Chapter 1

General Introduction

Among natural forces, the hydrophobic-lipophilic interaction is one of the most important and necessary forces for the formation of self assemblies of amphiphilic molecules e.g. association colloids or micelles, bilayers or vesicles, biological membranes and living cells [1-3]. Micelles (formed by ionic surfactants) are good model systems for ion binding properties of much more complex amphiphilic aggregates [4]. Micelles are known to provide various microenvironments that can provide various incorporation sites (of different polarities) for similar functionalities. In the fascinating world of surfactants, the rising demand for materials with improved and novel properties has changed the emphasis in surfactant research to study new phenomenon in solution (aqueous or polar). Surfactant micelles have been utilized as efficient material to enhance aqueous solubility of hydrophobic organic compounds. Polycyclic aromatic hydrocarbons (PAHs), due to their mutagenic and carcinogenic effects on both human and eco-system, are of environmental concern [5, 6]. PAHs are generally formed during pyrolysis of organic matter during forest fires, fossil fuel utilization and chemical production [7, 8]. Emissions of PAHs are increasing in developing countries [9]. The contamination of soil and aquifers by PAHs and their subsequent removal/biodegradation by natural processes has been hampered due to poor aqueous solubility. Surfactants based technologies are used to increase PAH solubility, bioavailability and subsequent biodegradability [10]. Surfactant enhanced remediation (SER) has been proposed as a promising technology for the removal of residual organics existing in the sorbed form at/in contaminated matrices [11].

Surfactant solutions have also attracted attention and exploited because of their applications in both academia and industry. The solutions containing surfactants are amendable because of their tendency of having versatile role in different phenomenon like detergency, wetting, foaming, emulsification, adsorption, electrochemical sensing, as template, dispersions and in different industrial areas like chemical (mineral ore, fuel additives, paints, coatings and adhesives) and oil industry (petroleum), pharmaceuticals and bio-industries. Various applications of surfactants in production and processing of food, agrochemicals, laundry products, and in paper and photographic film industries are also found in recent past [12-20]. Thus, wide spectrum of physical, chemical, biological and medical applications have seen. Tremendous new developments in the extraction / pre-concentration techniques are also traced which brings new challenges to the extraction field to increase the efficiency, sustainability and versatility in the conventional methods [21]. The search for new properties in the framework and to meet the societal eco-friendly requirements arise the demand of overcoming the extraction and other problems. Therefore, the research community is heading towards the challenges of the present century with continuous efforts to work upon the limits of the conventionally established extraction techniques. Surfactant based extraction is the beginning towards the application of potentially green methods.

Surfactants, surface active agents, also called detergents, are amphiphilic, organic or organometallic molecules where a polar group (head) attached to a long non-polar hydrocarbon chain (tail), provides distinct hydrophobic and hydrophilic functionalities [22]. Surfactants being amphiphilic in nature contain **hydrophobic tails** (usually a straight chain containing 8-18 carbon atoms) and water soluble **hydrophilic heads**. The hydrophobic part of the surfactant molecule, soluble in oil and other non-polar solvents but not very soluble in water and other polar solvents, is covalently attached to the polar functional portion, the so called hydrophilic head. The interfacial water in the immediate vicinity of hydrophobic and hydrophilic surfaces plays a predominant role in various phenomena of self assembly [23-25]. Due to the above mentioned two distinct groups, surfactant is also referred to as amphipathic, heteropolar or polar-nonpolar material. Figure 1 shows a general representation of a surfactant molecule.

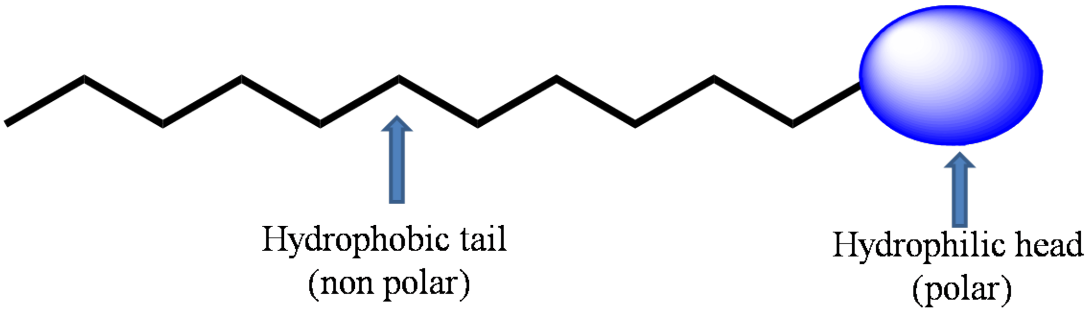

Figure 1. A typical Structure of a Surfactant molecule.

Surfactants have great potential because of their amphiphilic nature together with the molecular structural diversity and spontaneous self-assembling behavior [26, 27] in solution and at various interfaces. Inspite being amphiphilic, a surfactant molecule is not fully compatible with either of the medium (polar or non-polar). There is always a conflict between the affinity of head group and the tail in the solution. Generally, the aqueous surfactant solutions are more likely to be favored, due to the formation of 3D, H-bonded network in addition to the attractive Van der Waals interactions. It is known that amount of work required, to expand the air-water interface, is relatively high. When surfactant molecules are added into water, they get adsorbed at the air-water interface due to amphiphilic character. Here, the hydrophobic part interacts weakly with interfacial water molecules whereas the hydrophilic heads interact strongly via dipole or ion-dipole interactions, makes the surfactant soluble in water. This collaborative action of surfactant along with the 3D network of water, tend to throw the tails out of water and is responsible for the lowering of the surface tension. Thus, the amphiphilic nature forces them to adopt unique orientations in an aqueous medium to form organized assemblies which make surfactants more promising as far as the applications are concerned. In aqueous surfactant solution, at well defined concentration, the abrupt changes occur in several physical properties such as electrical conductance or surface tension among others. Above behaviours of surfactant can be explain in terms of formation of various organized assemblies like mono-layers, micelles, vesicles, emulsions / micro emulsions (both in aqueous and organic solvents) and reversed micelles (in organic solvents in presence of traces of water). After accumulation of monomers on the interface, at low concentration, amphiphilic nature derives them to arrange in various orientations (small organized assemblies) in the bulk at *critical micelle concentration, **cmc*** (would be discussed a little later) [26] (Figure 2).

