Chapter 1

General Introduction

Surface chemistry deals with the behavior of matter and its change during action of forces on the surface / interface. Conventionally, the term surface is used when liquid / solid is in contact of gas / air. Therefore, every surface can be called a part of interface. Interfacial phenomenon has significant role in pharmacy, medicine, cosmetics and other technologies [1]. Chemical reactivity at the surface / interface occupies a prominent place in catalysis. The domain of surface chemistry is perhaps one of the most multidisciplinary areas of science and technology [1*b*]. However, the importance of surface science has been known for more than a century. The formation of a liquid surface involves a change in surface free energy [1*c*, 2]. The surface free energy is the energy required to increase unit surface area. Surfactant is a substance, when present at low concentration, adsorbs on a surface and change the surface free energy required to expand the liquid surface as well as reduces the tension between two interfaces. Surfactant belongs to the most versatile chemicals, being key components in a diverse range of products and technologies such as petroleum industry, pharmaceuticals, detergents in personnel care / laundry products, firefighting, fuel additive, foams, inks, paints, adhesive, photographic films, electronic printing and biological and medical technologies [3].

1.1. Surfactant

Surfactant is derived from a phase 'surface-active agent'. Surfactant research has been continuously carried out in the last century [4]. They are usually organic compounds and their unique molecular structure contains two different / opposite groups. One is hydrophobic group / part ("tail") usually a straight hydrocarbon chain containing 8-18 carbon atoms while the other is a hydrophilic group ("head"), ionic / polar in nature. The hydrophobic part of the surfactant has a very little attraction to the water molecule (near to insoluble) but on the other hand hydrophilic part has strong attraction towards water (completely soluble). Due to the above two distinct groups, surfactant is also referred to as amphipathic, heteropolar or polar-nonpolar substances. The general representation of a surfactant molecule is shown in Figure 1. This polarity difference in surfactant molecule plays a vital role for various phenomena / unique properties in solution [5].

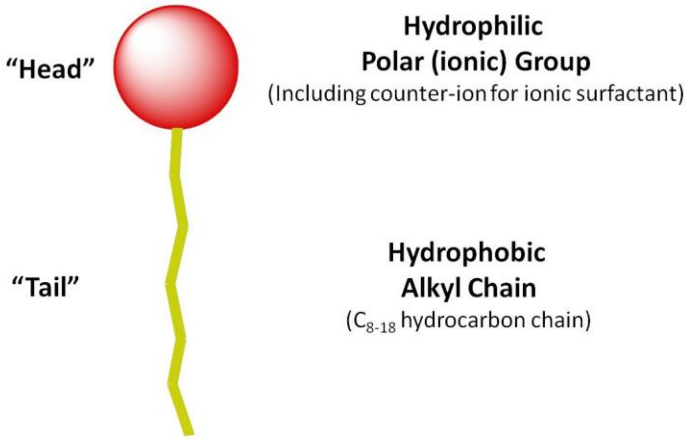


Figure 1. Simplified schematic diagram of a typical surfactant molecule.

When surfactant monomers are dissolved in polar solvents (*e.g.*, water), they adsorb at the surface of water because of their ion-dipole (or dipole-dipole) interaction of hydrophilic head group with water. Due to weak interactions of alkyl chains (hydrophobic part) and complex structure of water, the chain remains in the air (upward direction). On the other hand, presence of the hydrophilic group prevents the surfactant molecule from being expelled completely from water as a separate phase and mainly responsible for lowering the surface tension of water. After accumulation of monomers at the interface at low concentrations, amphiphilic nature forces them to adopt unique orientations to form organized assemblies (relatively small) in the bulk at higher concentration [6, 7] which make them more promising as far as the applications are concerned (Figure 2).

