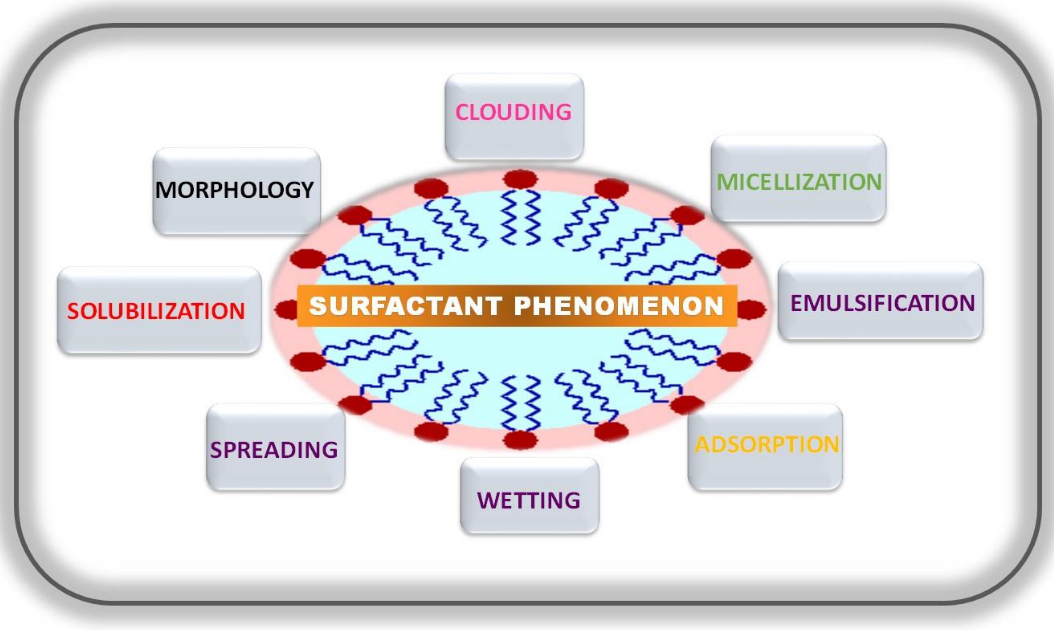
Chapter 1

General Introduction



Contaminated aquatic systems pose a serious problem for our environment. Organic contaminants are produced either by industrial development or natural and human activities [1-5]. These pollutants are moderately hydrophobic material with a varied degree of aqueous solubility (mostly towards the lower side) [6, 7]. Industrial effluents lead to migration of such pollutants to the soil and aquatic bodies (both surface and ground). This process adversely affects the quality of drinking/marine water and results in a life-threatening problem to the living system [8, 9]. In general, the contaminant can be a polyaromatic hydrocarbon (PAH), phenols, dyes, pesticides, drugs etc., individually or in the mixed form. Various attempts, involving physicochemical, biological or their combined strategies, have been adopted for aquatic remediation [10-19]. Among these treatments, adsorption is frequently studied/applied due to its effectiveness and ease of methodology. Both natural and synthetic adsorbents have received due attention for the adsorption of pollutants from the aqueous matrices [20]. Such remediation also includes desorption of contaminants or enhanced bioavailability for biodegradation [21, 22].

Under chemical science-based technologies, surfactant enhanced remediation (SER) processes are found a special place due to their versatility, efficient contaminant removal performances, and compliance with the principles of green chemistry [23-27]. In addition, surface active agents have also proved to be potential materials for the facilitation of microbial remediation by improving the accessibility of hydrophobic materials to micro-organism. The focus has been shifted towards designer adsorbents and their modification by various surfactants in order to improve their potential performance [28]. The work embodied in this thesis is related to the adsorption/ solubilization of a few classes of organic materials (PAH, dyes, drugs etc.) on pure or surfactant modified adsorbents (both natural and synthetic)/ in aqueous surfactant(s) solution. In this chapter (Chapter 1), brief descriptions related to surface active agents (or surfactants), micellization, morphological transitions, clouding, solubilization, adsorbents, surfactant modified adsorbents *etc*., are included together with the relevance of the present work and related bibliography.

1.1. Surfactant

Material which drastically lowers surface tension/ interfacial tension of air (or oil)/ water interface, due to interface accumulation, comes under the category of surfactants or surface-active agents. Surfactants are usually organic compounds with the special molecular structure of two opposite solvent loving/ hating tendencies (water-loving or hydrophilic and water-hating or hydrophobic). Due to the above two functionalities (hydrophilic head group attached with hydrophobic hydrocarbon tail), the surfactant is also known as amphipathic, hetero-polar or polar-nonpolar substances. The general depiction of a surfactant molecule is shown in Figure 1. This polarity gradient in a typical molecular structure originates various phenomena / unique properties in solution [29].

