultural and other industries.

8. PEO-PBO-PEO  

(Butylene glycols)  

Block copolymer micelles are widely used in drug delivery applications and synthesis of nanoparticles and other industrial application.
1. 6 Amphiphilic Ionic Liquids (AILs):

Ionic liquids (ILs), commonly referred as room temperature molten salts have recently attracted significant attraction and attention as a promising new class of benign green solvents for nanomaterial synthesis due to their unique physico-chemical properties such as high viscosity, high vapor pressure, high ionic conductivity, high thermal and chemical stability and negligible volatility [71,72]. Unlike conventional electrolyte aqueous solutions, IL solvents can dissociate into individual cations and anions rather than existing as intact molecules, due to their molten salt nature at room temperatures.

The room temperature ionic liquids (RTILs) are replacing the conventional solvents in numerous task specific applications, to overcome the nonapplicability and insufficient effectiveness of former. Besides, high thermal stability and electrical conductivity, large electrochemical window, ILs have low nucleophilicity and capability of providing weakly coordinating or non-coordinating environment. RTILs have very good solvent properties for a wide variety of organic, inorganic and organometallic compounds: in some cases, the solubility of certain solutes in RTILs can be several orders of magnitude higher than that in traditional solvents. There are number of different cation and anion combinations that may result in salts having low melting points and result in an ionic liquid (please see Fig. 1.3). One can select from dozens of anions and hundreds of thousands of large cations, such as 1-alkyl-3-methylimidazolium [mim]. ILs are thus known as designer solvents and their structure can be fine-tuned to suit a particular application such as dissolving certain chemical compounds in a reaction or extracting specific molecules from solution etc.
As a convention, a chemical compound with an organic cation or inorganic or organic anion with a melting point below 100 °C can be considered as ionic liquid. RTILs or ILs in general are more resistant than traditional organic solvents under harsh reaction or process conditions, such as those occurring in oxidation [73], photolysis [74] and radiation processes [75]. The ILs with [bmim]+ cation and a variety of anions such as [BF₄]⁻, [PF₆]⁻, [CF₃SO₃]⁻, [CF₃CO₂]⁻, [(CF₃SO₂)₂N]⁻ have been reported to be color less, even though they are not 100 % pure, usually the color of RTILs ranges from yellowish to orange and this is attributed to the use of raw materials with color or excessive heating during the synthesis. ILs have an inherent tendency to be hygroscopic and they become less viscous with increasing water content, so ILs need to be stored in inert atmosphere.

The degree of polarity can be varied by adapting the length of alkyl chain and the counter ion. Long alkyl chain ILs display liquid crystalline properties [76]. The anion chemistry has a large influence on the properties of ILs, for example [bmim][PF₆] is immiscible

**Fig 1.3 Cations, anions and alkyl chain used in amphiphilic ionic liquids**

As a convention, a chemical compound with an organic cation or inorganic or organic anion with a melting point below 100 °C can be considered as ionic liquid. RTILs or ILs in general are more resistant than traditional organic solvents under harsh reaction or process conditions, such as those occurring in oxidation [73], photolysis [74] and radiation processes [75]. The ILs with [bmim]+ cation and a variety of anions such as [BF₄]⁻, [PF₆]⁻, [CF₃SO₃]⁻, [CF₃CO₂]⁻, [(CF₃SO₂)₂N]⁻ have been reported to be color less, even though they are not 100 % pure, usually the color of RTILs ranges from yellowish to orange and this is attributed to the use of raw materials with color or excessive heating during the synthesis. ILs have an inherent tendency to be hygroscopic and they become less viscous with increasing water content, so ILs need to be stored in inert atmosphere.

The degree of polarity can be varied by adapting the length of alkyl chain and the counter ion. Long alkyl chain ILs display liquid crystalline properties [76]. The anion chemistry has a large influence on the properties of ILs, for example [bmim][PF₆] is immiscible

41
with water, where as [bmim][BF₄] is water soluble. ILs derived from polyatomic anions are dominating the commercial formulations (ILs based on acetylcholine chloride or amino acid derivatives are some examples).