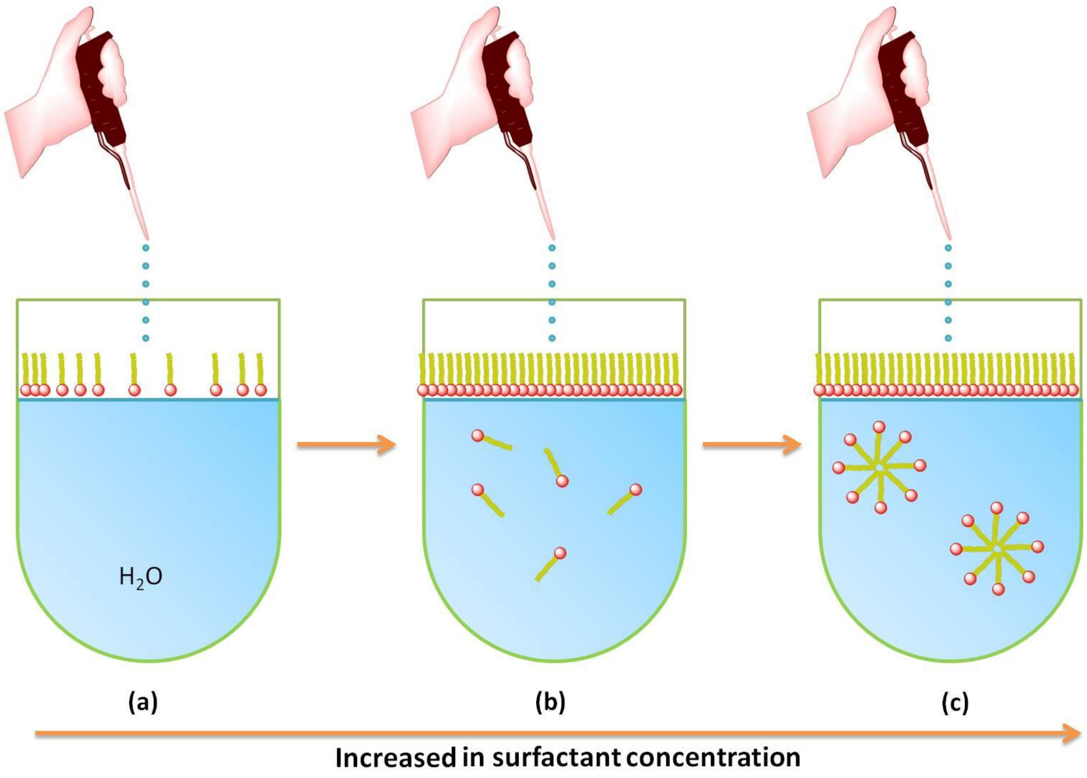


Figure 2. Schematic representation of surfactant monomer arrangements at air-water interface (*a* and *b*) at low concentrations and organized assemblies (spherical micelle) formed at high concentrations (*c*).

1.2. Classification of Surfactants

Surfactants can mainly be classified as according to their **nature of electrical charge** (positive or negative) on the polar head group (hydrophilic). A non-ionic surfactant does not have any charge on the head group. The four main classes are:

- Anionic
- Cationic
- Nonionic
- zwitterionic

***Anionic Surfactants*:** In aqueous surfactant solution, if the head group contains negative charge then the surfactant is called anionic surfactant. Examples of negative charged head groups (may be linear or branched) include sulfonates, sulphates, phosphates or carboxylates, *etc*. These are the oldest class of surfactants and still are in use. These surfactants are widely used as shampoos because of their excellent cleaning properties and least expensiveness [8]. SDS is a common example of anionic surfactant (Figure 3).

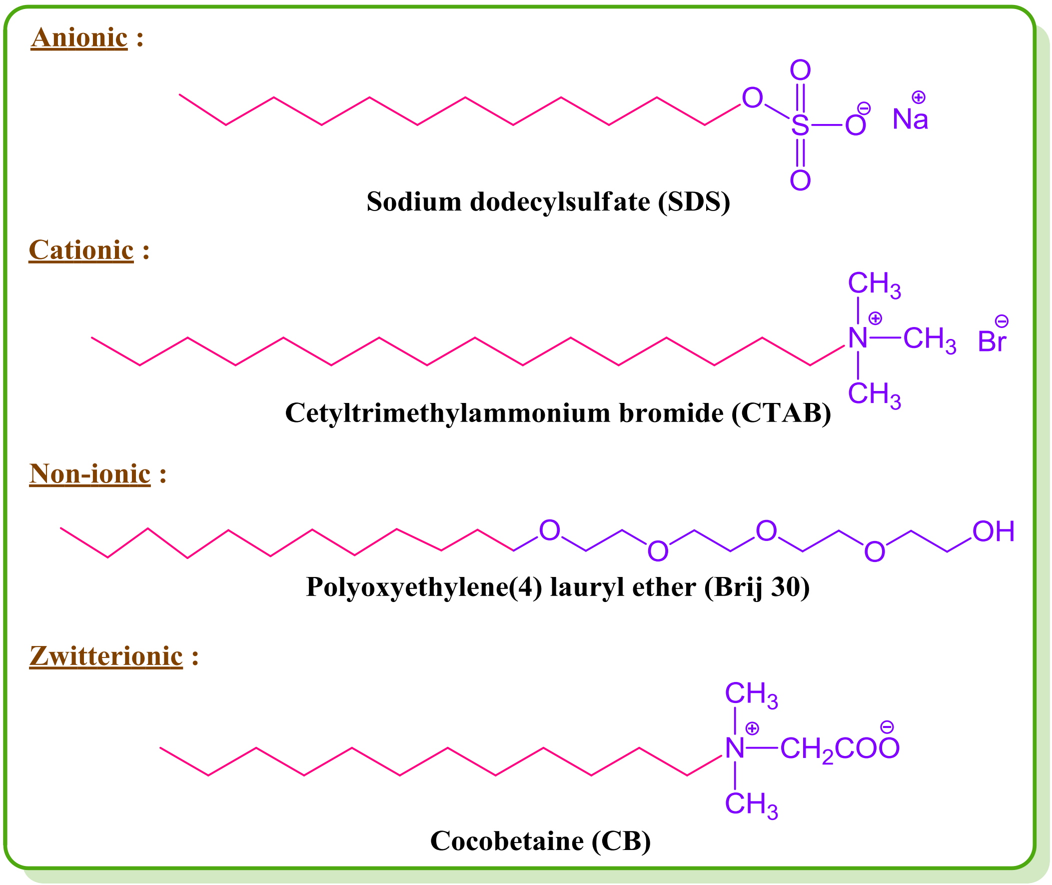


Figure 3. Structure of few typical surfactants according to the charge on the head group.