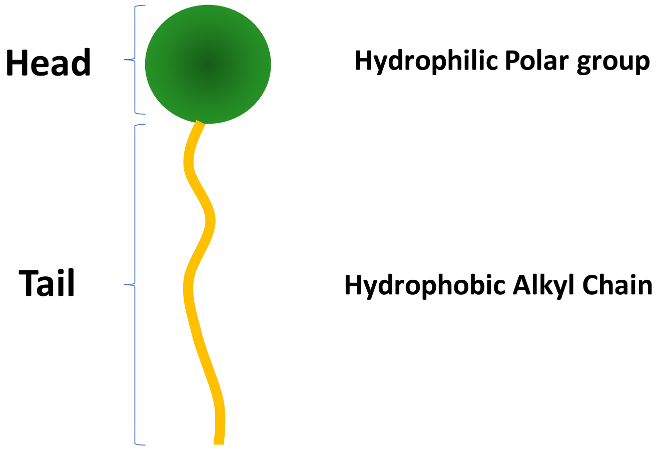


Figure 1. A typical structure of surfactant molecule

When a surfactant is dissolved in water, molecules adsorb at the air-water interface with a contact of the head group with the surface of water driven by ion-dipole (or dipole-dipole) interactions. Weak interactions/ complex structure of hydrophobic part drive alkyl chains away from the interface. However, the hydrophilic group prevents the surfactant molecule from being expelled completely from water and predominantly responsible for the lowering of the surface tension. After accumulation of surfactant monomers at the air-water interface (and its saturation), amphiphilicity forces monomers to adopts unique orientation to form organized assemblies (relatively small) in the bulk at an appropriate concentration [30, 31]. This concentration is called *critical micelle concentration* or *cmc* and assemblies are turned as '*micelle*' (Figure 2). Above two terms have a special place in the field of surface science and responsible for fascinating solution behavior [32].

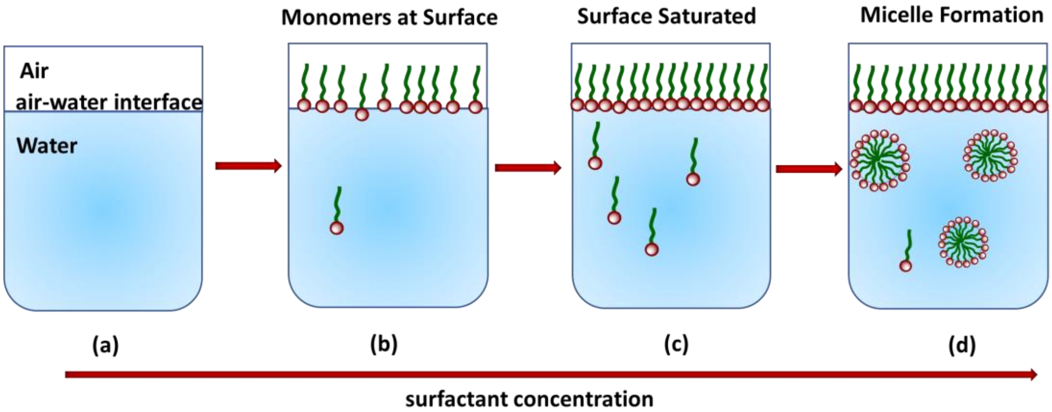


Figure 2. Schematic representation of monomers arrangements on the air-water interface (at low concentration) and organized assemblies (spherical micelle) formed at higher concentration (*cmc*).

1.2. Classification of Surfactants

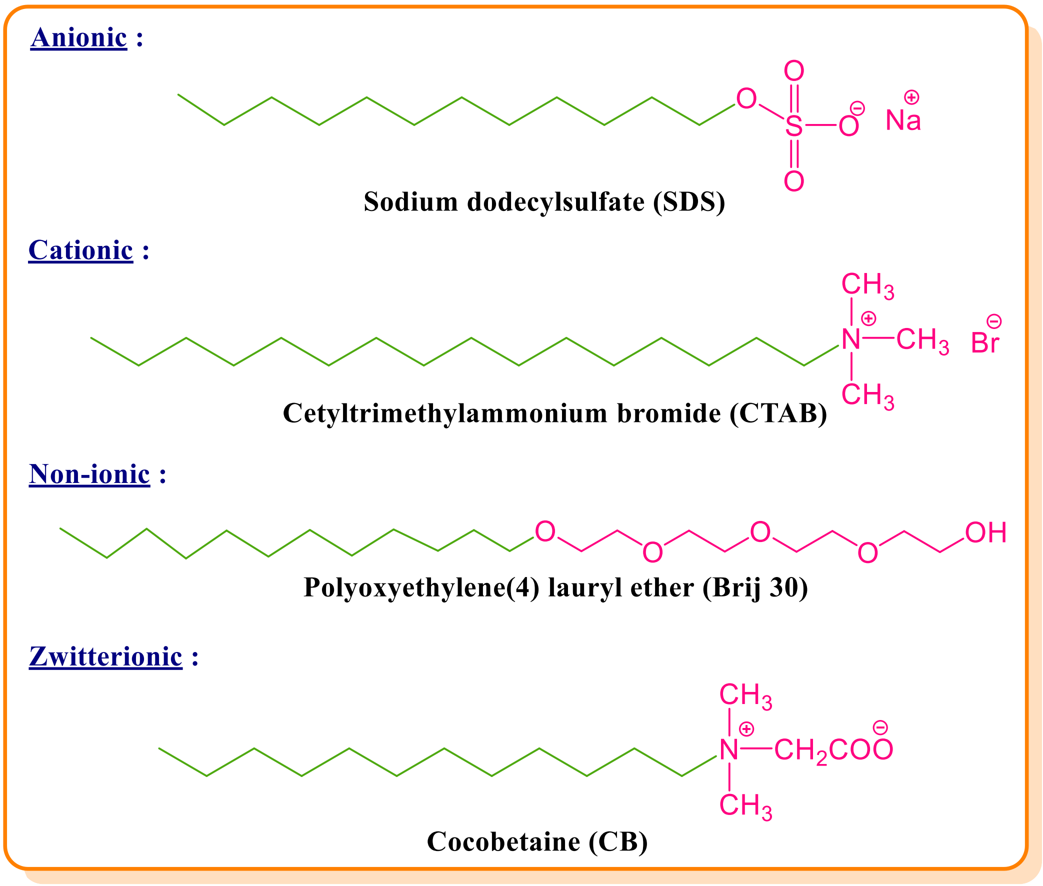
Surfactants can mainly be classified based on the head group charge (positive or negative or no charge). Accordingly, surfactants can be classified: cationic; anionic; non-ionic and zwitterionic.