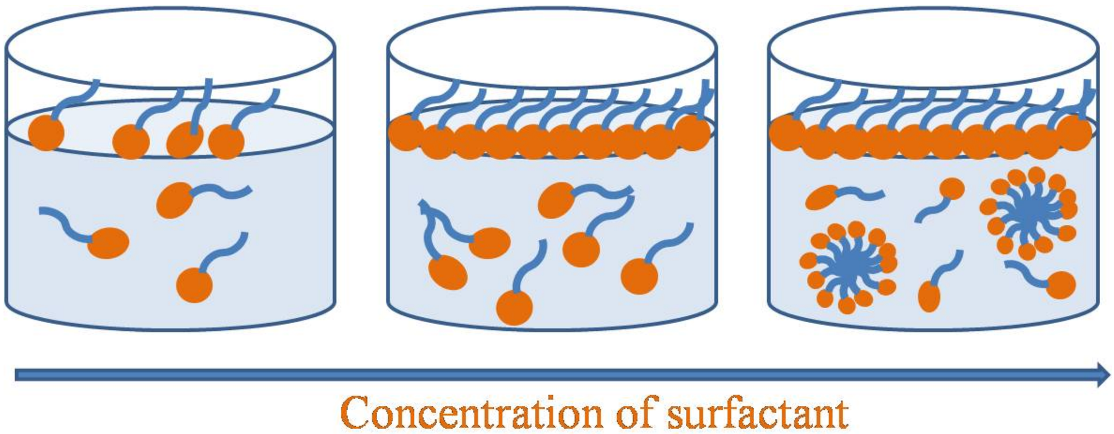

Figure 2. Schematic representation of monomers arrangement on air-water interface (at low concentration) and organized assemblies (spherical micelle) formed at higher concentration (*cmc*).

Classification of Surfactants

Surfactants can mainly classify 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 and zwitterionic.

Anionic Surfactants**:** In a typical surfactant monomer, if the head group contains negative charge then the surfactant called as *anionic surfactant*. Examples of negatively charged head groups include sulfonates, sulphates, phosphates or carboxylates. These are the oldest class of surfactants and still are in use for cleaning formulation such as shampoos because of their excellent properties and less expensiveness [22, 28-30]. SDS is a common example of anionic surfactant (Figure 3).

Cationic Surfactants**:** If the head group contains positive charge (hence cationic) and counter-ion has negative charge then the surfactant would be 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. Mostly, these surfactants are used as disinfectant / preservative as they have good antibacterial properties. The other prime use of cationic surfactants comes from their tendency to interact strongly with negatively charged species / surfaces e.g., binding with biological molecules (DNA, RNA or protein) [31]. 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**:** 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, sugar moieties. If hydrophobic portion 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 surfactants are of polyoxyethylene lauryl ethers (Figure 3).

Zwitter-ionic Surfactants**:** If the surfactant monomer contains two oppositely charged functionalities (positive and negative) on the same molecule, 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 iso-electric point. These types of surfactants have also been used as helping lipid with other surfactants in bio-medicinal applications. Cocobetaine (CB) is a well known example of this class of surfactants (Figure 3).

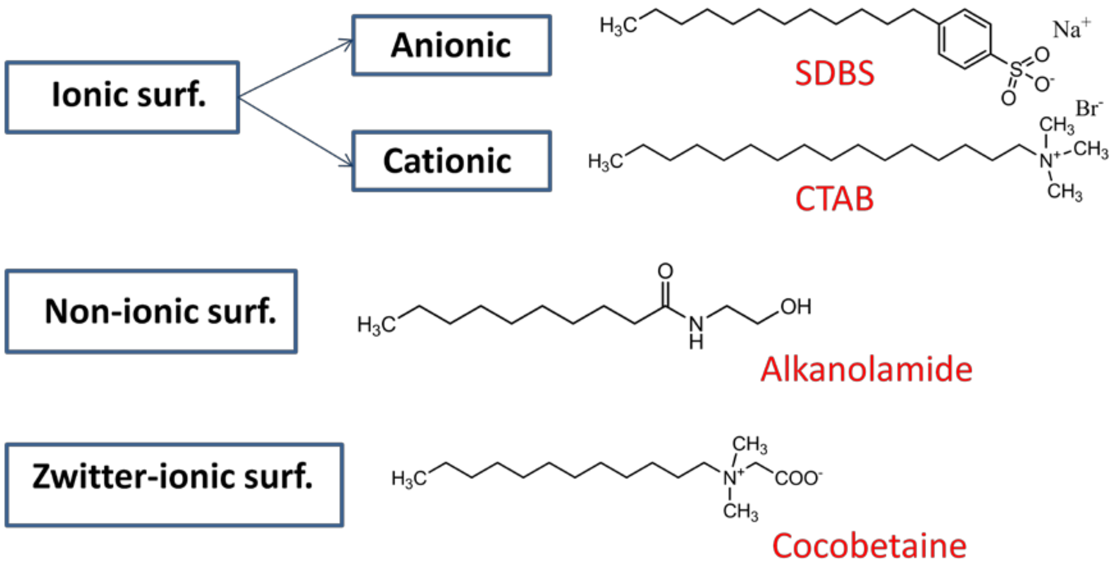

Figure 3. Structure of a few typical surfactants according to the charge on their head group.