***Cationic Surfactants*:** In solution, if the head group contains positive charge (hence cationic) and counter-ion has negative charge then the surfactant is cationic in nature. The positively charged head groups are quaternary ammonium, immidazolium, pyridinium, esterified quaternaries, *etc*. Among all head groups, quaternary ammonium surfactants are effective in neutral, alkaline as well as in acidic medium. These surfactants are mostly used for their disinfectant / preservation properties as they have good antibacterial properties. The other prime use of cationic surfactants is their tendency to interact strongly with negatively charged species, e.g., binding with nucleic acids (like DNA, protein, RNA) [9]. New applications include their use as antiseptic agents, textile softeners, corrosion inhibitors, foam depressants, flotation chemicals and petroleum derivatives. A well known cationic surfactant used in surfactant research is cetyltrimethylammonium bromide (CTAB, Figure 3).

Non-ionic Surfactants**:** In solution, if the head group has no charge then the surfactant is known as non-ionic surfactant. Typical head groups are alcohol ethoxylates, phenol ethoxylates, alkanolamides, alkanediols, mono- and disaccharides and sugar based. Hydrophobic part contains saturated / unsaturated fatty acid or fatty alcohols in the form of hydrogenated / fluorinated chain. These surfactants are excellent grease / oil remover and less sensitive to water hardness. According to their applications, non-ionic surfactants offer greater stability and flexibility but they rank after anionic ones. The most commonly used non-ionic surfactant is of polyoxyethylene(4) lauryl ether series (Figure 3)

Zwitter-ionic Surfactants**:** In solution, if the surfactant carries two oppositely charged functionalities (positive and negative) on same molecule then surfactant is zwitterionic (amphoteric) in nature. These surfactants can be called a combination of both anionic and cationic surfactants, where positive charge group is ammonium at most of the time but the source of negative charge may vary (carboxylate, sulfates or sulfonates). The charges on the head group mainly depend upon the pH of the solution. Surfactant can act as anionic surfactant at pH>7 or cationic surfactant at pH<7 and show the zwitterionic form around the isoelectric point. These types of surfactants have also been used as a helping lipid with other surfactants in biomedicinal applications. Cocobetaine (CB) is a well known example of this class of surfactants (Figure 3).

1.3. New Versatile Surfactants of Current Millennium

Based on demand of high performance, various new types of surfactant architecture have been successfully designed and developed in recent time *e.g.*, gemini surfactant, bolaform amphiphiles, polymeric surfactant, siliconic surfactant, hydrolysable surfactant, light sensitive surfactant, bio-surfactants, *etc* (See Figure 4). In this context, a few novel surfactants are discussed briefly in the following paragraphs.

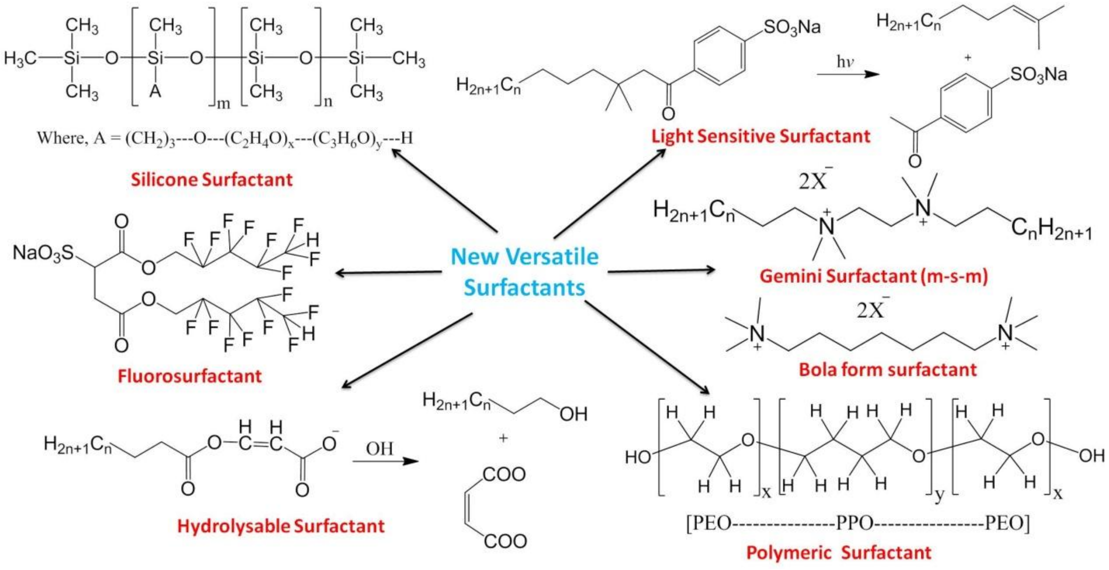


Figure 4. Different types of new versatile surfactant of current millennium with their molecular structures.