Anionic Surfactants**:** In surfactant solution, if the head group bears -ve charge then the surfactant is called *anionic surfactant*. Examples of anionic surfactants include linear or branched chain sulfonates, sulfates, phosphates or carboxylates. This is the oldest class of surfactant and widely used in cleaning formulations [33]. SDS is a well-known anionic surfactant and considered as the work horse of surfactant research (Scheme 1).

Cationic Surfactants**:** Similarly, if the head group bears +ve charge and attached to a long alkyl tail 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. A famous cationic surfactant in use is cetyltrimethylammonium bromide (CTAB, Scheme 1).

Non-ionic Surfactants**:** If the head group is neutral (un-ionizable) then surfactant is known as non-ionic one. Non-ionic head groups are: alcohol ethoxylates; phenol ethoxylates; alkanolamides; alkanediols; mono- and disaccharides. The hydrophobic part contains saturated/unsaturated fatty acid or fatty alcohols in the form of a hydrogenated/fluorinated chain. Polyoxyethylene (4) lauryl ether series compounds are well known non-ionic surfactants. (Scheme 1)

Zwitterionic Surfactants**:** When both charges are present in a typical surfactant molecule then the surfactant is known as zwitterionic or amphoteric one. Cocobetaine (CB) is a well-known surfactant of this category (Scheme 1).



Scheme 1. Structure of a few typical surfactants according to the charge on the head group.

Gemini Surfactants*:'Gemini surfactants'* consist of two amphiphilic monomers linked at the level of polar heads by a chain of spacer [34-38]. Various properties in gemini solution depend on the distance between the polar heads decided by nature and length of the spacer [39]. Among geminis, cationic bis(alkyldimethylammonium)alkane dibromides (represented by **m-*s*-m**, where **m** is the number of carbon atoms in hydrocarbon chain and ***s*** is the number of carbon atoms in the spacer) have studied many a time.

Gemini head group can be +ve (ammonium), -ve (phosphate or carboxylate), or neutral (polyether or sugar)**.** Structural variation exists in the nature of the spacer which can be short or long; rigid or flexible, polar or nonpolar and cleavable or non-cleavable [40]**.** It has been reported that the spacer hydrophobicity affects aqueous aggregate morphology [37]. A general structure of a gemini surfactant can be represented as shown in **Figure 3**.

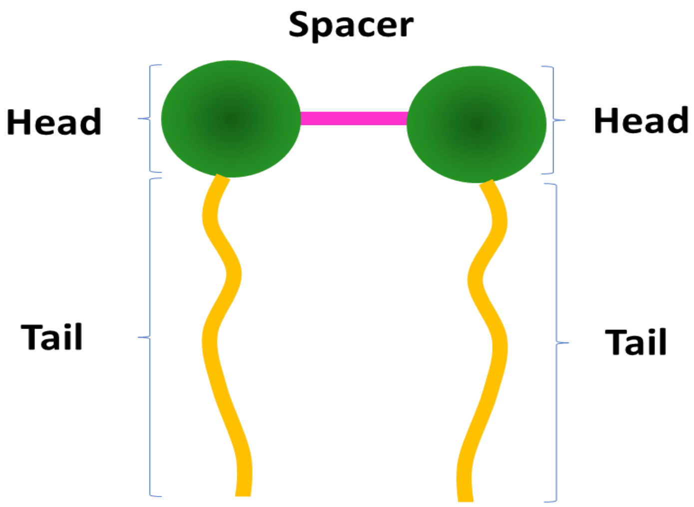


Figure 3. The general structure of a Gemini monomer

Gemini surfactant was synthesized and patented in 1935 [41]. However, they are reported (in open literature) by Bunton et al. in 1971 [42] and later named as 'Gemini' in 1991 by Menger and Littau [43]. Gemini possesses high surface activity and lower cmc, unusual viscosity changes with [surfactant], greater efficacy in decreasing the surface tension, improved wetting and solubilizing properties with unconventional micellar structure [44-48]. Due to above facts, geminis are also used in biochemical [49], pharmaceutical [50], petroleum [51], gene therapy [52], corrosion [53], and catalysis [54-56]. Aqueous gemini results vesicles, rod- or worm-like micelle, liquid crystalline phases and various complex morphologies over a broad concentration range.

1.3. Solution Behavior of Surfactants

Aqueous surfactants exhibit different phenomena/properties: *micellization*; *clouding; adsorption; spreading; wetting; solubilization; emulsification* etc (Figure 4). From the above surfactant properties, the work embodied here focuses on *micellization, morphological transitions, clouding*, *adsorption*, and *solubilization* [57, 58].

