CHAPTER 1

INTRODUCTION
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Introduction

The primary aim of this work was to synthesize anionic phosphate gemini surfactants based on higher fatty alcohols viz. tetradecanol, hexadecanol and octadecanol and then to study the physico-chemical and surface active properties of synthesized geminis. In chasing this goal, the present research has emphasized a broad range of fields, and this introduction provides a brief review of the surfactant in those areas. Section 1.1 of this chapter deals with the history, global production and consumption pattern, chemistry and mode of action of surfactants. Section 1.2 emphasizes on new class of surfactants i.e. gemini surfactants and their classification. Section 1.3 deals with gemini surfactants, and enlightens a few methods of synthesizing gemini surfactants specially the preparation of phosphate gemini surfactants and their characterization. Section 1.4 covers the properties of geminis, perhaps, the most congruous and Section 1.5 represents the applications of novel compounds i.e. gemini surfactants. The objective of study has been elaborated and has been covered in section 1.6.

1.1 Surfactants

Before studying the gemini surfactants and their novelty one should realize that they are basically surfactant molecule and show all the properties as depicted by conventional surfactants. Geminis are the recent innovations in the field of surfactants after 1988. Their maximum properties are like conventional surfactant molecules but their properties are much more modified and lowered. As geminis are the surfactant molecule so little information or knowledge
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of surfactant is essential to understand the gemini to their depth. The surfactant corresponds to contraction of surface active agents. Surfactants play a very vital role in our daily life as they have been used since morning to night. In morning soaps or gels have been used for showering which comprise surfactants, similarly creams and cosmetics also possess surfactants which meant to apply on skin. In addition, they are also present in many of the foods and in detergents which serve the purpose of cleaning. Besides that, surfactants are employed in different places such as personnel care, house hold, painting, coating, textile, dyes, polymer, food, agrochemicals, oils and other applications such as waste water treatment. Surfactants show dualistic character and possess a hydrophilic head group and a hydrophobic tail. The classification of modern surfactants takes place according to the nature of the hydrophilic head of the molecule or on the basis of sign of the charge they bear. Ionic surfactants are broadly categorized into four types; anionic surfactant (carry negative charge), cationic surfactant (carry positive charge), non ionic surfactant which comprises no charge and the fourth type surfactant is zwitterionic which carry both a positive and a negative charge. Millions of dollars would save with the development of new surfactants having novel performance properties and capability of enhancing the economics (Zana., 2005).

1.1.1 History

The oldest synthetic washing and cleaning agent was developed around 2500 B.C by Summerans (Fernandez et al., 2005). The synthetic surfactants (anionic, cationic, and non-ionic) became universally accepted in 1950, as organic substances having certain characteristics in structure and properties. Gemini surfactants came to known in the patent literature since 1935 (Zana., 2005). Bunton (Bunton et al., 1971) gave the first report on gemini surfactants in the
scientific literature in 1971. Colloid science had realized the unusual properties of defined surfactant dimers in mid 1980s. In the beginning of 1980s, surfactants having two hydrophilic head groups at opposite end of hydrophobic group were frequently referred to as bola surfactants. In 1990s, Zana and Menger saw the up rise of new generation surfactants due to their particularly appearing properties (Zana, 1998, Menger and Keiper, 2000, and Zana, 2002). These new generation surfactants were coined as “Gemini surfactants” by Menger in 1991 (Menger and Littau, 1993). In 1991, Menger reported surfactants as water soluble surface active agents comprising a hydrophilic group attached to a hydrophobic group (Menger and Littau, 1991). Therefore, surfactant dimers coupled via the end of the hydrophobic chain referred to as “bolas” whilst “Gemini’s” are dimers coupled via the hydrophilic head group (Laschewsky and Wattenbled, 2005).

1.1.2 Production and Consumption of surfactants

In 1996, the consumption of surfactants in Greater China, Southeast Asia, India and Pakistan was over 3.5 million tons. Total surfactant growth averaged 6.6 percent between 1992 and 1996. In 1997 the surfactant growth has slowed down due to the Southeast Asian economic crisis and the consumption of surfactants remained flat in 1998. In this region some countries have already shown signs of recovery and the consumption of surfactant was expected to grow at 4 percent per year after the year 2000. The data shown in Table I and Table II illustrates the vastness of surfactants markets. In 2010 the overall surfactant consumption in this region projected to grow at an annual rate of 3.9 percent per year to reach almost 5.8 million tons. The global surface active agents market is expected to reach US$16.65 billion in value terms by 2012, as stated by Global Industry Analysts, Inc. In volume terms, the market is expected to reach 17.8 million tons by
2015. Europe, with a share of 36% in volume terms represents the largest market, followed by US with a share of 32%. Asia Pacific is expected to offer the highest volume growth potential over the period 2001-2012, with a CAGR (compound annual growth rate) hovering around 6.04%, followed by Latin America with a CAGR of 4.4%. Anionic surfactants, accounting for a volume share of over 51%, represent the largest segment followed by nonionic surfactants. The market for amphoteric surfactants is expected to register a volume CAGR (compound annual growth rate) of 4.65%, while cationic surfactants are expected to be worth US$3.3 billion in 2013. Many large multinational companies are participating in the surfactant markets in Asia/Pacific either through wholly-owned companies or joint ventures. Some of these companies are Albright & Wilson, BASF, Clariant, Henkel, Kao, Lion, Rhodia, Salm, Stepan, Uniqema, Witco and, through a new joint venture called Optimal Group, Union Carbide. The large multinational consumer products suppliers that are active in standing alone or joint ventures in this region are Colgate-Palmolive, Henkel, Johnson & Johnson, Kao, Lion, Procter & Gamble and Unilever. Surfactant consumption in Asia/Pacific is being driven by the laundry sector and the development of the industrial base. Personal care products, although a faster growing market than the others, is relatively small and is not as developed as other major markets. Other major markets of surfactants are the major industrial markets including I&I cleaners, agricultural products, paints and coatings, pulp and paper, plastics and elastomers, and textiles in each country.