***Fluorosurfactants*:** Fluorosurfactants now constitute an important class and appear in a multiple range of utilities including biomedicine, firefighting, lubricants, and adhesives. A wide structural of two tail-three tail sulfosuccinate surfactants has been investigated. The terminal chain groups were varied to include fluoro alkyl, alkyl and aryl groups (Figure 4). Among them, fluoro alkyl material showed lowest surface tension at cmc. The potential of fluorochemical cleaning products (so called fluorosurfactants) has been reported long back in 1950s. The hydrophobic tail of fluorosurfactants display both oil and water repellency and, therefore, used as low surface energy coatings in textile / paper industry [3].

***Polymeric surfactant*:** These types of surfactants are attracting much attention in recent years due to their wide applications as stabilizers for suspensions / emulsions, wetting agent and especially for bio-applications [10, 11]. Different polymeric surfactants have been synthesized and some of them introduced as Hypermers of ICI (under special trade names) in the market. The one of the most common surfactants is pluoronic (repetitive block EO/PO/EO molecules, See Figure 4), where PO has more polarity than EO but they, generally, do not have high molecular weights. In some cases, silicone surfactants may also be considered as polymeric surfactant. However, in recent time, some graft polymeric surfactant (like “comb” structures) have also been introduced to obtain specific applications in dispersions.

***Bola forms*:** These are also called as *bolaphiles* or *alpha-omega-type surfactants*. Bola forms are the organic molecules which consist of two hydrophilic head groups, connected by a rigid / flexible long linear alkyl chain. The structure of bola form is interestingly fitting between single tailed and gemini surfactants (Figure 4). Compared to single-headed amphiphiles, the introduction of a second head-group generally induces a higher solubility in water, an increase in the *cmc*, and a decrease in aggregation number. Bola forms are, in general, less effective surfactants than conventional ionic ones. However, bolaform surfactants often show biological activity [12]. Some special bolaforms are capable giving rise to organized assemblies of peculiar structure [13].

Gemini Surfactants**:** Gemini (also called dimeric) a name itself suggests twins / two, which is similar to the zodiac sign (where two people / children are enclave together with hand to hand, see Figure 5). In last two decades, they are immerging as a *second generation surfactant* in surface chemistry due to their better physico-chemical properties over to single tailed as well as other classes of surfactants with respect to both industrial applications as well as academic point of view. These surfactants are a captivating class of surface active agents that are consisting of two identical monomeric surfactant molecules (single alkyl tail) covalently linked at or near to head groups by a spacer (can be hydrophilic or hydrophobic and flexible or rigid) [14].

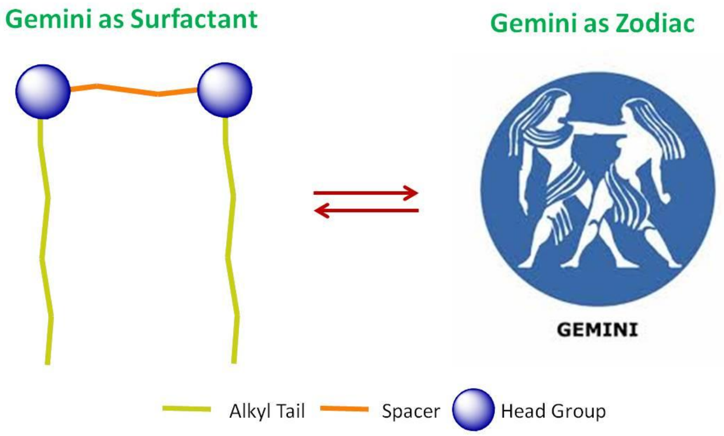


Figure 5. Schematic representation of gemini surfactant with comparison to zodiac sign.

Gemini surfactants, generally organic compounds, were first time architecturally synthesized and patented in 1935 [15]. However, they are reported (in open literature) by Bunton et al. in 1971 [16] and later named as ‘Gemini’ in 1991 by Menger and Littau [17].

1.4. Different Phenomenon in Aqueous Surfactant Solution

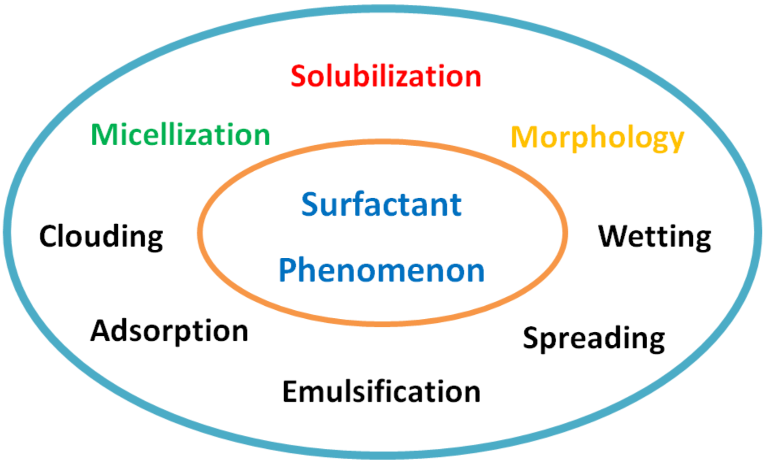


Figure 6. Representation of different phenonmenon / properties in aqueous surfactant solution.