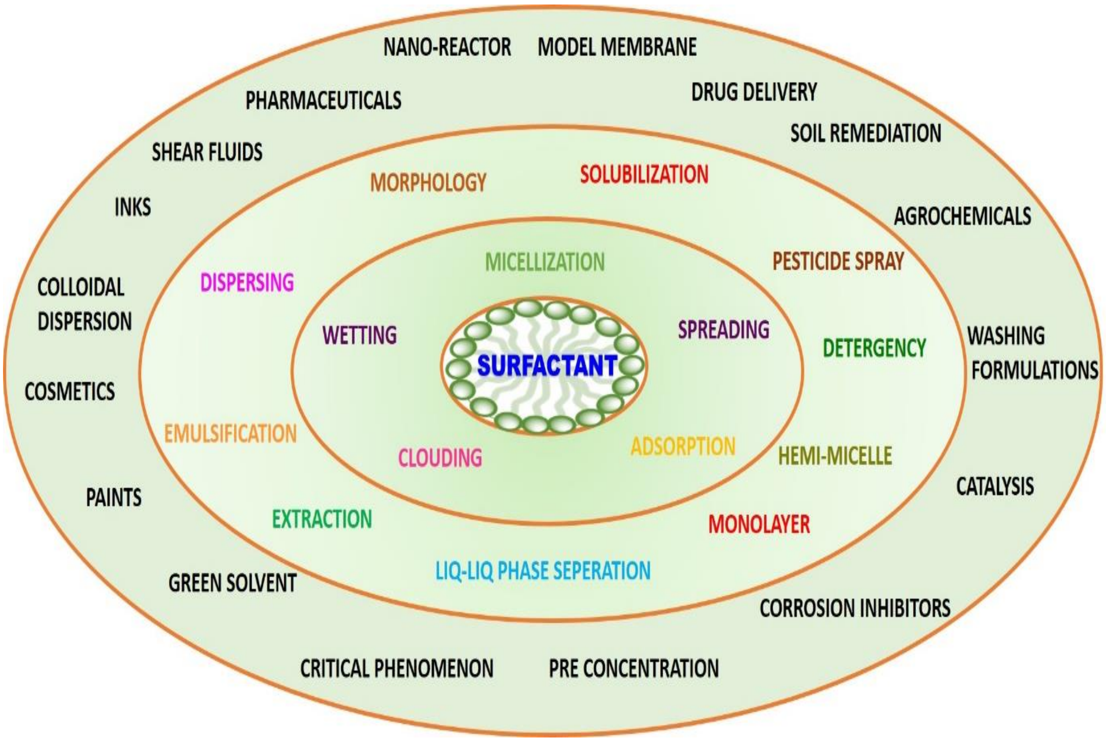


Figure 4. Representation of different phenonmenon / properties in aqueous surfactant solution.

Micellization

As mentioned earlier (Figure 2), aqueous surfactant monomers first accumulate at the air-water interface followed by formation of ***micelle*** (or normal micelle) at well-defined concentration referred to as ***cmc*** (at a given temperature) [59, 60]. 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 ($\geq C_8$) of the surfactant. ***cmc*** can be determined by various physicochemical methods with distinct changes in physical property (*e.g.*, specific conductance, κ) around it as illustrated in Preston's [61] classical graph (Figure 5). The idea about the magnitude of charge on the ionic micelle can be acquired by the degree of counter-ion dissociation (α). This can be determined by the ratio of slopes of straight lines, of the plot between κ *vs* [surfactant], post micellar and pre-micellar regions (before and after the distinct change, break). Average head group area of surfactant molecule (a_0) can also be computed by using the slope of the straight line portion of surface tension (γ) *vs* [surfactant] plot.

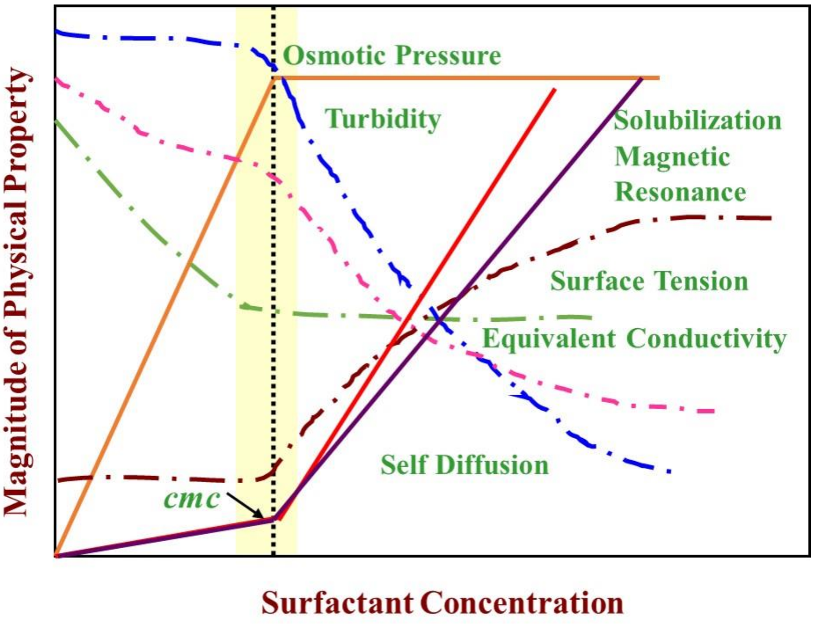


Figure 5. Different available methods to find cmc.

The name '*micelle*' (Latin meaning "small bit") was first coined by McBain [62] in 1920 for colloidal sized aggregates of soap molecules. The mechanism behind micelle formation is based on the cohesive force between two hydrophobic alkyl tails (hydrophobic interactions), forcing them to go towards interior part (proposed by G.S. Hartley in 1936 [63]) and electrostatic repulsion between head groups pointed towards the aqueous medium. The number of surfactant monomers that aggregate to form a micelle is called ***aggregation number*** (*N*agg). Monomers and micelles are in equilibrium but still, they rapidly assemble and disassemble in an 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. When a surfactant is dissolved in a non-polar solvent, having traces of water, results in an inverted structure with head groups towards the interior and a hydrophobic portion towards non-polar solvent. This arrangement of surfactant molecules is known as ***reverse*** or ***inverted micelle*** [64].

