Chapter 1

Introduction

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1.1 Introduction to Surfactants

Surfactants play a major role in nearly every aspect of our daily life from their commonly known applications in soaps and detergents to less commonly known applications in enhanced oil recovery and ore processing. The last decade has seen the extension of surfactant applications to high technology areas such as electronic printing, magnetic recording, biotechnology and microelectronics [1]. Therefore knowledge of fundamental understanding of their physicochemical properties, their any unusual properties and phase behavior is essential for chemists. Moreover, an understanding of the basic phenomena involved in the application of surfactants in the preparation of emulsion, foam, microemulsion and in wetting and adhesion is of vital importance in arriving at the right composition and control of the systems involved. Therefore it is necessary to know what exactly this surfactant / amphiphile molecule is?

The word amphiphile was coined by Paul Winsor 50 years ago. It comes from two Greek roots. First the prefix amphi which means "double", "from both sides", and the philos which expresses friendship or affinity. An amphiphilic substance exhibits a double affinity, which can be defined from the physico-chemical point of view as a polar-apolar duality. A typical amphiphilic molecule consists of two parts : a polar group containing hetero atoms such as O, S, P, or N, in functional groups such as alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide and apolar group which is in general a hydrocarbon chain of the alkyl or alkylbenzene type, sometimes with halogen atoms and even a few non-ionized oxygen atoms. The polar portion exhibits strong affinity for polar solvents, particularly water, and it is often called hydrophile or head. The apolar part is called hydrophobe or tail as shown in Figure 1.1.

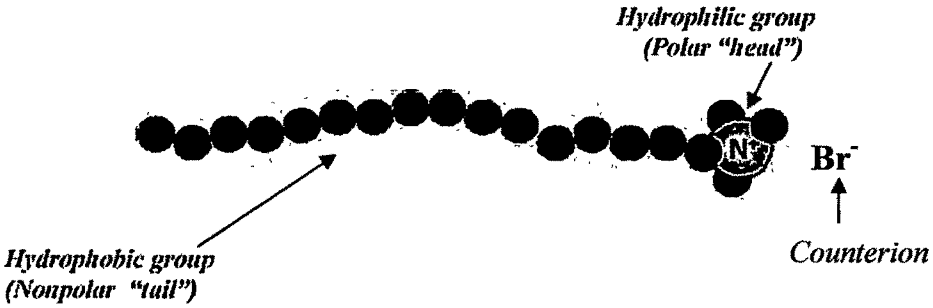


Figure 1.1 Schematic representation of a cationic surfactant molecule.

Because of its dual affinity, an amphiphilic molecule does not feel "at ease" in any solvent, be it polar or non-polar, since there is always one of the groups which do not like the solvent environment. This is why amphiphilic molecules exhibit a very strong tendency to migrate to interfaces or surfaces and to orientate so that the polar group lies in water and the apolar group is placed out of it and eventually in oil. Surfactant molecule is characterized by its tendency to adsorb at surfaces and inter-faces. The term interface denotes a boundary between any two immiscible phases such as,

- Solid-vapour
- Solid- liquid
- Solid- solid
- Liquid – vapour
- Liquid – Liquid

The driving force for a surfactant to be adsorbed at an interface is to lower the free energy at the phase boundary. The interfacial free energy per unit area represents the amount of work required to expand the interface. The term interfacial tension is often used instead of interfacial free energy per unit area.

Thus, the surface tension of water is equivalent to the interfacial free energy per unit area of boundary between water and air above it. When the boundary is covered by surfactant molecules, the surface tension is reduced. The denser the surfactant packing at the interface, larger the reduction in surface tension.

Surfactants may adsorb at all of the five types of interfaces listed above. The discussion here will be restricted to interfaces involving a liquid phase. The liquid is usually, but not always water. Examples of the different interfaces and products in which these interfaces are important are given in Table 1.1.

Table 1.1 Examples of interfaces involving a liquid phase.