Aqueous surfactant solution exhibits different phenomena / properties *e.g.*, micellization, clouding, adsorption, spreading, wetting, solubilisation, emulsification etc (Figure 6). Among all the properties, present work mainly focused on *micellization, morphological transitions* and *Solubilization*. The work on other phenomenon can be found in literature either in the form of published paper / monograph or text book [1, 18].

Micellization

It has been stated earlier that aqueous surfactant monomers well arranged at the interface after that they started to form organized assemblies / aggregates like micelle at well defined concentration (Figure 2). That concentration (generally a narrow range not a fixed value) referred to as critical micelle concentration ("cmc") at a given temperature [19, 20]. Still, micelles do not exist at all concentrations and temperatures. At cmc, these aggregates are in dynamic equilibrium with the monomers. From the structural point of view, micelle formation occurs at a certain hydrophobic alkyl chain length (>C10). The cmc generally drops as the chain length increases. However, cmc increases with the increase in number of the head groups. The micelles are also known as 'association colloids' in surface and colloid field due to their size range. However, below the cmc, surfactant molecules remain in monomer form. cmc can be determined by various physico-chemical methods with sharp inflected curve (distinct range), which is illustrated in Preston’s [21] classical graph (Figure 7).

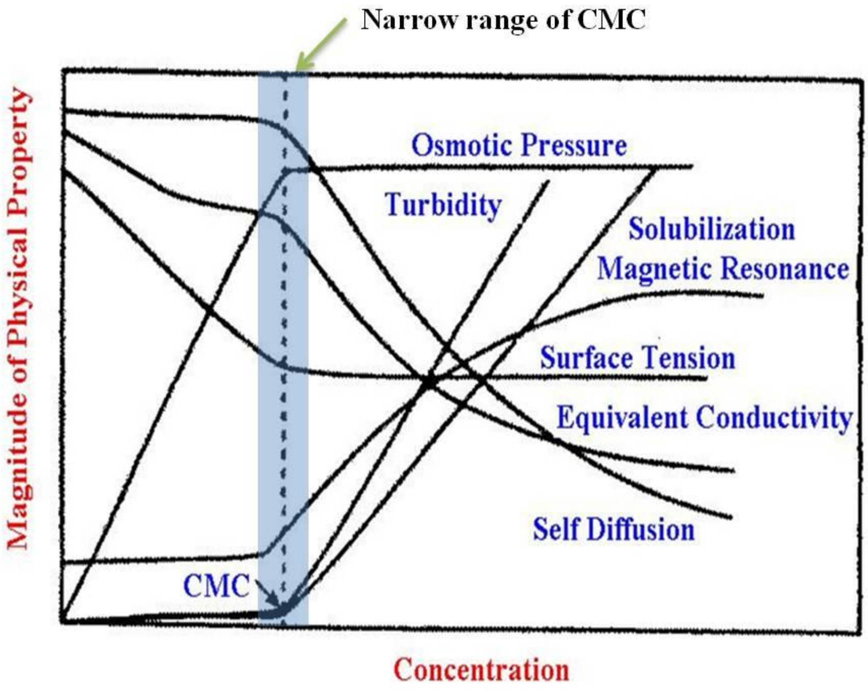


Figure 7. cmc determination by using various Physico-chemical methods.

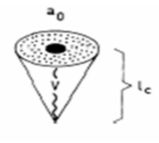
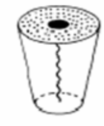
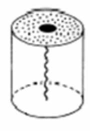
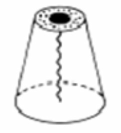
Due to these abrupt changes, micelle (Latin meaning “small bit”) was first described by McBain [22] in 1920 for colloidal sized particles of detergents and soaps. The driving force behind micelle formation is the cohesive force between two hydrophobic alkyl tails, forcing them towards interior part (proposed by G.S. Hartley in 1936 [23]) and electrostatic repulsion between head groups pointed towards the aqueous medium [8*a*]. In addition, individual micelles may experience an electrostatic repulsion from other similarly charged micelle of the same surfactant molecule in ionic surfactants solutions. These forces increase free energy of the system and sometimes oppose micellization [24]. The number of surfactant monomers that aggregate to form a micelle is called aggregation number (N_{agg}). The instinctively formed micelles above cmc may contain many surfactant monomers (approx 40-200) whose shape and size are governed by various factors. Monomers and micelle are in equilibrium but still they rapidly assemble and disassemble in aqueous solution which makes difficult to determine the exact size, shape or aggregation number. This arises due to a competition between adsorption and complete mixing of the surfactant molecules resulting in a lowering of surface tension. ‘Micelle’ is also a subject of a great interest to the organic chemist (unusual catalysis of organic reactions) [25] as well as biochemist (a model system for biological membrane or globular proteins) [26] for their simpler structure and easy modification.