The cations such as 1-alkyl-3-methylimidazolium ([$\text{C}_n\text{mim}]^+$), where $n \geq 4$, possess an inherent amphiphilicity and therefore ILs based on this cation could exhibit novel surfactant properties namely surface activity and self assembly into micelle-like aggregates with specific structure, shape and properties such as solubilization, detergency, wetting and dispersing etc. By simple fine-tuning of amphiphilicity of ILs by changing the alkyl chain length, the type of cations, and the nature counter ions, one can change or tailor the structure of the aggregates and hence their performance properties. The chemical structures of the some of the surface active and amphiphilic ILs are shown in Fig. 1.4.

![Chemical structures of the surface active imidazolium ILs used in this Study](image)
Till date, ionic liquids based mostly on alkyl methylimidazolium and to a less extent alkyl methyllpyridinium cations in combination with several anions such as bromide, chloride, iodide, tetrafluoroborate, hexafluorophosphate and bis-(trifluoromethylsulfonyl)imide etc, have been the focus of systematic investigations that deal with their synthesis, solvent properties and their thermophysical and colloid chemical behavior. Luczak et al [77] have reviewed the self organization of alkyl methylimidazolium ionic liquids in aqueous solutions. The ILs are also of great interest to surfactant chemists for multiple reasons. Firstly they have inherent amphiphilicity and hence are expected to possess unique surface / interfacial and aggregation properties in water. In terms of chemical structures, the ILs resemble to well known classical cationic surfactants based on alkyltrimethylammonium halides, linear alkyl chain pyridinium halides etc. Information about how the IL molecules align or adsorb at the air / water interface and also water / organic interface on one hand and the tendency of IL for self organization on the other hand is highly desirable for inventing new surfactant based applications such as wetting, dispersion, solubilization, detergency and soil remediation etc. It is also possible to propose potential green surfactants based on amphiphilic ionic liquids (AILs) once their adsorption and aggregation processes are fully understood and explained.

AILs based on pyridinium and pyridine derivative cationic rings have several advantages over AILs of imidazolium based rings. For example, not only the biodegradability of pyridinium based AILs is higher than the latter but also the rates of biodegradability increase with the increase in the length of the alky chains [78]. The pyridinium rings of neighboring molecules can mutually interact through \( \pi \)-electrons.
cloud and hence result into stalks of ordered structures. Pyridine and its derivatives are common laboratory solvents and hence the production of AILs based on these rings in large quantities for bulk use is more economically viable. N-Butylpyridinium tetrafluoroborate has been reported to be a better extractant of thiophene and benzothiophene from fuel oil as compared to imidazolium based ILs by oxidative desulfurization process [79]. Pyridine and substituted pyridines have required basicity to accept a proton, so that pyridine based ILs can be more useful as reagents in organic reactions involving proton transfer mechanism [80].