Mixed micelles

Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles and the phenomenon of aggregation is known as *mixed micellization*. Various physicochemical properties of the mixed system, compared to those of the single surfactant, are changed during mixed micellization. Packing of hydrocarbon chains (into the micelle) of the two components of the mixture has a role to decide the mode of interaction (synergistic or antagonistic). A typical structure of mixed micelle is shown in Figure 6. The resulted polymorphism of mixed micelle attracted increasing interest in experimental investigations and theoretical modeling [65].

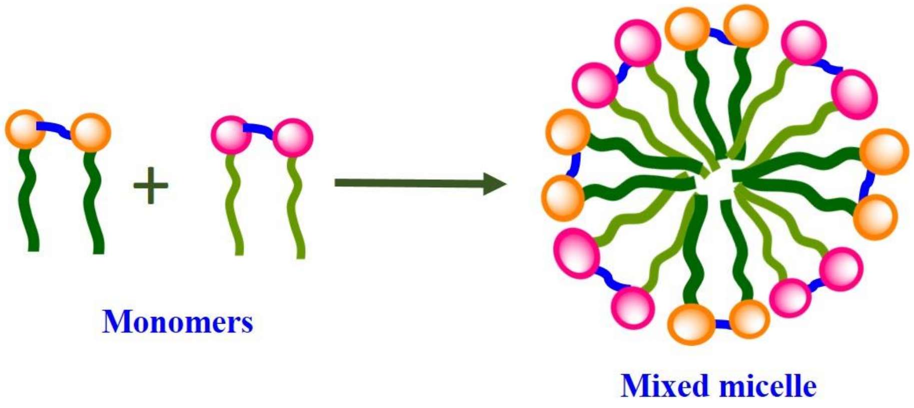


Figure 6. Schematic representation of the formation of mixed micelle by different surfactant monomers.

Morphological Modifications

Various morphological assemblies can be found in surfactant solutions under different experimental conditions. There are two factors (Figure 7) governing the micellar shape: i) the steric force of repulsion between two similar head group charges; and ii) hydrophobic interactions between two monomeric alkyl tails or the packing curvature related to Mitchell- Ninham parameter ($P=V/a_0\, l_c$, where V and l_c are the volume and length of the alkyl chain, respectively and a is the average head group area in a typical surfactant) [66]. The value of P depends on: i) optimal head group area (a_0) that indirectly depends on the amphiphiles (molecular structure), ionic strength, temperature/ pressure and nature of the solvent, ii) the volume of the alkyl chain (V) and iii) the critical chain length (l_c). The V and l_c can be calculated by empirical equations suggested by C. Tanford [67], while a_0 can be measured experimentally [68]. Due to the dehydration of counter ion and the surfactant head group, the counter ion binding takes place and responsible for deciding a_0 and hence the micellar morphology. The nature of counter ion plays an important role in the binding mechanism of a counter ion with a concomitant effect on P as well as resultant morphology (Table 1).

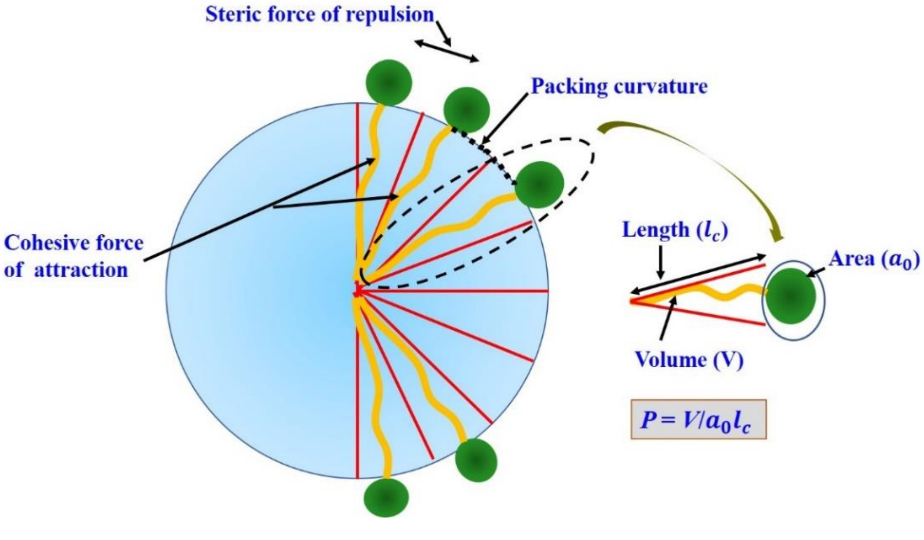
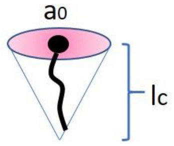
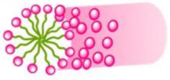
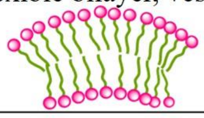
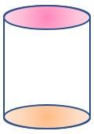
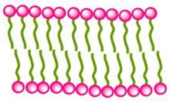
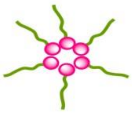