Gemini Surfactants: *Gemini* (also called *dimeric*), a name itself suggests twins / two, is similar to the zodiac sign (where two people / children are enclave together with hand to hand, Figure 4). In last two decades, geminies are immerging as a *second generation surfactant* in surface and colloid science due to their better physico-chemical properties over to single tailed as well as other classes of conventional surfactants (with respect to both industrial applications as well as academic field). 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) [32]. Gemini surfactant were synthesized and patented in 1935 [33]. However, they are reported (in open literature) by Bunton et al. in 1971 [34] and later named as 'Gemini' in 1991 by Menger and Littau [35].

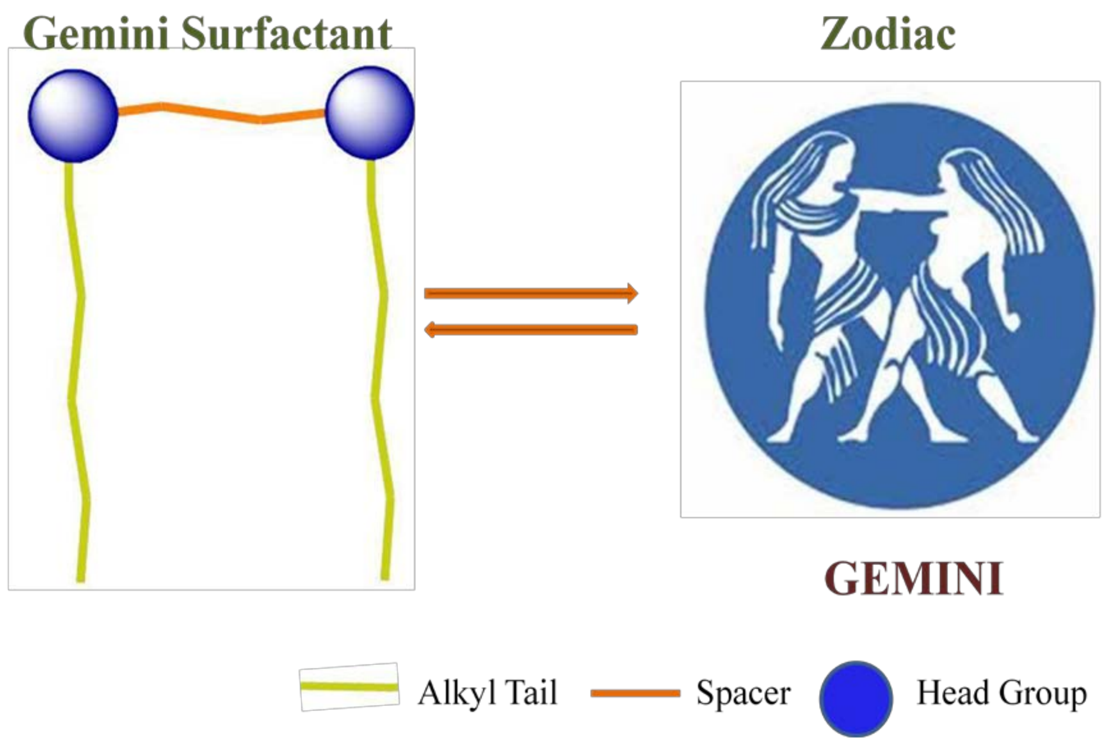

Figure 4. Schematic representation of Gemini surfactant with comparison to Zodiac sign.

They are represented by general formula, ***m-s-m*** (where ***m*** is the no of carbon atoms in hydrocarbon chain and ***s*** is the no of carbon atoms in the spacer joining the two chains. Gemini surfactant can also be anionic, cationic, non-ionic and zwitterionic in nature like conventional single chain surfactants).

Bio-surfactants

Bile salts are *bio-surfactants* important in the digestion process of food. They are produced by the liver from cholesterol, stored in the gallbladder and remain in the organism mainly as bile. Bile salts are amphiphilic molecules (also call facial amphiphile, most of these compounds are either anionic or neutral amphiphilic molecules) which do not have usual polar head and non-polar aliphatic tail as in the case of classical surfactants [36]. Due to this specific facial structure, bile salt molecules lie flat at the aggregate surface. Bile salts from different species differ chemically in the structure of side chain, distribution, position and stereochemistry of the hydroxyl group attached [37]. The hydrophobic part of the molecule is based on long-chain fatty acids, hydroxy fatty acids or α-alkyl-β-hydroxy fatty acids. The hydrophilic portion can be a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid or alcohol. Depending on the number of hydroxyl groups present bile salts are named as hydrocholate, deoxycholate and cholate in which they have one, two and three hydroxyl groups, respectively.

Bile salts solubilize hydrophobic material such as cholesterol, lipids, fatty acids, mono-glycerides, and vitamins. Martin et al. [38] reported that bile salts are metabolic together with phospholipids solubilize cholesterol-forming bile, stored in the gall bladder, assist favorable absorption of fat. It has been reported that sparingly soluble cholesterol get solubilized in the mixed micelle of bile salt and phospholipid [39]. Conjugate bile salts show powerful amphiphilic properties, important in stabilizing the supersaturated state of bile and in promoting fat digestion / absorption.