**Table 1 Consumption of surfactants in Asia / Pacific in 1996 and 2010**

<table>
<thead>
<tr>
<th>Consumption of surfactants in Asia/Pacific in 1996 and 2010 (thousand tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1996</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>Anionics</td>
</tr>
<tr>
<td>Nonionics</td>
</tr>
<tr>
<td>Cationics and Other</td>
</tr>
</tbody>
</table>
Table II Consumption of surfactants in Asia / Pacific by the end of 1996 and 2010

<table>
<thead>
<tr>
<th>Surfactant Consumption by end markets in Asia/Pacific 1996-2010 (thousands tons)</th>
<th>1996</th>
<th>2010</th>
<th>AAGR% (1996-2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Household</td>
<td>2743.9</td>
<td>4182.1</td>
<td>3.6%</td>
</tr>
<tr>
<td>Personal Care</td>
<td>101.3</td>
<td>289.3</td>
<td>7.7%</td>
</tr>
<tr>
<td>Industrial</td>
<td>673.0</td>
<td>1288.0</td>
<td>4.7%</td>
</tr>
<tr>
<td>Total</td>
<td>3518.6</td>
<td>5759.5</td>
<td>3.6%</td>
</tr>
<tr>
<td>Includes Soap</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.1.3 Chemistry of surfactants

In order to understand the relationship between the surface activity of a given material and its chemical structure, it is useful to have a handle on the chemistry of the individual molecular components that produce the observed phenomena. The most common taxonomy of modern surfactants divides them according to the nature of the hydrophilic ‘head’ of the molecule. These are the salts in which the head group carries a charge and is associated with a counterion. In “standard” surfactant terminology, the “head” refers to the solubilizing group—the lyophilic or hydrophilic group, in aqueous systems—and the “tail” refers to the lyophobic or hydrophobic group in water. The properties of surfactants arise from the different solubilities of the head and tail of the surfactant. Polar and non polar parts of surfactants perform extraordinary feats of self-assembly in order to preserve a delicate thermodynamic balance and thereby remain solvated. The phenomenon of surfactant adsorption has been studied to determine the measure of coverage of surface/interface by the surfactant, which in turn determines the performance of surfactant in many industrial processes such as foaming/defoaming, detergency and emulsification. The adsorption properties of surfactants provide information on the type and the mechanism of any interactions between the surfactant molecules at the surface/interface and their efficiency.
as a surface-active agent. Various forces like electrostatic attraction, covalent bonding, hydrogen bonding, hydrophobic bonding and solvation were used to evaluate the behaviour of surfactants at the interface of various species (Somasundaran and Huang, 2000). Affinity to water is the characteristic property of hydrophilic solid materials. The formation of water film or coating on the surface of hydrophilic solid materials leads to the wetting of these materials following the surface chemistry. Hydrogen bond with water is formed because of the ability of surface functional groups. The solid-liquid interface is considered to develop a surface charge as a result of surface equilibrium involving potential determining ions which give rise to positive, negative and for some systems, neutral surface sites. The charge on the surface depends on the nature of the colloid, pH, ionic strength, and other solution conditions (Robertson and Leckie, 1997). In simple electrolyte solution the charge is typically positive at low pH, the charge decreases and eventually becomes negative as pH increases. This charge variability is caused by the release and uptake of protons or hydroxyls. Generally, the H⁺ and OH⁻ are the potential determining ions. There are number of mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution (Rosen, 1978). In general, the adsorption of surfactants involves single ions rather than micelles (Griffith et al., 1967). The adsorption of surfactants is normally governed by following mechanisms:

i. Ion exchange: Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions.

ii. Ion pairing: Adsorption of surfactant ions from solution onto oppositely charged sites unoccupied by counter ions.

iii. Hydrophobic bonding: Adsorption occurs by this mechanism when there is an attraction between a hydrophobic group of adsorbed molecule and a molecule present in the solution.
iv. Adsorption by polarization of p electrons: When the surfactant contains electron-rich aromatic nuclei, the solid adsorbent has strongly positive sites and attraction between electron rich aromatic nuclei of the adsorbate and positive sites on the adsorbent results in adsorption.

v. Adsorption by dispersion forces: Adsorption by London-vander Waals force between adsorbate and adsorbent increases with the increasing molecular weight of the adsorbate.

1.1.4 Mode of action of surfactants

The work of surfactants at the core is related to chemistry. The basic molecular structure of all the surfactant is similar i.e. a hydrophile attached to a lipophile and it is this nature that makes them adsorb at surfaces. The hydrophile is attracted to water whereas the lipophile is attracted to lipid-like substances (hydrocarbons such as oil and grease). It is the amphiphilic nature of surfactant molecules that makes them bifunctional. This can be seen when oil/grease and water come together. No matter how much energy is expended in getting them to mix, the oil and water will always separate into two distinct phases. The intermolecular forces between water molecules and between oil molecules are stronger than the forces between water and oil molecules. Added surfactant molecules adsorb at the oil-water interface, where they orient themselves such that the hydrophile is in the water and the lipophile is in the oil. With a little agitation the oil becomes dispersed in the water and the surfactant acts as an emulsifying agent.