In spite of these promising advantages, there are only very few studies that deal mostly with the monitoring of bulk interactions through various thermo-physical properties and heat capacities for binary mixtures of 1-butyl-3-methylpyridinium tetrafluoroborate \([C_{4}mpy][BF_{4}]\) with water or alcohols [81-84] and very few on colloidal [85-87] aspects of N-butyl-3-methylpyridinium chloride \([C_{4}mpy][Cl]\) in water. Singh and Kumar [86] have investigated the aqueous solutions of 1-butyl-3-methylimidazolium tetrafluoroborate \([C_{4}mim][BF_{4}]\) and 1-butyl-3-methylpyridinium chloride \([C_{4}mPy][Cl]\) through \(^1\)H NMR and steady state fluorescence spectroscopy. It was emphasized that a strong correlation exists between the aggregation patterns of these two ILs in water. It was argued that \(\pi\ldots\pi\)-interactions are more predominant and facilitate the stacking of the rings upon the aggregation. It was further explained that \(BF_{4}\) anion interacts more strongly with the water molecules than with aromatic ring protons and similarly the less acidity of ring protons of pyridine and the lone electronegative nitrogen in pyridine ring favor \(\ldots\) IL interactions. Critical micelle concentrations and surface active parameters for a series of 1-alkyl-3-methylpyridinium chlorides, \([C_{n}mpy][Cl]\) with varying alkyl
chain lengths \((n = 10, 12, 14, 16 \text{ or } 18)\) have also been reported using fluorescence, interfacial tension and \(^1\text{H} \text{ NMR}\) spectroscopy methods [87]. The authors compared the data on surface active parameters of methylpyridinium and methylimidazole ionic liquids and suggested that the adsorbed \([\text{C}_n\text{mim}]\text{[Cl]}\) molecules have a higher degree of packing over the adsorbed \([\text{C}_n\text{mpy}]\text{[Cl]}\) molecules. This conclusion is rather surprising as one would expect that the aromatic pyridine rings facilitate a close packing of molecules due to their stalking through \(\pi\) electron clouds. Does similar effect translate into closely packed aggregates in bulk aqueous phase? Therefore, it would be very interesting to investigate the effect of these interesting interactions on the aggregation characteristics of AILs with different cation rings in aqueous solutions. Before one arrive at well meaning conclusions, more data on surface active and aggregation characteristics of pyridine ring based AILs in aqueous media is desired. As far as we are aware, till date there are no studies on colloidal aspects of pyridine ring based AILs in water.

Structural features of aggregates of short alkyl chain AILs namely 1-hexyl-, and 1-octyl pyridinium chlorides in water have been reported [88]. It was suggested that a minimum of six carbon atoms is required in the alkyl branch for the formation of micelle-like aggregates. Otherwise the clustering of molecules occurs through an open aggregation process. Small angle neutron scattering (SANS) and Small angle x-ray scattering (SAXS) results indicated that the clusters of closely packed molecules or small aggregates occur through several types of interactions, namely \(\pi\ldots\pi\) interactions between the pyridine rings of cations and H-bonding interactions between the cations of the ILs and halide ion, the water and halide ions, ring acidic protons and water etc. The methyl group in substituted pyridine hinders the close packing of molecules sterically and
hence addition of NaCl has opposite effect on the growth of aggregates of simple octyl based pyridines ILs as compared to the methyl substituted pyridine AILs. Triolo et al [89] indeed reported from the X-diffraction studies on pure ILs based on alkylimidazolium cations (butyl to decyl) and tetrafluoroborate anion that structural organization exists at nanometer scale both in their liquid and super cooled state. The nano-domains are built of aggregates of neutral alkyl tails surrounded by strong electrostatically-interacting charged species. These already self organized molecules get completely disturbed in aqueous media, so that well defined associates are formed analogous to classical surfactants in water. It would not be totally unexpected to find some of the residual organized nano-structures of ILs in aqueous media. More over the pyridine rings in cations would further aid the self organization through close stalking of aromatic rings. More systematic measurements on higher homologues series of AILs of type 1-alkyl pyridinium of methylpyridinium chloride [C\textsubscript{n}\text{py} or C\textsubscript{n}\text{mpy}][\text{Cl}] where n = 8, 10, 12, 14, 16, 18 etc are required to understand and analyze these systems further.