Different Phenomenon in Aqueous Surfactant Solution

Aqueous surfactant solutions exhibit different phenomena / properties *e.g.*, micellization, clouding, adsorption, spreading, wetting, solubilization, emulsification, etc (Figure 5). Among above properties, present work mainly focused on *micellization, clouding phenomenon* and *Solubilization*. The work on other phenomenon can be found in literature either in the form of published paper /monograph or text book [3, 40-47].

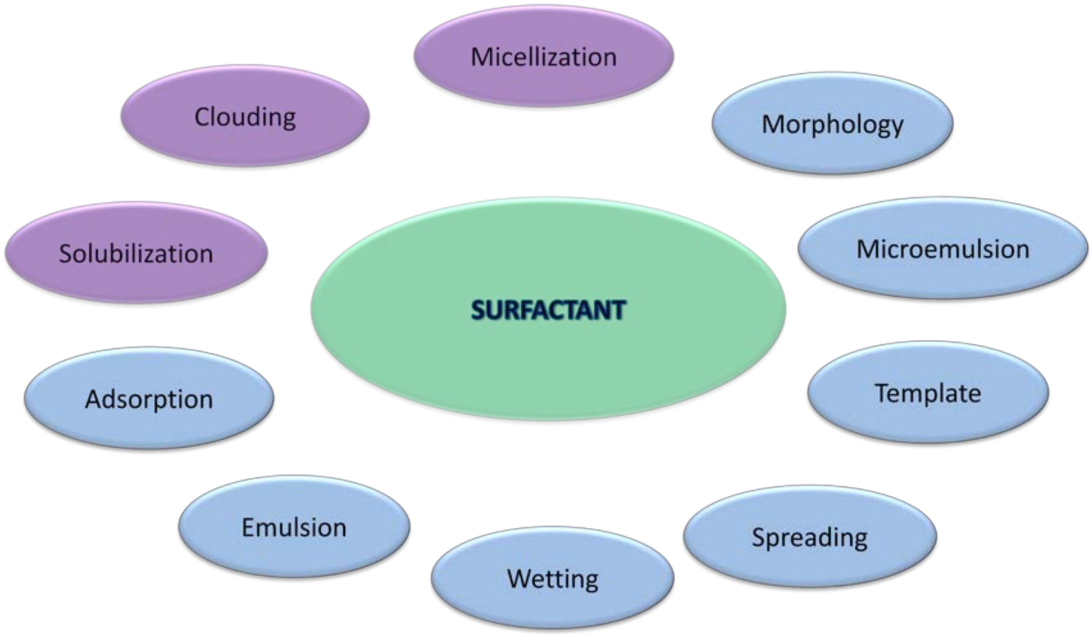

Figure 5. Representation of different phenomenon / properties in aqueous surfactant solution.

Micellization

As mentioned earlier, aqueous surfactant monomers first accumulate at the interface followed by formation of organized assemblies / aggregates called ***micelle*** at well defined concentration (Figure 2). This concentration (generally a narrow range not a fixed value) referred to as ***cmc*** at a given temperature [48, 49]. At ***cmc***, micelles are in dynamic equilibrium with the monomers present at the air-water interface. From the structural point of view, micelle formation occurs at a certain hydrophobic alkyl chain length (≥C8). The cmc generally decreases with the chain length of the hydrophobic tail. However, cmc increases with the increase in the number and size of the head group. ***cmc*** can be determined by various physico-chemical methods with sharp changes in physical property (*e.g.*, specific conductance) around it as illustrated in Preston's [50] classical graph (Figure 6).