Interface	Type of system	Product
Solid-liquid	Suspension	Solvent-born paint
Liquid-liquid	Emulsion	Milk, cream
Liquid-vapour	Foam	Shaving cream

In many formulated products several types of interfaces are present at the same time. Water-based paints and paper coating coloures are familiar examples but, from a colloidal point of view, very complicated systems contain both solid-liquid (dispersed pigment particles) and liquid-liquid (latex or other binder droplets) interfaces. In addition, foam formation is a common (but unwanted) phenomenon at the application stage. All of the interfaces are stabilized by surfactants. The widespread importance of surfactant in practical applications and scientific interest in their nature and properties have precipitated a wealth of published literature in the subject. Several books and reviews related to surfactants have been published in the past which are the indicators of their importance in daily life [2-20].

1.2 Classification

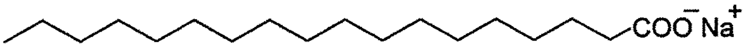
Surfactant is an amphiphilic substance consisting of a long chain hydrophobic hydrocarbon " tail" and a hydrophilic polar "head" which may be ionic or nonionic. Based on the charge on the polar head group and its molecular structure, surfactants have been classified in four main classes namely

- Anionic.
- Cationic.
- Non-ionic
- Zwitterionic

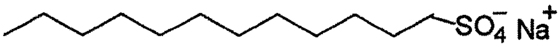
They can further be sub classified as

- Polymeric surfactants
- Silicone surfactants
- Bolaform surfactants
- Multiheaded single-chain surfactants
- Hybrid surfactants and
- Gemini surfactants.

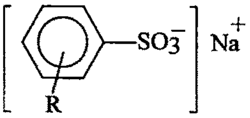
Anionic surfactants give rise to a negatively charged surfactant ion and a positively charged counter ion upon dissolution in water. Examples of anionic surfactant groups include sulfonic acid salts, alcohol sulfates, alkyl benzene sulfonates, phosphoric acid esters, and carboxylic acid salts. Anionic surfactants tend to be good solubilizers and are relatively nontoxic. They have been used in petroleum oil recovery operations as well as in contaminant hydrogeology remediation applications. They are the oldest class of surfactants and are still used extensively. Some representative structures are given below.



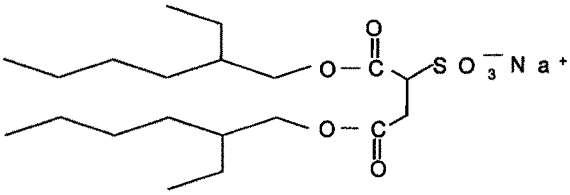
Sodium stearate



Sodium dodecyl sulphate (SDS)



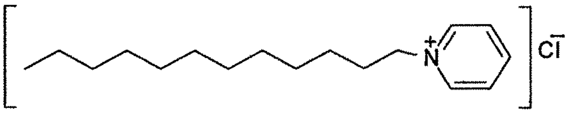
Sodium alkyl benzene sulphonate



Sodium bis (2-ethylhexyl) sulphosuccinate (AOT)

Cationic surfactants yield a positively charged surfactant ion and a negatively charged counter ion upon dissolution in water. Cationic surfactants first became important when the commercial potential of their bacteriosidic properties was recognized by Domagk in 1935 [21]. From this came a proliferation of hundreds of commercial products. Today, cationic surface active agents with antibacterial properties continue to play an important role as sanitizing and antiseptic agents, as components in cosmetic formulations and as germicides and fungicides. New applications include their use as antistatic agents, antiseptic agents, textile softeners, corrosion inhibitors, foam depressants, flotation chemicals and petroleum derivatives. Two common types of cationic surfactants are long chain amines and quaternary amine salts. The long chain amine types are made from natural fats and oils or from synthetic amines. They are soluble in strongly acidic medium but become uncharged and insoluble in basic medium. Quaternary amine type cationic surfactants are very important as fabric softeners. They adsorb on the surface of fibers with their hydrophobic groups oriented away from the fibers. This reduces the friction between fibers and imparts a soft, fluffy feel to the fabric. The same mechanism accounts for the behavior and use of cationic surfactants as hair conditioners. Quaternary ammonium salts are effective in neutral and alkaline as well as acidic medium. Following are some examples

Tetradecyl trimethyl ammonium bromide (TTAB)