1.2 Gemini surfactants

Gemini surfactants comprise two hydrophilic groups and two hydrophobic groups connected with proper spacer group as shown in Fig 1. Gemini surfactants came into existence before 1988. However, the first report on gemini surfactants was published in 1988. This report documented
the properties and structures of gemini surfactants universally (Zhu et al., 1988). Spacers are playing a very important role on the end properties of surfactants. Rigid spacer groups comprise aromatic (Hattori et al., 1998) or unsaturated groups (Menger et al., 2000), while flexible linkers include long methylene chains (Song and Rosen, 1996). Spacers may be hydrophobic (e.g. alkyl- or aryl-based), or inclusion of ethylene oxide units serve as hydrophilic groups (Dreja et al., 1998). The length of the spacer is also of great interest, since varying it affords control over the distance between the head groups (Zana et al., 1991). On the basis of polar head group, the geminis are classified into zwitterionic, nonionic, cationic, and anionic gemini surfactant as shown in Fig 2, and the classification chart is shown in Fig.3. When a single gemini surfactant molecule exhibit both anionic and cationic dissociations it is called amphoteric or zwitterionic. Nonionic gemini 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 these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the poly condensation of ethylene oxide. 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 ammoniums. Anionic gemini surfactant carries negative charge. In water anionic gemini surfactants are dissociated in an amphiphilic anion, and a cation, which is in general an alkaline metal (Na⁺, K⁺) or a quaternary ammonium. They are the most commonly used surfactants. Anionic gemini surfactants have two hydrophobic chains and two hydrophilic head groups attached to a spacer group. Spacer can be polar (polyether), non polar (aliphatic or aromatic), rigid (stillbene or benzene) or flexible (methylene chains). In universities, the research on gemini surfactants is expanding as well as they establish their feet in chemical
industries too. Condea (now Sasol GmbH, Marl, Germany) is the company which introduced formulations based on anionic gemini surfactants into the market. In order to make the products more effectual gemini surfactants have been suggested in formulating products for more effective wetting, solubilizing, dispersing, thickening, making of microemulsion, antimicrobial activity, and other industrial uses. Research on gemini surfactants now have ongoing by many surfactant-producing companies. One company, Sasol (formerly Condea, located in Marl, Germany), is already offering formulations (Ceralution) based on anionic gemini surfactants, which can be used as dispersing or emulsifying agents, for foam production, and so forth (Kwetkat., 2001).

Fig. 1 Schematic representation of gemini surfactant

```
\[ R \]
\[ \downarrow \]
\[ O \]
\[ \downarrow \]
\[ O-P-O(CH_2)N^+(CH_3)_2 \]
\[ \downarrow \]
\[ O \]
\[ R', R = C_8H_{17} \sim C_{18}H_{37} \]
```

Zwitterionic gemini surfactant

\[ [C_{13}H_{27}C(O)NCH_2(CH_2)\text{CHOH}_4CH_2OH]_2(CH_2)_5 \]
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Nonionic gemini surfactant

\[ \text{Br}^+(\text{CH}_3)_2\text{N}^+\text{Y}(\text{CH}_2)_y\text{N}^+(\text{CH}_3)_2\text{Br}^- \]

(A)

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2 \quad &\quad \text{CH}_2(\text{CH}_3)_2\text{N}^+\text{C}_m\text{H}_{2m+1} \\
\text{NH} \quad &\quad \Phi \text{2Br} \\
\text{C}=0 \quad &\quad \text{2Cl}^- \\
\text{CH}_2 \quad &\quad \text{H}_3\text{CN}^+\text{CH}_3 \\
\text{H}_3\text{CN}^+\text{CH}_3 \quad &\quad \text{CH}_2(\text{CH}_3)_2\text{N}^+\text{C}_m\text{H}_{2m+1} \\
\text{C}_{12}\text{H}_{23} \quad &\quad \text{C}_{12}\text{H}_{23}
\end{align*}
\]

(B)

where,
R = C_mH_{2m+1} or C_mH_{2m+1}CO_2CH_3
Y = CH_2, O, S, CHOH, N(CH_3), (CHOH)_2
Φ = refers to phenylene ring
(CH_3)_y = no. of methylene chains

Cationic gemini surfactant

\[ \text{O}^- \quad 2\text{Na}^+ \quad \text{O}^- \]

\[
\begin{align*}
\text{O} &= \Phi - \text{CH}_2 - \text{CH}_2 - \Phi - \text{O}^- - \text{P} = \text{O} \\
\text{O} &= \text{C}_m\text{H}_{2m+1} \\
\text{O} &= \text{C}_m\text{H}_{2m+1}
\end{align*}
\]

where,
Φ = refers to phenylene ring

Anionic gemini surfactant

Fig. 2 Types of gemini surfactants
Fig. 3 Classification of gemini surfactants

1.3. Synthesis of anionic gemini surfactants

This thesis deals with the synthesis of anionic phosphate gemini surfactants, therefore, it is worth mentioning the most common methods used in synthesizing anionic gemini compounds. Anionic geminis were classified into four types on the basis of the molecule responsible for surface activity. Anionic gemini surfactants, includes sulfates, sulphonates, carboxylates and phosphates. Variety of anionic gemini structures, have been synthesized using various synthetic methods. Zhu(Zhu et al., 1988, 1990, 1991, 1993, and 1993) prepared anionic gemini surfactants (sulfates, sulphonates, phosphates), by using a three-functional epichlorohydrin, as shown in Scheme 1.
1.3.1 Synthesis of sulphate anionic gemini surfactants

When two sulphate head groups are attached to two hydrophobic chains via spacer, then this type of anionic gemini surfactant comes under the category of sulphate anionic gemini surfactants. In this case, surface activity is possible because of sulfate headgroups. Sulphate anionic gemini surfactants were synthesized by Zhu (Zhu et al., 1990). Disulfate gemini was prepared by Zana (Zana et al., 1997) using epoxyalkane as shown in Scheme 2. Renouf (Renouf et al., 1998) synthesized asymmetric gemini surfactant with two different head groups, one sulfate and one nonionic, from oleic acid via epoxidation.
1.3.2 Synthesis of sulphonate anionic gemini surfactants