Micelles of ionic surfactants [90-97] and block copolymers [98-101] can get transformed from spheres into rod-like, thread-like and other higher ordered structures including vesicles, liquid crystalline phases etc upon increase in the concentration or increase in temperature or upon addition of additives. In hydrotope additives, the co-ions affect the electrical and hydration characteristics of micelle surface through various mechanisms that result in a decrease in area per head group, increase in packing parameter without significantly affecting the surfactant volume. Additives such as sodium salts of salicylate or benzoates and hydroxyl compounds such as naphthols [102,103] have been reported to interact specifically with the charged head groups and
induce not only micellar shape transition but also formation of gel like structures with viscoelastic behavior. Therefore, it is thought that investigations on effect of various hydrotopes that promote the growth of the micelle – like aggregates of AILs in aqueous media would be quite useful from technology viewpoint. Few recent studies reported the use of ionic liquids in dissolution and regeneration of cellulose [104], preparation of gel material from cellulose solutions [105], acetylation of chitin [106], preparation of chitin/cellulose, cellulose / starch composite gels and films [107-109]. Utilization of tunable ionic liquid aggregates in aqueous media in these processes is expected to yield better and structured gels or films with easy process and wide applications ability.

Garcia and coworkers [110], reported that 1-butyl-3-methylimidazolium salts exhibited higher toxicity to the cladoceran invertebrate Daphnia magna compared to the salt water bacteria Photobacterium phosphoreum. The fact that toxicity increases with the alkyl chain length of the 1-alkyl-3-methylimidazolium class of ILs strongly suggests that the hydrophobicity of the IL can cause intercalation into the cell membrane resulting in its loss of integrity [111]. Up to this date, no literature report has extensively studied the surface tension lowering efficiency or determined the critical micelle concentration (CMC) values for a variety of structurally related dialkyl chain imidazolium based AILs. Therefore, we synthesized and studied this type of AILs. These AILs consist of various lengths of alkyl substituent appended to the one and three positions of the imidazolium cation.

In view of the above, the present thesis mainly focuses on synthesis and characterization of new and novel amphiphilic ionic liquids (AILs) based on 1-alkylpyridinium chloride [Cₙpy][Cl] (n = 10, 12, 14, 16, 18), 1,3- dialkylimidazolium
chloride \([([C_n]_{2\text{imi}})[\text{Cl}])\] (n = 4, 6, 8, 10, 12), 4-hexadecyl-4-methylmorpholinium chloride \([C_{16}\text{mmor}][\text{Cl}])\), 1-hexadecyl-1-methylpiperidinium chloride \([C_{16}\text{mpip}][\text{Cl}])\), 1-hexadecyl-1-methylpyrrolidinium chloride \([C_{16}\text{mpyrr}][\text{Cl}])\) and 1-hexadecyl-4-methylpyridinium chloride \([C_{16}\text{-4mpy}][\text{Cl}])\). The above AILs are further studied for their surface active, self aggregation behavior and rheological behavior using several independent methods such as surface tension, electrical conductivity, steady state fluorescence, static light scattering (SLS), density, ultra sound velocity, rheology, small angle neutron scattering (SANS) measurements. The comparison of the surface active and micellar features of AILs with similar head group but different alkyl chain lengths and micellar features of same chain length with different head groups are made and discussed. The micro structural features of the aggregates namely size, shape, fractional charge, number density, water content and aggregation number were obtained across the concentration using fluorescence quenching technique employing pyrene and benzophenone as the probe and quencher respectively. Static light scattering measurements (SLS) in Debye and Zimm models were made to collect scattering intensities of a given solution at different angles and also adjudge the strength of the solute-solute interaction, SANS measurements enabled to analyze the cross-section versus scattering vector profiles in terms of particle form factor and structure factors applying different models that assume a given shape to the micellar aggregates.

The thesis is divided into SIX Chapters.

Chapter 1 provides the detailed literature survey on the general introduction along with the objectives of the work. The unique features of ionic liquids namely nature of cation-anion, design and their novel properties are mentioned.
Chapter 2 gives the details of experimental measurements and methods. Besides listing the source and purity of the chemicals and reagents used, the synthesis schemes for the preparation of AILs and their characterization is described. The details of each of the methods along with the data treatment procedures are also presented. The instrumentation details for measuring surface tension, electrical conductivity, density, speed of sound, steady state fluorescence quenching, static light scattering, SANS and dynamic rheology measurements described. This chapter also gives a separate subunit in describing the basis and analysis of the experimental data to obtain surface active parameters, thermodynamic parameters of aggregation, size related parameters, shape related parameters, aggregation number, fractional charge of aggregates and water content etc. The procedure for obtaining zero shear viscosities from shear rate dependent viscosities data on iongels, storage ($G'$) and loss ($G''$) modulus is also described.