Figure 7: Various factors governing the micellar morphology

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

Effective Shape of the surfactant molecule	**Packing Parameter**	**Aggregate Morphology (Geometry of micelles)**
 cone	< 1/3	Spherical Micelle 
 Truncated cone	1/3- 1/2	Cylindrical Micelle 
 Truncated cone	1/2 -1.0	flexible bilayer, vesicles 
 Cylinder	~ 1	planer bilayer 
 Inverted cone	> 1.0	Reverse Micelle 

Clouding

Clouding (or liquid-liquid phase separation) is the physical change occurring in the aqueous surfactant solution on heating. Generally, the solution behavior of two types of surfactant (ionic and non-ionic) is in sharp contrast with respect to the influence of temperature. Non-ionic surfactant solutions (e.g. *CiEj* type, where *i* and *j* are the number of carbon atoms in tail and number of oxyethylene group, respectively) cannot bear heating beyond a certain temperature and resulted in turbidity followed by phase separation into two isotropic liquids, surfactant lean- and surfactant-rich phases. This critical temperature is known as ***cloud point (CP)*** [69]. CP of aqueous surfactant solution can be tuned by adding various additives [70-75]. It is always advantageous to have clouding phenomenon near ambient temperature in order to reduce the requirement of any kind of heating. It is reported that progressive dehydration takes place when the salt is added to the nonionic surfactant solution resulting in a smaller effective headgroup area provoking a shift in CP to lower temperature. Thus, the change in the micelle morphology also takes place. Clouding may also affect with the change in pressure. A study of the transition from spherical micelles to wormlike micelles to vesicles (micellar growth) in a non-ionic aqueous system (on heating) with strong electrostatic interactions and subsequent network formation is also reported using Cryo-TEM [76].

Solubilization

Another interesting property of surfactants is their ability to enhance the aqueous solubility of a hydrophobic compound which otherwise is insoluble in an aqueous medium. This solubility increase, resulted from hydrophobic interactions, is referred to as *solubilization*. Due to the amphiphilic nature and the spontaneous self-assembling behavior, surfactants possess versatile applications for solubilization of the insoluble substrates. The nature of the surfactant morphology plays an important role in deciding the solubilization efficacy of a typical aqueous surfactant system. It becomes interesting to see how an additive at different micellar solubilization sites can influence physical properties and the morphology involved therein. The amphiphilic characteristics of surfactants, past long, have extensively been utilized in eco-friendly aqueous solubilization of organic materials, drug carriers, and probing of biological systems [77-79]. Thus the key property of micelles is to enhance aqueous solubility of organic compounds by enabling multiple solubilization sites (Figure 8) of interaction where solutes can partition according to their hydrophobic or polar nature.

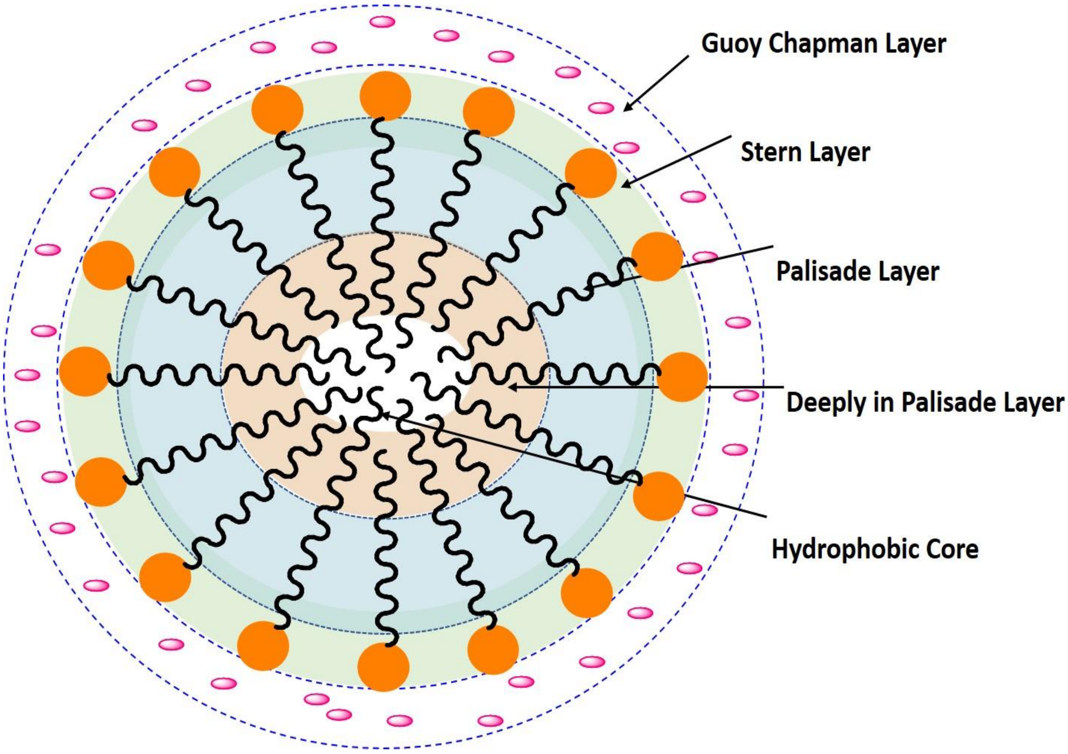


Figure 8. Various solubilization sites of the normal micelle.

1.4. Adsorption Phenomenon

The term adsorption is defined as the adhesion of atoms, ions, biomolecules or molecules of the gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent (Fig. 9). It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. The term adsorption was given by Keyser in 1881.