Sulphonate anionic gemini surfactants have two hydrophilic sulphonate head groups attached to two hydrophobic chains through a spacer group. In this type of anionic gemini surfactant, sulphonate group is responsible for the surface activity. Sulphonate anionic gemini surfactant were synthesized by Zhu (Zhu et al., 1990, 1991, and 1992). Sulfonate-nonionic asymmetric gemini surfactant with different head groups was produced by Alami and Holmberg (Alami and Holmberg, 2001) as shown in Scheme 3. Kokai (Kokai, 1994) patented the synthesis of sulphonate gemini surfactants by connecting the two acid molecules via esterification with α,ω-
diiodohydroxyalkane or oligoxyethylene glycol or via amidation with α,ω-diaminoalkane.
Anionic gemini surfactant with sulfonate head groups

Scheme 3 (Alami and Holmberg, 2001)

1.3.3 Synthesis of carboxylate anionic gemini surfactants
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Carboxylate anionic gemini surfactants consist two hydrophobic chains and two hydrophilic carboxylate head groups attached through a spacer. The surface activity is shown by carboxylate head groups. The synthesis of carboxylate anionic gemini surfactant was carried out by Kokai (Kokai., 2000) as shown in Scheme 4.

\[
\begin{align*}
\text{CO}_2\text{Na}^+ & \quad \text{CO}_2\text{Na}^+ \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{O} & \quad \text{O} \\
\text{CH}-\text{CH}_2\text{Y}-\text{CH}_2\text{-CH} & \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{O} & \quad \text{O} \\
\text{C}_{11}\text{H}_{21} & \quad \text{C}_{10}\text{H}_{21}
\end{align*}
\]

**Anionic gemini surfactant with carboxylate head groups**

![Scheme 4](image)

**Scheme 4 (Jpn. Tokkyo KoKai Koho 2000)**

1.3.4 Synthesis of phosphate anionic gemini surfactants
Phosphate anionic gemini surfactants are those anionic gemini surfactant which consist two phosphate hydrophilic head groups and two hydrophobic chains separated via spacer group. Phosphate shows the surface activity in this type of anionic gemini surfactant. Phosphate anionic gemini surfactants were synthesized by Zhu, Menger and Engbert team (Zhu et al., 1991, Menger and Littau, 1993, and Engbert et al., 1997). In the synthesis of phosphate gemini surfactant spacer undergoes a nucleophilic substitution reaction with a mono alkyl phosphate anion to yield bis-(phosphoric diester) di anion i.e. a phosphate gemini surfactant. The synthesis of phosphate gemini surfactant involves the reaction of alcohol and POCl₃ (Eilbs method) as depicted in Scheme 5. In this method, alcohols are refluxed with di hydroxy stilbene in the presence of tri ethyl amine. However, POCl₃ is also not easy to handle as it reacts exothermically (with possible spattering) with water to form fumes of phosphoric acid, hydrogen chloride, and possibly spontaneously flammable phosphone gas (Aswal et al., 1999, De Soma et al., 1999, and Yuhai et al., 2007). Phosphate gemini surfactants were also prepared by phosphorylation of ethleyne glycol with polyphosphoric acid, which produces dihydrogen phosphates with polyether functionalized spacers (Zhu et al., 1991, and 1992). The synthetic route for this method is shown in Scheme 6 but in this method hybrid reagents have been developed during phosphorylation. Reaction of simple alcohol with 117% polyphosphoric acid is reported to produce 21.0 to 23.8% pyrophosphoric acid (Clark and Lyons., 1966, Tracy and Reierson., 2002). An alternative method for the preparation of bis phosphatae geminis, involves the reaction of alcohol and pyrophosphoric acid (Bauman method) as depicted in Scheme 7. In this method mono alkyl phosphates were refluxed with α,ω alkyl dibromide. This method was found to be convenient for the preparation of phosphate gemini surfactants and therefore has been widely studied (Menger and Littau, 1993, Bauman, 1974, and Zana and Xia, 2000). Although this reaction can
sometimes take days to complete due to the low reactivity of the halide but the phosphate gemini surfactant is generally obtained in high yield. This method turned out to be an excellent procedure for the synthesis of these phosphate gemini surfactants, however, one has to be careful in controlling the formation of different undesired products, especially the dialkyl mono phosphates. This method and variations on it have been used to produce anionic geminis with a variety of sizes and functionalities.

Scheme 5 (Aswal et al., 1999, Desoma et al., 1999, Yuhai et al., 2007)
Scheme 6 (Zhu et al., 1991, 1992)

Scheme 7 (Bauman, 1974, Menger and Littau, 1993, Engbert et al., 1997 and Zana and Xia 2000)

1.3.5 Characterization of gemini surfactants

The characterization of the gemini is an important aspect because the presence of traces of impurities, can change the surface activity. Nuclear Magnetic Resonance (NMR) spectroscopy ($^1$H, $^{13}$C, $^{31}$P), mass spectroscopy (fast atom bombardment), Fourier-transform infra red
spectroscopy (FT-IR) and elemental analysis are used worldwide for the characterization of
gemini surfactants.

1.4 Properties of anionic gemini surfactants

Anionic gemini surfactants show all properties which were shown by conventional ones. This
thesis mainly relates to anionic geminis, so almost all properties of anionic dimers are depicted
here.