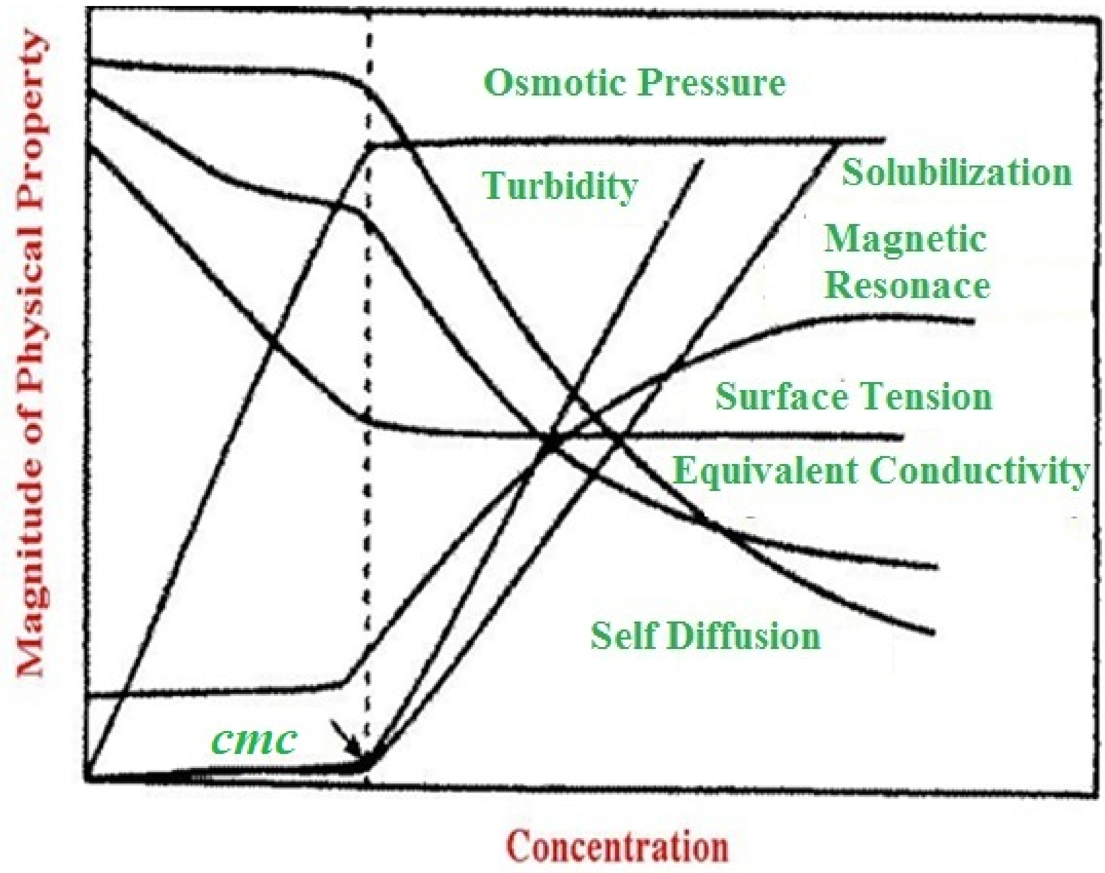

Figure 6. Variation of different physical properties with surfactant concentration **(**different techniques to find ***cmc***).

Due to the abrupt changes, micelle (Latin meaning "small bit") was first described by McBain [51] in 1920 for colloidal sized particles of amphiphilic molecules (detergents or 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 [52]) and electrostatic repulsion between head groups pointed towards the aqueous medium. 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 the free energy of the system and sometimes oppose ***micellization*** [53, 54]. 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 such as electrostatic interactions, hydrophobic interactions, hydration forces among ohthers. Monomers and micelles 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 at ***cmc***. 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) [55] as well as biochemist (a model system for biological membranes or globular proteins) [56-60] for their simpler structure and easy modifications.

Mixed Micelles

Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles. When more than one surfactant are added simultaneously in water, several physicochemical properties of the mixed system compared to those of the single surfactant, are changed. The negative and positive variations from *ideal* ***cmc*** (computed from regular solution theory [61]) indicate synergistic and antagonistic interactions in various surfactant mixtures. Probably, packing of hydrocarbon chains (into the micelle) of the two components of the mixture has a role to decide synergistic or antagonistic effect. The mixed system almost invariably yields enhanced interfacial properties (*e.g.* decreased *cmc*, higher surface activity, lower head group area *etc.*) with respect to the individual surfactants (termed as *synergism*) [62]. The structure of mixed micelle is shown in Figure 7. Rich polymorphism in bulk solution has attracted increasing interest in experimental investigation / theoretical modeling.

Mixed micellization is a special case of solubilization compared to pure micelles, mixed micelles have been shown to have considerable solubilization capabilities toward nonelectrolyte [63, 64]. Mixed micelles have been used in the pharmaceutical field for increased solubilization of various water insoluble drugs for the last two decades. Mixed micelles have been particularly employed for parenteral [65], oral [66], and dermal routes [67].

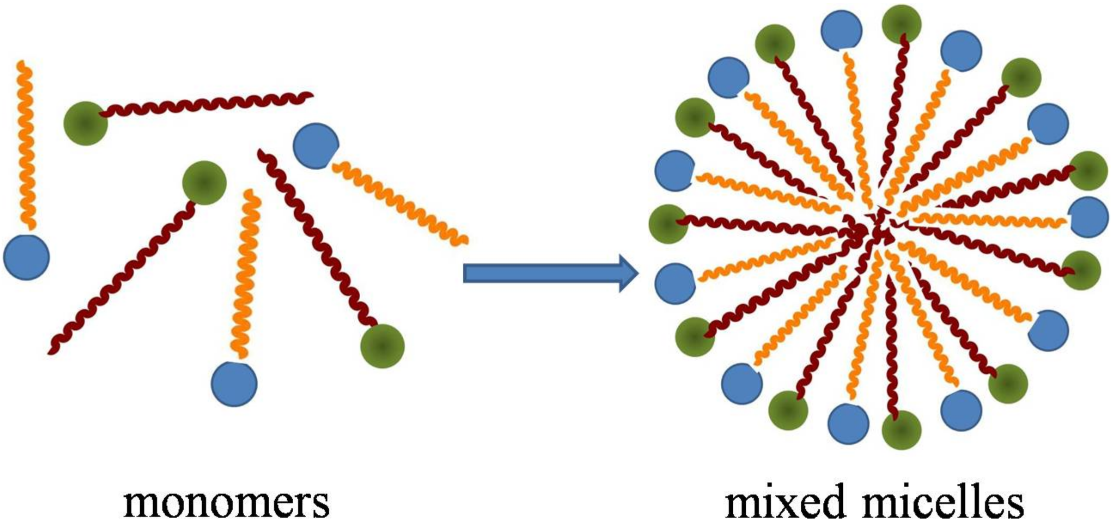

Figure 7. Schematic representation of formation of mixed micelle by individual surfactants monomers.

Clouding

Clouding (or liquid-liquid phase separation) is the physical change occurring in the surfactant solutions on heating. Generally, the solution behaviour of two types of surfactant (ionic and non-ionic) is in sharp contrast with respect to influence of temperature. Non-ionic surfactant solutions (e.g. *CiEj* type, where *i* and *j* are number of carbon atoms in tail and number of oxyethylene group, respectively) cannot withstand elevated temperature and undergo clouding followed by phase separation into two isotropic liquids, surfactant lean and surfactant rich phases, at a well defined temperature known as ***cloud point (CP)*** [68].