The adsorption is of two types i.e. Physisorption and chemisorption. Physisorption is physical adsorption involving intermolecular forces (Van der Waals forces), which do not involve a significant change in the electronic orbital patterns of the species [80]. The physisorption decreases with increase in temperature [81].

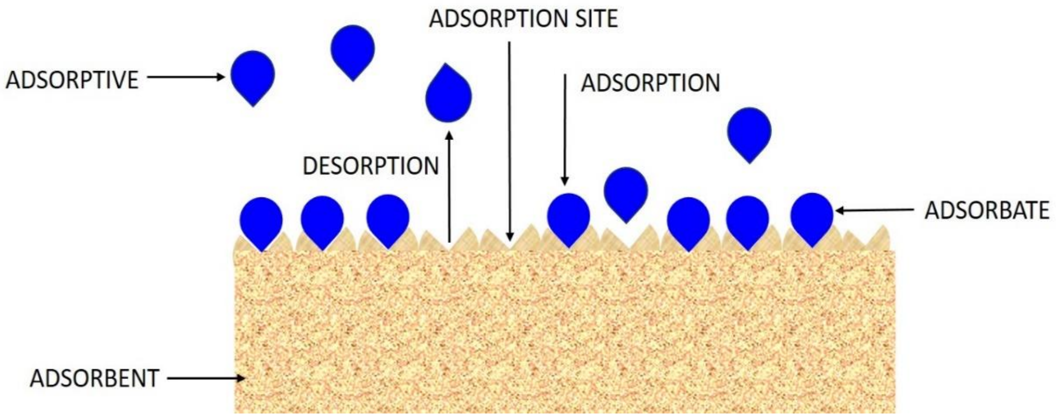


Figure 9. Pictorial representation of adsorption phenomenon

In physical adsorption, equilibrium is established between the adsorbate and the solid phase resulting in multilayer adsorption. Physical adsorption is relatively non-specific due to the operation of weak forces of attraction between molecules. While chemical Adsorption is due to the formation of chemical linkages between adsorbate and adsorbent surface. The chemical adsorption is generally nonreversible and it increases with temperature. It is characterized by a large heat change during adsorption. Adsorption process depends upon the nature of adsorbent and the solutions. It is also dependent upon the surface area, functional groups, pore sizes, morphology and surface charge of the adsorbents. Adsorption properties are dependent upon pH, temperature, the concentration of the adsorbates, dosages of adsorbent and equilibrium time.

Adsorbent and modified adsorbent in the removal of organic pollutants

Adsorption is one of the most important processes for the removal of heavy metals, dyes, organic and inorganic pollutants from the industrial effluent by conventional and non-conventional adsorbents. The adsorption technique is considered better than other purification processes because of simplicity of operation, economy, user-friendly, and ease of design. Adsorption is a mass transfer step via which a pollutant can be selectively removed from a water body by preferentially transporting it (adsorbate) towards adsorbent-water body interface. The method finds wide utility in the selective removal of dye from background aqueous media. Dyes are used for coloring textile, wool, leather, paper, fibre etc. Synthetic dye substituted natural ones based on economy and variety of colors. The aqueous solubility of dyeing material leads wide dissemination into the outer world, thus making them hazardous to crops, aquatic/ wild life and human health [82]. Colored water show resulted contains a distinct amount of various dyes and must be removed to bring down their content within the permissible level. To achieve and sustain the required recovery of the above water, optimization of the adsorbent material is of great importance [83]. Both natural and synthetic adsorbents are used for the removal of various dyes from effluent water. A few of them are rice husk [84], wheat straw [85], wheat shell, almond shell [86], hazelnut [87], orange peel [88], coffee waste, tea waste [89], fly ash [90], etc. Activated carbon and clay are also used regularly in the adsorption technique due to their specific properties (adsorption capacity or varied plasticity) [83]. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost and poor regeneration capacity [91], [92]. Synthetic adsorbents (nano-materials, graphene or graphene derivatives) are now attracting many researchers due to excellent properties or novel structures [93]. As an efficient adsorbent, graphene can offer a wide range of potentialities such as high surface area, mechanical stiffness, and flexibility. However, the adsorption capacity of graphene nanosheets is restricted if the surface is not optimally functionalized.

Nowadays, people are even interested to modify graphene structure and synthesizing more versatile graphene composites [94]. Graphene-based materials can interact with dye/PAH molecules (present in a water body) via electrostatic interactions, hydrogen bonding, π-π stacking in addition to physisorption. Therefore, understanding organic molecule adsorption by such material is essential to decide the fate and transport of organic contaminants and for designing novel adsorbents. However, long equilibrium period and aggregating tendencies make them less attractive for the adsorption process. To address the above problems, functionalization by metal oxide nanoparticles and organic molecules is often recommended [95]. This is a novel approach to obtain a hybrid/functionalized composite material with added properties (increased mechanical strength or thermal stability). In this direction, the use of a surfactant is also an attractive alternative as the process requires a simple mixing of graphene composite and surfactant. Schematic representation, of organic molecule adsorption phenomenon on surfactant modified adsorbent surface, is depicted in Figure 10.