1.4.1 Surface activity

At the cmc of a surfactant the surface tension of water (72 mNm$^{-1}$ at 25 °C) is normally reduced
to value of 30-40 mNm$^{-1}$. Surface activity has wide industrial applications. C$_{20}$ is the term used
to report the surface activity. C$_{20}$ value corresponds to the surfactant concentration that reduces
the surface tension by 20mNm$^{-1}$. Rosen (Rosen, 1989) found that C$_{20}$ is a comparative measure
of the ability of surfactant to adsorb at the air-water interface. C$_{20}$ values are determined by the
length and structure of the linkage between the two hydrophilic groups. Geminis are found to be
3 orders more surface active than conventional surfactants. Anionic geminis are used in various
applications in the industry for detergency and emulsification because of higher surface activity.
Geminis aggregate more readily with a flexible hydrophilic spacer in comparison to a rigid
hydrophobic one (Song and Rosen., 1996). More cohesive and stable interfacial films are
produced by the higher packing of the hydrophobic group of the gemini surfactants in
comparison to conventional surfactants. The higher packing of the hydrophobic group of the
gemini surfactants indicates greater emulsion stability and greater foam stability. About 0.1 %
geminis may be used as emulsifying agents to make stable emulsions. Zhu (Zhu et al., 1993)
observed that the smallest $C_{20}$ values appear to arise with spacers that are short or slightly hydrophilic or hydrophobic or flexible. The adsorption of the surfactant at the interface is greatly related to the surface tension or the interfacial tension of a surfactant. Fatma (Fatma, 2009) showed the lower cmc values for anionic geminis, which indicates their enhanced surface activity.

1.4.2 Critical micelle concentration

Critical micelle concentration (cmc) is the keystone for all surfactant research. The concentration above which monomeric surfactant molecules abruptly assemble into aggregates is called cmc and aggregated molecules are known as micelles. As the surfactants show good inclination to assemble in water, therefore, determination of cmc is important aspect. Surfactants with longer tail show lower cmc. The electrostatic repulsion among the ionic head groups opposed by hydrophobic forces at the micelle surface, drive the micellization. Micelles are known to be disorganized assemblies with interior consisting of mobile hydrocarbon chains. Bai (Bai et al., 2001) reported the thermodynamic parameters for micellization of geminis with varied spacer length (m-s-m, m = 12). Anionic gemini surfactants have much lower cmc than their cationic counterpart. Hait and Moulik (Hait and Moulik, 2002) found that the critical micelle concentration of anionic geminis decreases with increasing spacer length. It was found that anionic gemini surfactants have remarkably low cmc value as compared to the corresponding surfactants of equivalent chain length (neglecting the spacer). Rosen and Liu (Rosen and Liu, 1996) observed that anionic geminis have lower cmc value than their cationic counterpart. Because of much lower cmc, geminis produces less skin and eye irritation. Yoshimura and Esumi (Yoshimura and Esumi, 2004) have investigated surface properties and
aggregation numbers of anionic gemini surfactant 1,2-bis(N-b-carboxy propanoyl -N-alkylamino) ethane with two carboxylate groups and concluded that the gemini surfactants show fairly low cmc and high efficiency in lowering surface tension but poor performance in dynamic surface tension. Li (Li et al., 2007) have investigated cmc and aggregation behavior of alkyl benzene sulfonate gemini surfactants by fluorescence measurements. Aswal (Aswal et al., 1999) have studied two series of gemini surfactants 12–m–12, 2Na⁺ and 16–m–16, 2Na⁺ systems in which two phosphate centers are attached at the level of polar head group by a polymethylene spacer chain (CH₂)m. They investigated their micellar morphology by SANS. It was found that the effect of m-value becomes more pronounced with the increase in the hydrophobic tail.

1.4.3 Micelle shape

The shape of micelle is very complicated as it depends on surfactant structure. In addition to surfactant structure, it also depends upon solution conditions such as concentration, temperature and ionic strength. The micelle shape affects rheological and solubilization properties and these properties are very important from practical view point. The main role of length of spacer is to control the shape of micelle rather than cmc. The shape of micelle is prolate with spacers of 5-carbon chain or more. Cryo-transmission electron microscopy studies on 12-n-12 and 16-n-16 have produced interesting morphologies. The giant, elongated worm like micelles has been documented for12-n-12 lowest spacer length region and as length of the spacer increases in the range of 4-12, produces spherical micelles. On further increasing the spacer length to 16, the micelle acquires the shape of vesicles. Some relevant points regarding micelle shape are as follows (Menger and Littau, 1993):
a) Hydrophobic spacers with short spacer length produces non spherical micelles ("threads") where as long hydrophobic spacers lead to rod like micelles.

b) Hydrophilic spacers show more or less spherical micelles.

c) The cmc get reduced due to bending stiffness in hydrophilic spacers and increases with the bending stiffness of the hydrophobic spacer.

d) The morphologies of the ionic and nonionic geminis are identical whatever is the nature of spacer.

1.4.4 Solubilization

Micellar surfactants dissolve many organic compounds to a greater extent which are normally insoluble in water, or only slightly soluble. Solubilization means the increased solubility to form thermodynamically stable and isotropic solution. Solubilization is an important phenomenon of homogenizing (Hait and Moulid, 2002). Due to low cmc values geminis are better solubilizers. Solubilization power increases with the increase in surfactant chain length and tends to diminish with the branching of surfactant. Solubilization usually follow the sequence nonionic > cationic > anionic (Satio, 1967). Kraft point temperature is the characteristic temperature at which solubility of surfactant becomes equal to cmc. Kraft point temperature has to be below room temperature for considering the surfactant to be soluble. McBain and Richards (McBain and Richards, 1946) found that potassium laurate micelles solubilized 0.23 moles of cyclohexane per mole of soap. Kleven (Kleven et al., 1946) reported that sodium dodecyl sulfate solubilized 0.87 moles of n-heptanol per mole of surfactant. Disulfonate, disulphate and diphosphate anionic geminis have low Kraft point temperature than those of comparable conventional surfactants. The new surfactant prepared by Laschewsky and Wattebled (Laschewsky and Wattebled, 2007)
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had a Kraft temperature below 0°C and a very low critical micellization concentration compared to the monomeric reference sodium laurate. This makes it attractive for the solubilization of hydrophobic substances at low surfactant content.