Clouding is also known as lower consolute behaviour or coacervate phase behaviour. *CP* can be lower consolute solution temperature (LCST), the temperature above which the two phases appear or upper consolute solution temperature (UCST), below which the two phase region appears (Figure 8).

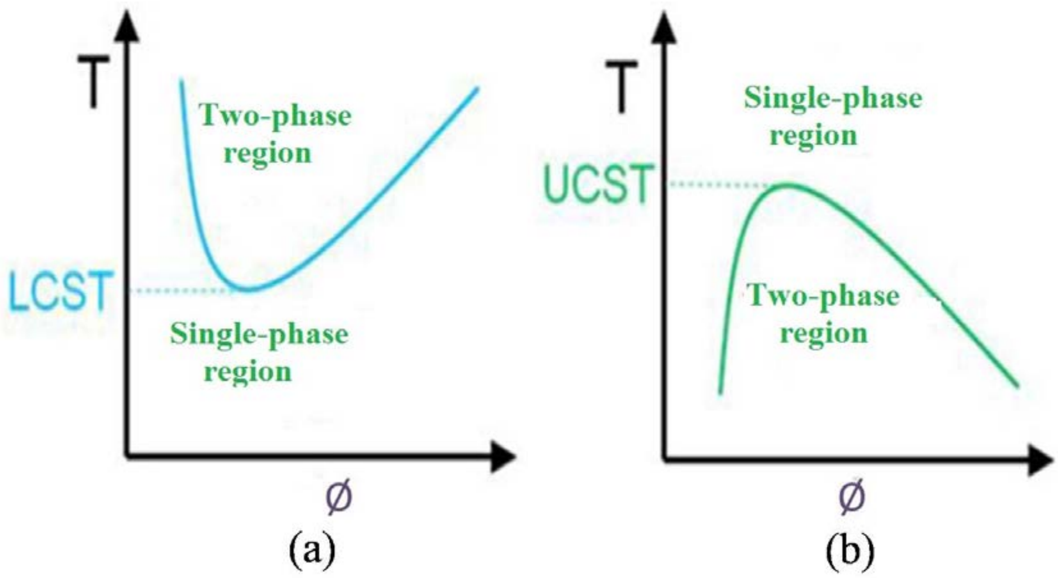

Figure 8. Temperature v/s Surfactant Volume Fraction (ϕ).

A number of applications have been reported for the CP phenomenon in diverse fields, [69-72] but the mechanism by which it occurs is not yet clear and a source of controversy among different groups [73]. The phenomenon has been a consequence of efficient dehydration of hydrophilic portion of micelles on heating. The Langer-Schwartz theory [74] predicts that the nucleated phase may appear as a cloud of small droplets that grow slowly beyond the critical droplet size or it may form as an isolated droplet that rapidly grow to a very large size. The analogy has been draw to surfactant solution in which liquid-liquid immiscibility occurs above LCST or CP. Micelles attract each other and form clusters [75] on approaching CP. Earlier, the phase separation was attributed to the micellar growth, the micellar coacervation, or the changes in poly (oxy ethylene) chain conformations with temperature [76-78]. The roles of oscillation in the critical concentration and of micellar growth as mechanisms for the clouding phenomenon are still debated [79-81]. Another group proposed that clouding phenomenon is due to the interaction of non-ionic surfactant micelles via an attractive potential whose well-depth increases with temperature [82]. According to lattice gas theory, CP appears from a sudden increase in rotational entropy caused by rapid breaking of H-bonds between water and head groups [83]. In recent reports, it has been proposed that the formation of the connected micelle network or strongly orientation dependent interactions [69, 84] between water and head groups could be responsible for the clouding phenomenon. The value of CP depends on the structure and concentration of the surfactant and the resulting hydrophobicity in presence of additives. A progressive dehydration takes place when the salt is added to the nonionic surfactant solution resulting in a smaller effective headgroup area causing a lower CP. Thus, change in micelle morphology also takes place. Moreover, it is also well established that the addition of an ionic surfactant increases the CP of their non-ionic counter parts. Valaulikar and Manohar interpreted CP increase in terms of the surface charge per micelle, responsible for electrostatic repulsion between the micelles [85]. Clouding may also occur with the change in pressure or due to the presence of appropriate additives. Cryo-TEM study showed the first direct evidence for the existence of connected topology in the system showing clouding [86]. It has been proposed that clouding and phase separation do not occur in aqueous ionic surfactant solutions due to the existence of the electrostatic repulsion between the charged headgroups / micelles. In ionic surfactant solutions, water-headgroup interactions are also stronger due to ion-dipole interactions making difficult for H-bonds to break on heating: the prime cause of clouding in non-ionic surfactant solutions. However, cloud point was first reported by Yu and Xu [87] with aqueous tetrabutylammonium tetradecyl sulfate (TBATS), an anionic surfactant. It has been observed that CP decreases with increasing [TBATS]. The micellization and phase equillibria in aqueous solutions of cationic quaternary ammonium bromide surfactants (alkyl tri-methyl-, -ethyl-, -propyl-, -butyl-, -pentyl-ammonium bromide) was also investigated as a function of alkyl chain length, electrolyte concentration and temperature. But no phase separation phenomenon was reported with head groups containing lower alkyl chains [88]. The change in head group from tri-propyl to tri-butylammonium in a cationic surfactant causes the appearance of clouding on heating. Thus, it was concluded that with solutions of alkyltributylammonium bromides presence of a large hydrophobic headgroup, is responsible for clouding [89-92]. In contradiction to above results, no clouding was observed with tetrabutylammonium dodecanoate [93], tetradecanoate, octadecanoate, docosanoate or tetracosanoate [94] up to 98°C. Other conventional anionic surfactants (*e.g.*, SDS) having inorganic counter ions, are not prone to clouding. Few studies with ionic surfactants in presence of high salt concentration, salt free aqueous solution of certain ionic surfactant with large head group or large hydrophobic counter ion such as tetra-*n*-butylammonium perfluroalkanoate and some mixed cationic and anionic surfactant solution showing clouding phenomenon were reported in recent past [95-106]. There have been only a limited number of investigations of such ternary systems and the electrolyte was always presumed necessary to suppress the electrostatic interactions. Detailed studies of SDS in presence of simple inorganic salts are vast and can be found in literature. In contrast to the inorganic counterions, symmetrical quaternary cations are essentially non-hydrated and the positive charge is buried in paraffin shell due to which the unusual phenomenon can be expected with such counterions. Subsequent studies with number of inorganic, organic and quaternary bromides with SDS in presence or absence of different additives in combination were performed to generalize the clouding phenomenon. Recent reports show that only a few quaternary bromides / chloride are effective in producing clouding in a limited concentration range [107]. Above survey point out that nature of headgroup and the effect of counterion on the micellar surface region seem to be of prime importance to observe clouding in ionic surfactant solution. The clouding phenomenon of sodium linear alkylbenzene sulfonates in presence of various quaternary organic salts has also been reported. [107-109]. It has been found that, CP can be tuned with [surfactant] and [counterion]. An increase / decrease in CP with the increase in [surfactant] or the increase in [quaternary ion] has been reported [102, 104, 110]. Keeping above views in mind, few researchers have studied variety of systems in context of clouding in charged micellar solutions in presence of different additives [111, 112].