Morphological Transition

Till date, aggregation of surfactant monomers is a complex phenomenon but few intelligent mechanisms are now available to understand the process [24]. Israelachvili et al. [27] have developed a general theoretical relationship between secondary structures (formed by surfactant monomers in aqueous solution) and molecular architecture of surfactant molecule. This relationship can be represented by the Mitchell-Ninham packing parameter ($R_p=V/a_0l_c$, where V and l_c are the volume and length of the alkyl part of surfactant chain, respectively, and a_0 is the area of a typical surfactant head group) [28]. The value of R_p mainly depends on optimal head group area (a_0) that indirectly depends on the amphiphiles (molecular architecture), ionic strength, temperature/ pressure and the solvent; the volume of alkyl chain (V) and the critical chain length (l_c). The V and l_c can be calculated by empirical equations given by

Tanford [8*a*], while a_0 can be measured experimentally as reported by Lantzsch et al. [29]. The relationship of the aggregate morphology with R_p is shown in Table 1.

Table 1. Dependence of shape on critical packing parameter **($R_p=V/a_0l_c$).**

Effective Shape of the surfactant molecule	**Packing Parameters (R_p)**	**Aggregate Morphology (Geometry of Micelle)**
 Cone	< 1/3 (0.33)	Spherical Micelle
 Truncated Cone	1/3 – 1/2 (0.33-0.5)	Ellipsiodal Micelle
 Cylinder	1/2 – 1.0 (0.5 – 1.0)	Rod like, Vesicle, Bilayer Micelle
 Inverted Cone	> 1.0	Reverse Micelle

Morphological transitions not only dependent on their molecular structures but other factors are equally important (e.g., nature of surfactant monomer, concentration, [30], counter-ion distribution or condensation [31], pH [32], temperature, and/or the presence of additives [19, 33]). Single-tail surfactants usually form spherical micelles in aqueous solution above their cmc which eventually grow to other shapes with increasing concentration. Above cmc, more number of micelles is formed and responsible for a decrease in the average distance between two micelles (resulting into more inter-micellar repulsions) [34]. In order to accommodate such repulsions, spherical micelles may transform into rod shape, where the distance between aggregates increases again. The size of these micelles has been found in micrometer range and shows different flow properties, which may found application in food or petroleum industry [35]. On further increase in concentration of surfactant, micelle structure may rearrange into higher order aggregates like wormlike micelle, vesicle, tubular, helical, *etc* (Figure 8).

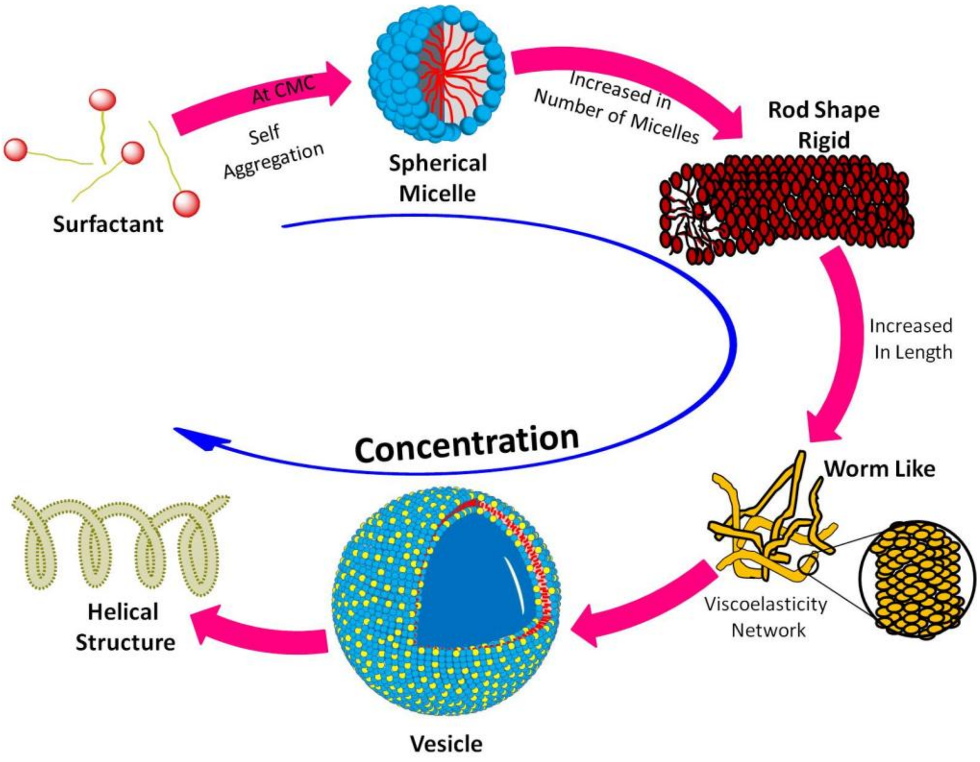


Figure 8. Different surfactant morphologies with increase in concentration.

Solubilization

Another interesting property of surfactant is micellar solubilization, which refers to as an enhanced solubility of hydrophobic compounds in aqueous medium through micelle formation (Figure 9). This property has extensively been utilized in *eco-friendly* way of solubilizing of certain amount of organic compounds or drugs in past decades [20, 36]. Amount of organic moieties can be increased with the increase of micelle dehydration using various stimuli (additives or temperature), resulting in to more hydrophobic environment [25].