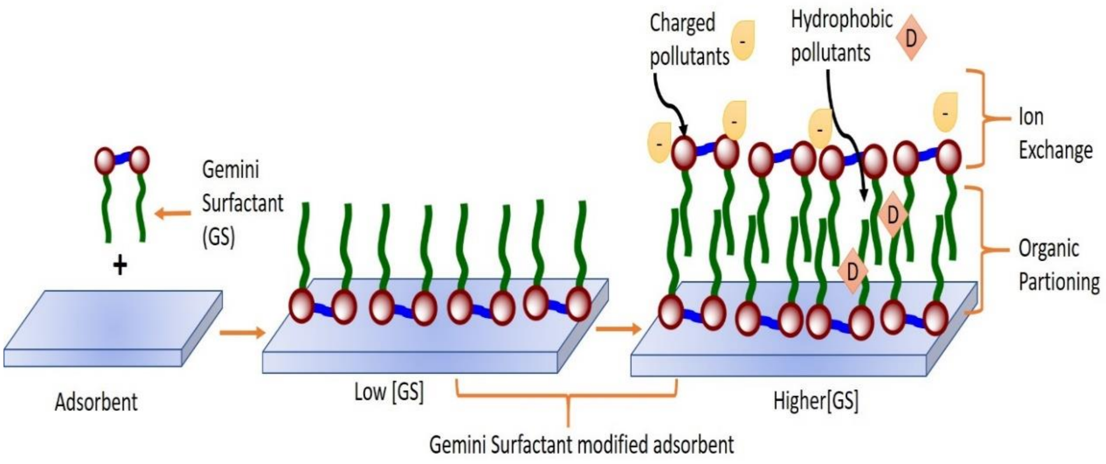


Figure 10. Adsorption of the pollutant on gemini surfactant modified adsorbent.

Recently, adsorptive removal of organic pollutants using surfactant-modified solid matrices have attracted great attention. Materials, thus modified with a surfactant, contain micelle-like structures on their surfaces with the potential to solubilize organic molecules within the structures formed. These structures are called *hemimicelle* or *ad-micelle*, and the phenomenon is called *ad-solubilization*. Surfactant-modified metal oxides have also been used for studying the physicochemical aspects of the phenomenon using different hydrophobic compounds. Even mixed surfactant systems were used to test the efficacy of the *ad-solubilization* of the organic pollutant on functionalized adsorbent [96-97].

Cationic surfactant (*e.g.,* CTAB) functionalized bentonite has attracted great interest due to its high affinity for hydrophobic material [98]. CTAB modified silica particles facilitate the adsorption of ionic dyes [99]. Anionic surfactant modified alumina has been found very effective in the removal of Malachite green (a toxic cationic dye) from the aqueous environment [100].

Gemini modified clays have been used in removing organic dyes [101]. Similarly, Gemini modified silica has been used for the removal of 2-naphthol [102]. It has further been reported that gemini functionalized clay is more effective in removing to 2- naphthol and 4-chlorophenol. A potential recyclable surfactant modified nano-adsorbent has been reported for the removal of toxic dyes from wastewater [103].

1.5. Relevance of Research Work

As mentioned above, numerous structural modifications to the adsorbent material have been carried out in order to enhance their performance or to make them application specific. Surfactant functionalized adsorbent material (natural or synthetic) shown potential application toward both highly water-soluble (*e.g.,* dyes) or slightly water-soluble (PAHs) organic compounds. However, the removal of water-soluble dyes from water is still a big challenge. Similarly, removal of PAH from aqueous (industrial effluent) or solid matrices (contaminated soil) is equally challenging.

To address the above problems, various strategies are planned and compared with the existing methods reported in the open literature. In this direction, graphene-based composite has been synthesized by mixing with zirconium oxide nanoparticles (a potential adsorbent) followed by its characterization. This material was modified using both conventional and gemini cationic surfactant. Modified material then used for the study of adsorptive removal of two anionic azo-dyes. In a separate study, solution behavior of a surface active ionic liquid (SAIL) has been modified (system starts showing clouding phenomenon) in the presence of an anionic gemini surfactant. Effect of some bio-additives has also been seen to tune the clouding behavior and its subsequent use in cloud point extraction methodology (CPEM) for PAHs. Liquid-liquid phase separation was achieved in PAH solubilized gemini-SAIL aqueous system at CP. On standing the system at CP, accumulation of PAH takes place in the surfactant-rich phase (*pre-concentration step*). The surfactant-rich phase has been treated with graphene- zirconium oxide nanocomposite for adsorptive removal of PAH. In another set of experiment interaction of oppositely charged gemini surfactants has been studied conductometrically. cmc data were computed and used for the determination of the nature of interaction using various regular solution theories.

Internal modification in micellar morphologies has been studied using various related parameters: composition; chain length; spacer nature; temperature etc. Various scattering/ microscopic techniques were used to establish morphologies and their inter-conversion. In a separate study, efforts have been devoted to facilitating aqueous solubility of PAHs using various morphologies so obtained from the above study. Both single solubilization and co-solubilization of various PAHs (pyrene, anthracene, fluorine or phenanthrene) have been checked in order to see the effect of various solubilization sites available in a typical morphology.

The thesis consists of seven chapters including: i) ***General Introduction***; ii) ***Materials and Methods;*** iii) ***Adsorption of anionic azo-dyes using Surfactant modified synthetic and natural adsorbents*** iv) ***Solution behavior of anionic Gemini modified surface active ionic liquid: interaction; clouding and solubilization.*** v) ***Mixed Micellization and Interaction of oppositely charged Gemini surfactants;*** vi)

Structural modification in Self-assembly of Aqueous oppositely charged Mixed gemini surfactants; vii) ***Solubilization of polyaromatic hydrocarbons in various morphologies based on mixed gemini surfactants;*** viii) ***Overall Conclusion.***

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