The chapters 3 - 5 would present the actual experimental work, results and discussion. Each of these chapters would be self containing and would have the introduction part specific to the type of study.

Chapter 3 is divided into two parts. Part A describes the surface active and aggregation behavior of amphiphilic ionic liquids mostly based on cationic rings 1-alkyl pyridinium chlorides of type, general formula $[\text{C}_n\text{py}][\text{Cl}]$ ($n = 10, 12, 14, 16, 18$). The results on critical aggregation concentration (CAC), surface active parameters namely effectiveness of surface tension reduction, $\gamma_{\text{CAC}}$, adsorption efficiency, $\text{pC}_{20}$, surface excess, $\Gamma_{\text{max}}$ and minimum area per ionic liquid molecule, $a_i^*$, thermodynamic parameters namely counter-ion binding of aggregates ($\beta$), standard molar Gibbs free energy, $\Delta G_a^0$, enthalpy,
ΔH\textsubscript{a}^0 and entropy of aggregation ΔS\textsubscript{a}^0 have been calculated. The micro structural features including micellar size i.e. semi major axis b, semi minor axis a, fractional charge α, aggregation number N, root mean square radius, weight average micellar molar mass, second virial coefficient A\textsubscript{2} and mass average aggregation number have been determined from SANS and SLS measurements. The aggregation numbers of micellar systems are also calculated from the other independent methods such as fluorescence quenching, density, isentropic compressibility and compared with each other.

**Part B of Chapter 3** deals with the studies on influence of two hydrotope additives namely sodium benzoate (SB) and sodium salicylate (SS) on surface chemical and aggregation characteristics of 1-alkyl pyridinium chlorides, [C\textsubscript{n}py][Cl] (n = 10, 12, 14, 16, 18) in aqueous solution.

**Chapter 4** reports the conditions for the growth of worm-like micelles of AILs of type [C\textsubscript{n}py][Cl] where n = 12, 14, 16, 18 in presence of hydrotopes, SS or SB. The individual mixture solutions of AILs / SS or SB in water were prepared and mixed in different mole ratios to get highly viscous to gel solutions. The zero shear viscosities (η\textsubscript{0}) of the solutions or gels were obtained by scanning viscosities in a shear rate range of 0.1 to 100 \text{sec}^{-1}. The mole ratio in each of the AIL / SS or SB mixtures corresponding to maximum η\textsubscript{0} was located. Here, we find that SS is more preferable for gel preparation rather than SB. These gel like systems were further analyzed through oscillatory shear measurements to obtain storage modulus (G'), loss modulus (G''), and complex viscosity [η*], assuming that, gel solutions consist of highly grown worm-like micelles. Relaxation times were evaluated from the experimental data of storage modulus, G'.
Chapter 5 reports the surface active and aggregation behavior of dialkyl chain imidazolium based ionic liquids, 1,3-dialkyl imidazolium chlorides \([\text{[(C}_n\text{)}_2\text{imi}][\text{Cl}]\) (n = 4, 6, 8, 10, 12). The results of CAC, surface active parameters, thermodynamic parameters, counter-ion binding of aggregates, micellar size i.e. semi major axis, semi minor axis, fractional charge, aggregation number, root mean square average radius, weight average micellar molar mass, second virial coefficient and weight average aggregation number are calculated and discussed. Aggregation numbers were also determined by fluorescence quenching, density and isentropic compressibility data.

Chapter 6 provides the summary of the results.
1. 7 References:


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79. D. Zhao, Y. Wang, E. Duan, Molecules 2009, 14, 4351.