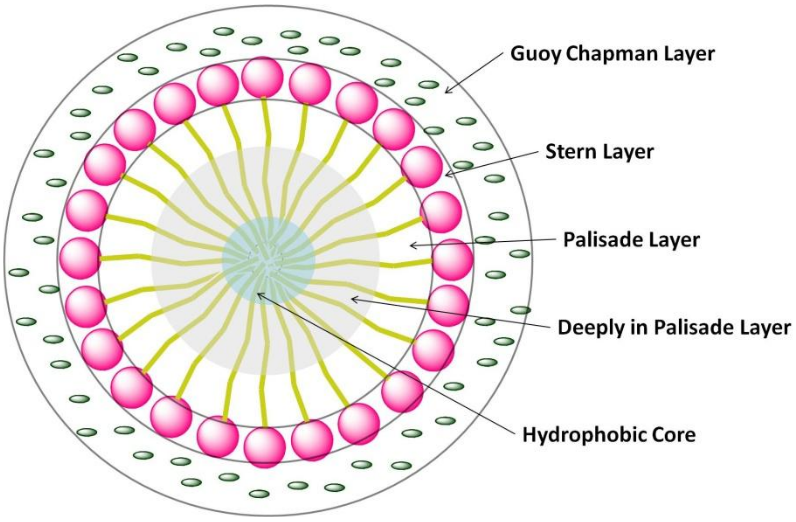


Figure 9. Various solubilization sites of the normal micelle.

Many studies have been performed to determine the location of a solubilizate within a micelle at various sites [37]. The site of additive solubilization may be one of the following depending upon its polarity / charge,

1) Small polar molecules (oppositely charged hydrophobic species) close to the surface in the palisade layer or adsorption at the micelle-water interface.
2) Short chain phenols (solubilized in nonionics) located between the polyoxyethylene chains.
3) Large polar molecules (dyestuffs) in the palisade layer.
4) Saturated aliphatic and cyclic hydrocarbons in the inner core of the micelle.
5) Aliphatic hydrocarbons of higher alkyl chain length are solubilized in the interior of the micelle.

However, depth of the penetration in the palisade layer depends on the ratio of polar to non-polar structures in the solubilizate molecule. Longer-chain and less polar compounds penetrate more deeply than short-chain and more polar material. Most interestingly, solubilizate molecule (with its amount) can also affect the final micellar shape, size and its surface active (physiological) properties [38].

1.5. Gemini over Conventional Surfactants

The growing interest for gemini surfactant (see Figure 5) is due to their unusual physicochemical properties over conventional surfactant, which mainly dependent on three structural elements (two polar head groups, two aliphatic chains and one spacer) [39, 40]. However, comparing it with the single tailed surfactant, only spacer has been found as the main difference. Due to this most of the dramatically superior properties are observed such as,

1) one to two order of magnitude lower cmc (means required less amount needed to achieve the same activity),
2) lower surface tension or C_{20} value (a measure of their tendency to adsorb at an interface) / increased surface activity with respect to same molar concentration of conventional surfactant,
3) interesting viscoelasticity (effective thickening),
4) better solubilizing power with lower Krafft temperature (with hydrophilic spacer),
5) better wetting capacity, good foaming ability and improved gelification.

1.6. Brief Review on Work with Gemini Surfactants

Recently, researchers have shown much attention on cationic gemini surfactants than anionic / non-ionic gemini counterparts due to their ease of synthesis [41], better physicochemical properties [42, 43], greater ability to bind negative charged moiety (e.g., DNA or bovine serum albumin), relatively low cytotoxicity towards animal cell lines [9, 24*b*, 41*a*, 44, 45], potential gene delivery agent [41*a* and *b*],better drug entrapment and release [41*c*], advanced antimicrobial activity [41*d*], as a templates for nano particles synthesis [41*e*], as corrosion inhibitors [41*f*] and as erythrocyte protectors against hypotonic hemolysis [46].

Mostly, researchers have mainly focused on cationic geminis with quaternary ammonium head groups, linear hydrocarbon tail groups, polymethylene spacer and dihalide counter-ion (also called bisQuats, Figure 8), which are referred to as ***m*-*s*-*m***, where ***m*** and ***s*** stand for the number of carbon atoms of the alkyl chain and the spacer, respectively (Figure 9) [14, 42, 47]. However, bisQuats are very stable molecules with a poor chemical and biological degradability. This may cause a risk of toxicity to aquatic organisms, which could make them ecotoxicologically and environmentally unacceptable.

Now the need of environment, consumers as well as from legislation pressure, it is required to develop new *eco-friendly* and cost effective greener surfactants. In Europe and United State of America (USA), some established surfactants (toxic) had already vanished out and replaced by lesser toxic amphiphiles. There are several trends to make “greener” surfactant as follows [48],

a) synthesize the surfactant from *natural building blocks*,
b) use both *natural and synthesized material* as a precursor,
c) insert one or more *labile (weak) group* in to the skeleton of surfactant (ester, amide, ether, alkenes, etc).