1.4.5 Aggregation numbers

Aggregation number (AN) is a means to report the number of surfactant monomers required to form a micelle. There are several methods for the determination of aggregation number namely light scattering, small angle neutron scattering and fluorescence method. Out of all three methods, fluorescence method is widely used as light scattering method is tedious and small angle neutron scattering method is very costly. In fluorescence method, the fluorescence of a probe molecule formed from pyrene, anthracene, sulphonate, etc is quenched by a quencher molecule (usually cetyl pyridinium chloride) and aggregation number is determined by following the two equations. These two equations were reported by Moulik (Moulik et al., 1996) and Turro (Turro et al., 1979 and 1980).

\[ \frac{I_0}{I} = \exp \left( \frac{[Q]}{[M]} \right) \]

\[ AN = \frac{([S]\text{-CMC})}{[m]} \]

where,

\[ [Q] = \text{Concentration of quencher} \]

\[ [S] = \text{Concentration of surfactant} \]

\[ [M] = \text{Concentration of micelle} \]

\[ I_0 = \text{Fluorescence emissions in the absence of quencher} \]

\[ I = \text{Fluorescence emissions in the presence of quencher} \]
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Moulik and Turro (Moulik et al., 1996, Turro et al., 1979) found that AN increase with increasing concentration of surfactant as well as it also increases on increasing the hydrophobic chain length. AN value is found to be 35 when m is 10 for m-3-m geminis and the value of AN increases to 45 for m = 12. The AN value is 74 at 2.5 mM and increases to 138 at 50 mM for 16-5-16 compound. The reports on the temperature dependence of CMC and AN are rare but Menger (Menger et al., 2000) gave a report on 12-s-12 (s=2, 3, 4) and showed that cme values increases with temperature for 12-s-12 surfactants. Manne (Manne et al., 1997) investigated the controlled geometry for the aggregated geminis at different surfaces (mica, graphite) and in solution. Bhattacharya (Bhattacharya et al., 1999) characterized the anionic gemini surfactants with phosphate head groups by SANS (small angle neutron scattering) and fluorescence spectroscopy and found that ellipsoidal micelles were formed with short spacer having C_{12}H_{25} hydrophobic tails. Laschewsky and Wattenbled (Laschewsky and Wattenbled ., 2007) showed that small micellar aggregates were formed, between pH 7 and 12.

1.4.6 Wetting and foaming properties

Geminis possessing short and branched alkyl chains show excellent dynamic wetting properties. Geminis having short linkage between the hydrophilic ends also show excellent dynamic wetting properties. Wetting properties considerably increases with weakly water soluble surfactant in aqueous media. Geminis easily foams and the foaming properties of geminis surfactant found to depend upon the chain length of the hydrophobic groups, and on the length and nature of the spacer between them. Compounds of structure \( \{RN[C_2H_5O]_nH\}-C(O)\}_{2}CH_2CH_2 \), where R=2-
ethyl hexyl, and C$_2$H$_5$C(OH)C=C(OH) CCH$_3$C$_2$+, have been reported to be excellent hydrophilic soil wetting agents (Zana, 2005). Rosen (Rosen et al., 1992 and 1992) found that wetting time at 0.1% concentration were 6 and 16s for di carboxylate anionic geminis having structure [C$_{10}$H$_2$I(OCH$_2$CH(OCH$_2$COO$^-$Na$^+$) CH$_2$]$_2$Y, where Y =O (CH$_2$)$_6$O or O(CH$_2$CH$_2$O)$_x$. An alkylated di phenyl ether sulfonate type anionic gemini (disodium didecyl diphenyl ether sulfonate) was found to be a good solubilizer by Rosen (Rosen and Zhu, 1993) as it dissolved water insoluble nonionic surfactants more efficiently and more effectively than its monomeric analogs. Anionic gemini surfactants having carboxylate head group of structure (C$_{11}$H$_{23}$)$_2$C(OCHCO ONa)$_2$, were observed to foam more than their conventional surfactants as C$_{11}$H$_{23}$COONa. Compounds of structures C$_{10}$H$_2$I(OCH$_2$CH(OCH$_2$COO$^-$Na$^+$)CH$_2$]$_2$ Y, where Y = -O-, -O CH$_2$CH$_2$ O- found to be a better foaming agent. Improved foaming behavior at 0.1% concentration of the sodium laurate was shown by dicarboxylate anionic geminis having structures [C$_{10}$H$_2$I(N(COCH$_2$CH$_2$COO$^-$Na$^+$)CH$_2$]$_2$ CHOH (Kitsubi et al., 1998). Zhu (Zhu et al., 1991) showed that anionic gemini surfactants of structure \{C$_m$H$_{2m}$ $^1$OCH$_2$CH(CH$_2$) [OP(O)(O$^-$ Na$^+$)(OH)]]$_2$Y, where Y =O(CH$_2$CH$_2$O)$_x$, having phosphate head groups at 0.1% concentration had excellent foaming properties. The analogous of gemini surfactants i.e tetra sodium phosphates at 0.1 concentration showed almost no foaming.