Clouding phenomenon is widely exploited for the extraction and pre concentration of various analytes. This approach was originally introduced by Watanabe *et al* [113]. Since last two decades the cloud point extraction (CPE) has gained many fold interest over coventional extraction techniques (*e.g.*, solvent extraction) for the separation of environmental [113-122] and biological [123, 124] samples of interest. Later on, the method was extensively exploited as a primary isolation step in purification of proteins [125]. Paleologos *et al*. compiled an excellent overview on the fundamentals, methodology and applications of the CPE technique [126]. Till date, mostly CPE is used for pre-concentration of analytes using non-ionic surfactant systems [127]. The CPE method has usually limited capabilities for the extraction of thermally-labile compounds if the surfactant solution has a high CP or if much higher temperature than the CP is needed to be maintained for a long time in order to allow maximum extraction [128-131]. This problem can be solved by using surfactants that have CP near room temperature. Unfortunately, the application of ionic supramolecular assembly-based separations has been hindered in practice, as the phenomenon rarely occurs for charged surfactant systems [94]. Conditions leading to clouding in ionic supramolecular systems are, therefore, interesting from theoretical and practical points of view. Recently, there was a comprehensive review on using supramolecular solvents in the extraction of organic compounds [132]. The extraction methodologies involving cloud point are known as *cloud point extraction methodologies* (**CPEM**). CPE has the potential to replace hazardous solvent extracting systems and, therefore, beneficial from the point of view of green chemistry approaches.

Solubilization

Another interesting property of surfactant solutions is micellar solubilization, refers to as an enhanced solubility of hydrophobic compounds in aqueous medium through micelle formation (Figure 9). This property has extensively utilized, in *eco-friendly* way of solubilizing certain amount of organic compounds or drugs, in the last few decades [132, 133-135]. Above the ***cmc,*** the solubility of sparingly soluble organic compounds increases in aqueous medium [136, 137]. This solubility enhancement of organic compounds is due to their dissolution at / in different solubilization sites, of varied polarity (polar → non-polar towards micellar core), provided by the micellar aggregates. Many studies are performed to determine the location of a solubilizate within a micelle at various sites [9, 10, 138-143]. 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 non-ionics) 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) and PAHs (with more than one aromatic ring) are solubilized in the interior of the micelle.