In the last decade, cationic gemini surfactant has been architecturally modified by various research groups worldwide [7, 35, 44, 49]. However, the basic structure (like quaternary ammonium head group) has been remained same. Researchers have mainly focused to make gemini more greener by changing,

(i) The nature of the head group such as pyridinium [50], immidazolium [50*c*, 51], dimethyl and diethyl quaternary ammonium [52], pyrolidimium [53], piperidinium [54] or amino acids [55],

(ii) alkyl tail part such as cholesterol [56], pyrenyl [67], esterquat [58], alkenes and symmetrical and asymmetrical alkyl tail [39] and

(iii) in the spacer (most of the change has been limited to its alkyl length) [24*b*, 39, 44, 52*b*, 59].

Only a few reports are available on changing the nature of the spacer [56*b*, 60]. Further, very little work is available regarding biocompatible spacers [61]. However, by modifying the any structural part of gemini surfactant, it is bound to have changed physico-chemical properties. Several reviews, scientific articles and patents are now available [24*b*, 39, 49*i*, 62]. With change in nature of the spacer (like introducing labile group or natural building blocks), more and more dramatic changes are observed in their physico-chemical properties (like lower cmc, higher α, lower N_{agg}, lower free energy) compared to hydrophobic spacers [39].

Menger et al [62*c*] have reported threefold increase in cmc value for disaccharide (sugar) spacer based geminis compared to polymethylene spacer based gemini surfactants. Bhattacharya *et al* have also prepared mono-, di-, or trioxyethylene spacer based hexadecyl gemini surfactants with lower fractional charge and higher cmc [63]. On the other side, Holmberg [58] and other research groups [64] have reported some esterquat and adamantine-amide, serine-amide and ester spacer based gemini surfactants with better physiochemical properties (e.g., lower cmc, lower Krafft temperature). Therefore, no correlation has been established between the biodegradable (hydrophilic / flexible) spacer based gemini surfactant and their physico-chemical properties.

On application front, the presence of a labile group in the spacer can influence the several parameters and can facilitate the pH induced mobility in entocytosis process. They can easily (enzymatically) be hydrolyzed to non-toxic molecules and safely removed from the living organisms [65]. Though, conventional bisQuats have extensively been studied for some biomedical applications [9, 24*b*, 39, 41*c*, 44-46, 62*c*, 66], the role of greener spacer based geminis is not much studied.

Relevance of the Research Problem

As mentioned above, numerous structural modifications to the gemini surfactant architecture have been carried out in order to enhance their performance or to make them application specific. The nature and structure of a spacer are the key factors which distinguish gemini surfactants form their conventional counter-parts. The spacer can be utilized to tune the hydrophobic / electrostatic interactions. However, not many manipulations are available with regard of spacer as compared to head group / alkyl tail. The effect of spacer has been discussed with respect to its conformation and its location in various surfactant association structures [14].The aggregation behavior of gemini surfactants with partially fluorinated spacer has also been investigated [67]. Besides the constant challenges of finding ways to minimize the manufacturing cost for existing surfactants, the market pull for ‘greener’ products is the overriding driving force for surfactant development. With the aim to develop greener gemini surfactants, change in nature of the spacer has been utilized as a tool to synthesize biocompatible material. The labile groups, such as diester isosorbate, ester or amide, are used as spacer to obtain various gemini surfactants and their solution behavior have been studied / compared with cationic gemini surfactants having polymethylene spacer. The purpose of the work is to get greener surfactant without compromising their physico-chemical properties (*e.g.*, cmc). The synthesized material has also been used for various physico-biochemical activities such as cytotoxicity, DNA interaction or PAHs solubilization. A preliminary study related to gene transfection, *in vitro*, has also been performed in order to show that the present surfactant systems can be a potential candidate for the purpose.

Constitution of the Thesis

The present Thesis comprises in six chapters (including general introduction as **Chapter 1**). Various abbreviations and symbols, to be used throughout, are included in tabular form before the beginning of the **Chapter 1**.

On the basis of literature survey (included in **Chapter 1**) various cationic gemini surfactants, with varying alkyl tail (***m*** = 12, 14, 16) and spacer (polymethylene, diester, diamide and diester isosorbate), are synthesized and characterized (**Chapter 2**). In addition to this, an anionic gemini surfactant (***m*** = 12) with phosphate head group has also been synthesized / characterized for comparison purposes.

Chapter 3 includes physico-chemical studies (micellization, aggregation number, surface parameter, U-shaped behavior, monomers arrangement and micellar size) of both geminis as well as their conventional counter-parts. Different techniques (conductometry, tensiometry, fluorescence, dynamic light scattering and 2D NOESY) are utilized for the purpose.

Morphological transitions in a typical isosorbide spacer based gemini (with ***m*** = 16) are investigated in **Chapter 4**. Different stimuli (concentration, pH, temperature, organic / inorganic salts) are tested to know about the mechanism of various structural transitions.

Solubilization data related to solubility of various polycyclic aromatic hydrocarbons (PAHs) have been obtained (spectrophotometically) with various surfactants (gemini / conventional) and are compiled in **Chapter 5**.

In **Chapter 6**, various synthesized gemini surfactants are used for a few biological applications (cytotoxicity, DNA binding, transfection, *in vitro*).

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