1.4.7 Lime soap dispersing ability

Rosen and Kwetkat (Rosen et al, 1992, Rosen and Zhu, 1993 and Kwetkat and Hulsag, 1997) observed that anionic gemini surfactants have much better soap dispersing ability. Anionic geminis can be used in the presence of hard water in cleaning and other industrial processes because of their low sensitivity to Ca$^{++}$ and Mg$^{++}$. Zhu (Zhu et al., 1990) showed that lime-soap
dispersing requirement was about six for sulfated geminis with two decyl groups and exhibited improved lime soap dispersing ability in comparison with normal surfactants with one lipophilic chain and one functional group. Okahara (Okahara et al., 1989) compared the lime soap dispersing ability of sulfated geminis with two decyl groups with the terminal amide type of alcohols ethoxylates. As the amide groups have strong affinity to calcium ions, therefore, it may make a positive contribution to the lime soap dispersing ability. Zhu (Zhu et al., 1991) showed that sulphonate anionic geminis have much better lime-soap dispersing ability than that of single chain surfactants having one sulphonate head group.

1.4.8 Skin and eye irritation

Sulfo esters type anionic geminis of structure \([\text{C}_{12}\text{H}_{25}\text{CH(SO}_3\text{Na)}\text{COOCH}_2\text{Na}]_2\) was tested by Okano (Okano et al., 1997) on human arms by protein denaturation and found to be superior to single chain sulfo monoester. Lower protein denaturation was subjected to this type of surfactants by factor of 10 and when 5% solution applied to human arms depicted no redness or skin rashes. Sulfated gemini surfactants of structure \([\text{C}_{12}\text{H}_{25}\text{N(COCH}_2\text{CH}_2\text{CH}_2\text{O}_3\text{SO}_3\text{Na})\text{CH}_2\text{CH}_2\text{OH}]_2\) patented by Kitsubi (Kitsubi et al., 1998) tested on the abdominal region of guinea pigs and showed no irritancy while methylene bis (alkylphenol) sulfates of structure \([\text{C}_{12}\text{H}_{17}\text{C}_9\text{H}_8\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{SO}_3\text{Na}]_2\) patented by Tracy (Tracy et al., 1998) tested as mild surfactants.

1.4.9 Hydrotrropic properties

The ability to inhibit the formation of aggregated crystalline or liquid crystalline structures in the aqueous phase is called as hydrotrropic properties of surfactant. Good hydrotopes have large
hydrophilic parts in comparison to their hydrophobic portions. Mono alkylated disulphonates (MADS) claimed to be the best hydrotropes as it have the largest ratios of hydrophilic region than hydrophobic groups whereas the gemini di alkylated disulphonate (DADS) with two hydrophilic groups were reported to be a better hydrotropes than the conventional analogs. Menger and Littau (Menger and Littau, 1993) showed that N-alkyl ethylene diamine triacetate have hydroscopic properties even in highly alkaline medium.

1.5 Applications of anionic gemini surfactants

Anionic geminis displays wide applications and they have been utilized in every phase of life. But amidst all applications, anionic gemini's are more effectual in the lowering of surface tension and show much lower cmc. Because of their peculiar properties these compounds are broadly used as effective emulsifiers, bactericidal agents, dispersants, antifoaming agents, detergents etc.

1.5.1 Detergent and cleaners

Soaps and detergents are the primary traditional applications of surfactants and used for a wide variety of cleaning processes. Environmental impact of detergents have reduced due to gemini surfactants because to perform the same function, a little amount of surfactants will be required, for example anionic gemini surfactants of structure $[R_1-N=R_2-Y]_2R_3$ with $R_1=R_4-B-R_5$ ($R_4$=hydrophobic group, $B$=amide group, $R_5$=alkylene group), $R_2$=alkylene or its hydroxyl-substituted derivative, $R_3$=alkylene or alkylaryl spacer, and $Y=SO_3^-Na^+$ or $COO^-Na^+$ patented by Tracy (Tracy et al, 1998) were found to be mild and biologically compatible in ecologically sensitive environment. They also showed lower toxicity and irritancy and efficiently dissolved
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water-insoluble material. Anionic gemini surfactants \[(C_8H_{17}C_6H_{25}O(C_2H_4O)_7SO_3^-Na^+)_2\ CH_2\]
patented by Tracy (Tracy et al., 1998) revealed good wetting ability with Draves wetting times of 5.7 s at 0.1 % concentration. Geminis \[(RC_9H_{18}SO_3^-M^+)_2\ O\]
illustrated the enhanced solubilization of water-insoluble matter and have the ability to remove stains from inks, paints, and other coloring materials from skin and clothing (Kaiser, 1996, and Rosen and Tracy, 1998).

1.5.2 Cosmetics and personal care

A vast multi-billion-dollar market is captured by cosmetics and personal products universally. As a result of improved living standards and continuing cultural driving forces, this market continues to grow. Primarily, these products have been made from fats and oils, which often are perceived to have the advantage of occurring naturally in the human body but show fewer problems in terms of toxicity, allergenicity, and so on. Modern surfactant and detergent formulations have made it possible for us to attain the same or better results. Gemini surfactants and detergent formulations attracted the attention of manufacturers of cosmetics, shampoos, lotions, and personal care products to attain the better results in terms of their mildness, soft feeling, and absence of skin irritation. Gemini sulfoesters (Okano et al., 1997) of structure \[C_{12}H_{25}CH(SO_3^-Na^-COOC H_2)\]
gave lower protein denaturation by a factor of 10 and illustrated no redness or skin rash on applying 5% solution to human arms for 5 days. Bacterial decomposition of perspiration, particularly in the underarm region cause troublesome body odors and to eliminate these body odours usually deodorants are used. Formulation comprising gemini surfactant such as (dimeric alcohol sulfate or alcohol ether sulfate, or trimeric alcohol-triether
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sulfate (Raths et al., 2001), aluminum chlorohydrate, an esterase inhibitor, a bactericidal agent, and a bacteriostatic agent) found to be very effective on serine esterases and serine proteases without impairing the biological equilibrium of the skin flora. They also found to enhance the compatibility between skin and cosmetics and also known to suppress the activity of esterolytic enzymes, even in the lower parts per million (ppm) ranges. In the production of hair shampoo, hair lotion, foam baths, and cream gels or lotions these Gemini surfactants have been exploited. At pH 6, the effectiveness of the formulation was characterized by inhibition of esterase in a concentration of 100-6000 and results demonstrated that on the addition of 10-100 ppm of dimeric alcohol sulfate, esterase activity reduced from 100% to 0% whereas in the presence of 2000 ppm aluminum chlorohydrate the activity remained at 100% (Raths et al., 2001). Good mildness to skin and environmental safety was pictured by anionic geminis such as \([C_{14}H_{25}CONHCH_2CH_2NCH_2CH_2COO^-Na^+]_2CH_2CH_2\) (Li et al., 1997).