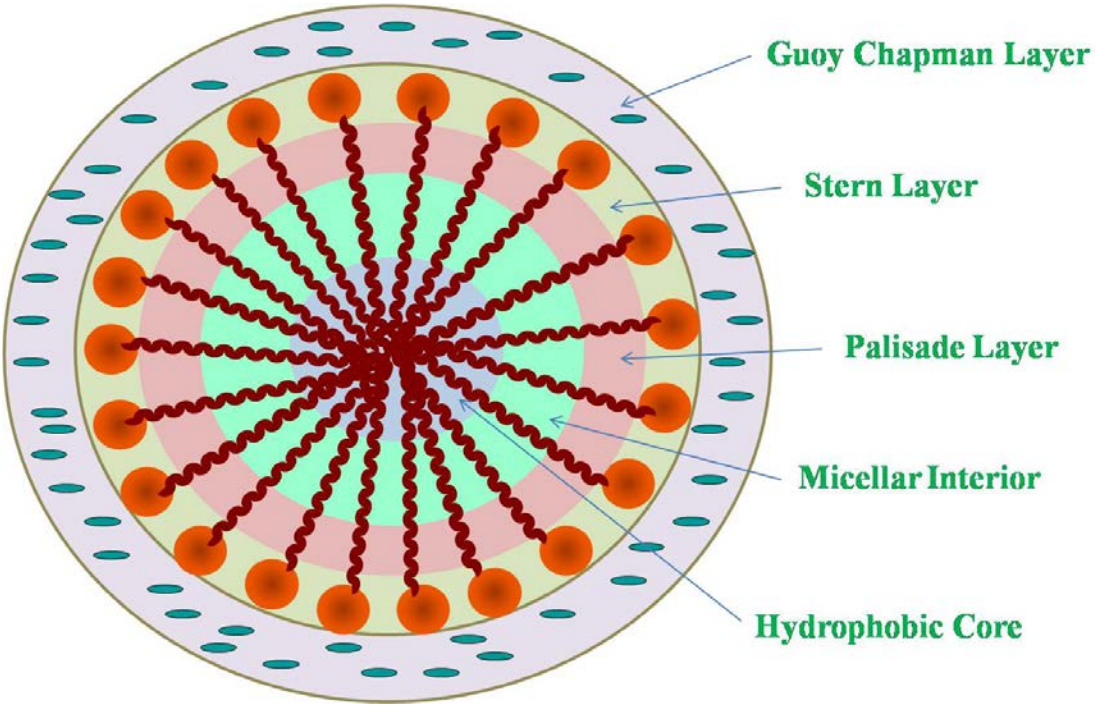

Figure 9. Various solubilization sites of the normal micelle.

However, depth of the penetration in the palisade layer depends on the ratio of polar to non-polar structures in the solubilized 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 [25, 144-150].

Surfactant solutions have also been studied and assist as effective systems for enhancing aqueous solubility, and thus bio-availability of a typical PAHs for its biodegradation [151, 152]. Much of the PAH solubilization work has been performed with single surfactants [153-157]. As mixed surfactant systems show better properties than the single surfactant, these have been preferentially used in solubilization studies in recent time [9, 10, 158]. The mixed micellar structure may have dramatic influences on solubilization behaviour of PAHs due to possible polarity modification.

Gemini over Conventional Surfactants

The growing interest for gemini surfactant (Figure 4) is due to their improved physicochemical properties over conventional surfactant, which mainly dependent on three structural elements (two polar head groups, two aliphatic chains and one spacer) [159, 160]. However, comparing it with the single tailed surfactant, only spacer has been found as the major architectural difference. Due to this most of the dramatically superior properties are observed:

1) one to two order of magnitude lower cmc (means required less amount needed to achieve the same activity);
2) lower surface tension or C20 value (concentration required to decrease surface tension of water by 20 dynes/cm, a measure of their tendency to adsorb at an interface) and 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.

Relevance of the Research Problem

For various applications, surfactants are required to be present simultaneously with different additives (another surfactant, salt, hydrocarbons, bile salts etc.) to improve their performance through synergistic interactions. Studies on surfactants and their mixtures with a variety of additives in aqueous solutions are, therefore, of interest regarding their technical applications. The key question here is to understand the magnitude and nature of the additives as well as the mechanism involved so that suitably modified systems, having desired mode of action can be designed. Accordingly, a fundamental understanding of additive effect on the micellization, clouding in aqueous surfactant solutions may lead to a more effective utilization of these systems in various practical applications (single or with other additives). Not many structure-property relationship work have been performed involving ionic surfactant-quaternary salt combination with respect to clouding phenomenon. As has been mentioned earlier, ionic surfactants produce clouding seldomly in pure state and with inorganic salt. However, quaternary salts can produce clouding with ionic surfactants without any predictiveness. Literature survey shows that a typical quaternary salt produces clouding with one class of anionic surfactant (alkyl sulfate) and fails to do show with another class (soaps).

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. 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 novel surfactant systems.

With the increasing demands at technological fronts, a search for potential surfactant material is constantly increasing. After exploiting the good properties of gemini surfactants, the focus has now been shifted towards gemini-conventional mixture which would be superior to the desired application. The presence of two ionic head groups in a typical gemini facilitates synergistic interaction with the neutral and oppositely charged surfactants than that single tailed mixture.

When ionic geminies are mixed with neutral / oppositely charged conventional surfactants, show better properties towards specific application (e.g. PAH solubilization). However, the potential of the mixing of oppositely charged gemini surfactants has not been exploited. Even only scanty reports are available in the literature regarding mixed micellization of oppositely charged gemini surfactant [161, 162].

Above facts prompted to perform the studies on micellization of conventional and cationic gemini surfactants mixed with quaternary salts and oppositely charged anionic gemini, respectively. A relationship between headgroup / counterion nature with clouding phenomenon is established. Effect of different classes of additives on CP has also been investigated. Micellization studies with oppositely charged gemini surfactants have provided various compositions which were utilized to perform solubilization studies of various PAHs.

Constitution of the Thesis

- The thesis comprises of six chapters (including **Chapter 1,** as general introduction). Chapter 1 provides an up to date literature related to the research problems addressed in the thesis. At the start of the **Chapter 1**, various abbreviations and symbols (used throughout the thesis) are included in a tabular form.

- **Chapter 2** details about various material used and methodologies adopted. The chemical structures of the surfactants and additives used throughout are provided in Chapter 2.

- **Chapter 3** contains studies related to micellization and mixed micellization of anionic surfactants with various quaternary salts. This chapter also includes mixed micellization of oppositely charged amphiphilic molecules (gemini surfactants and bile salts).

- **Chapter 4** contains studies related to clouding phenomenon with various anionic surfactants in presence of quaternary salts. The CP data with and without additives have obtained and complied in this chapter.

- Solubilization studies related to solubility of various polycyclic aromatic hydrocarbons (PAHs) have been complied in **Chapter 5**. The data obtained from the present studies are compared to the reported solubilization data in the literature.

- **Chapter 6** deals with over all conclusion of the studies performed on various aqueous surfactant systems (gemini or conventional) with or without another surfactant/quaternary salt/additive/solubilizate.

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