1.5.3 Miscellaneous

Phosphate-based Gemini surfactants constituting the shortest possible spacer (viz. a single oxygen atom) found to be cleavable and can be converted into non surfactants or daughter surfactants by cleavage at a functional group (Jaeger et al., 2002). The self-assembly of small molecules in solution into very elongated aggregates is necessary for the formation of gels. Estroff and Hamilton (Estroff and Hamilton, 2000) showed that bis-urea dicarboxylic acid Gemini surfactants displayed occurrence of gelation with water. Surface and aggregation properties that are sensitive to UV irradiation assigned by photosensitive Gemini surfactants with a stilbene spacer constitute much lower surface tension in the process. Karthaus (Karthaus et al., 1996) reported that the photosensitive mono layers were formed at the surface of
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water by the surfactant containing stillbene \([C_{15}H_{31}C(O)NH]_2C_6H_5(2-SO_3^-Na^+)CH=HCC_6H_5(2-SO_3^-Na^+)\). To remove oily pollutants from water efficiently Yan (Yan et al., 2002) proposed that the systems constituted by anionic resins saturated by bound 12-s-12 gemini surfactants can be used. Moreover, environmental surfactants, such as bis(sulfonate) or bis(carboxylate) gemini surfactants containing C=C groups in the hydrophobic moiety or spacer are cleaved by ozone and exhibit much higher degradability than for conventional surfactants such as LAS, SDS, for instance (Masuyama et al., 2000, 1998). Currently gemini surfactants show their proficiency in the solubilization of dyes and pigments in the textile industry (Choi et al., 2000), gene therapy (Camilleri et al., 2000), and the synthesis of highly mesoporous materials (Collart et al., 2001). Geminis reflect better solubilizing and foaming properties than their monomeric counterparts (Li et al., 2009, and Sen et al., 2006). Gemini surfactants also accounted for better control of stability, floatation, and rheology of dispersed system in different technological process (Azzam, 2001, Azzam et al., 2007). Moreover, geminis also contributes to biodegradability as the protection of environment is the main concern. Researchers (Holmberg et al. and Youguo et al.) carried out several investigations in order to prepare the biodegradable gemini surfactants and finally got succeeded to introduce weak bonds (ester bonds) in order to show good biodegradability (Holmberg et al., 2000 and 2003, and Youguo et al., 2005). (Chanda and Bandyopadhyay., 2003 and Atkin et al., 2003) mentioned that the surfactants play a very vital role at interfaces and because of their superior interfacial properties and molecular geometries gemini surfactants have become a topic of scientific interest in industrial process.

1.6 Objective of study
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The novel properties associated with gemini phosphate surfactants have motivated efforts to synthesize new gemini surfactants. The research on gemini surfactants with phosphate head groups have been performed by teams of Menger, Engberts and Bhattacharya. They synthesized the phosphate gemini surfactants with lower fatty alcoholic chains i.e. C₈-C₁₂ except Bhattacharya, who worked on C₁₄ alcohol, after that none of the researcher had tried to synthesize gemini surfactants with phosphate head groups using higher fatty alcoholic chains. In literature it is reported that the long hydrocarbon chain tends to increase the surface activity of the gemini surfactants (Hait and Moulik, 2002).

Therefore, the main objectives of the proposed research are given hereunder:

1) The first objective of the proposed research work is to prepare mono alkyl phosphates with higher fatty alcoholic chains i.e. C₁₄-C₁₈ at slightly higher temperature instead of room temperature for better surface properties by following the method of Nelson and Toy (Nelson et al, 1963).

2) The second objective is to prepare the phosphate gemini surfactants by Bauman method using higher fatty alcoholic chains i.e. C₁₄-C₁₈ with three different α-ω-alkyl dibromides viz. 1,4 dibromo butane, 1,6 dibromo hexane and 1,8 dibromo octane at 35⁰C.

3) The third objective of the study is to convert the synthesized phosphate gemini surfactants to their disodium salts to make them water soluble.

4) The fourth objective of the research work is to characterize all synthesized chemical molecules, intermediates and final products by modern instrumental techniques viz. FT-IR, ¹H-NMR, ¹³C-NMR and elemental analysis.
5) The next objective is to evaluate the physico-chemical properties of synthesized gemini surfactants viz. anionic content, foaming, wetting, emulsification, dispersing ability and solubility which are very important for the detergency.

6) Furthermore, the last objective of present study is to determine the surface properties of synthesized gemini surfactants such as surface tension, interfacial tension and critical micelle concentration.
References


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32. Kokai Koho Jpn. Tokkkyo (1994) Japanese patent to Lion Cooperation , 6-65592 and 6-330084