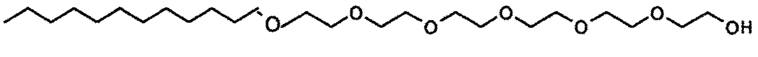


Dodecyl pyridinium chloride

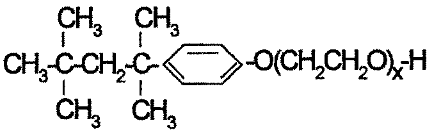
Generally cationic surfactants are more expensive than anionics. Hence, cationic surfactants are commercially used only if there is no other substituent. They are found as antistatic agents in fabric softeners and hair rinse formulas. They are used in textile manufacturing to delay dye adsorption. In this application they compete with dye and thus slow down their adsorption and help attaining an uniform colouration. Their action as corrosion inhibitor in acid environment is similar, but in this case they compete with hydrogen ions. Collectors for mineral floatation are often ammonium salts or quats. Asphalts emulsions for roadway pavement and protective coatings and paints are often stabilized by fatty amine salts (at acidic pH) or quats (at neutral pH). Benzalkonium and alkyltrimethyl ammonium chloride or bromides are used as antiseptic agents, desinfectants and sterilizing agents. They are also incorporated as additives in nonionic detergent formulations for corrosion inhibition purposes, and in very small quantity in anionic powdered formulas to synergize detergency.

Nonionic surfactants are characterized by hydrophilic head groups that do not ionize in water. Examples include polyoxyethylenated alkyl phenols, alcohol ethoxylates, alkylphenol ethoxylates and alkanolamides. Nonionic surfactants tend to be good solubilizers and are relatively nontoxic. They are usually easily blended with other types of surfactants and therefore have found widespread uses. The performance of nonionic surfactants, unlike ionic surfactants, is relatively insensitive to the presence of salts in solution. Examples of nonionic surfactants are

$C_{12}E_6$ $C_{12}H_{25}(OCH_2CH_2)_6OH$

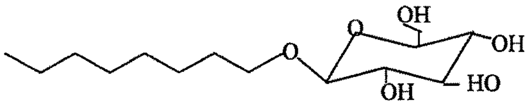


Hexa oxyethylene n- dodecyl ether



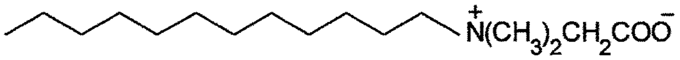
where x = 9 or 10

Poly oxyethylene t-octyl phenyl ether (Triton X 100)



Alkyl Poly Glycoside e.g Octyl β-D glucoside

Zwitterionic surfactants contain two charged groups of different signs. The positively charged group is almost invariably ammonium, whereas the source of negative charge may vary, although carboxylate is by far the most common. Zwitterionics are often referred to as amphoteric; but the terms are not identical. An amphoteric surfactant is one that changes from net cationic via Zwitterionic to net anionic on going from low to high pH. Neither acid nor the base site is permanently charged, i.e. the compound is only zwitterionic over a certain pH range. The change in charge with pH of the truly amphoteric surfactants naturally affects properties such as foaming, wetting, detergency etc. These will all depend strongly on solution pH. At the isoelectric point the physicochemical behavior often resembles that of nonionic surfactants. Below and above isoelectric point there is gradual shift towards the cationic and anionic character, respectively. Zwitterionics as a group of surfactants are characterized by their excellent dermatological properties. Due to lower eye irritation they are frequently used in shampoos and other cosmetic products. Following are some of the examples.



N-Dodecyl-N,N-dimethyl glycine

3-(Dimethyldodecylammonim)-propane-1-sulfonate

1.3 Novel Surfactants

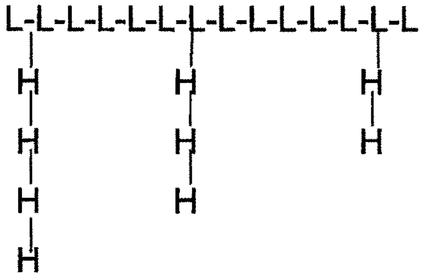
The last decade is known for the extension of use of surfactants in high-technology areas such as electronic printing, magnetic recording, biotechnology and microelectronics. As decreasing the quantity of surfactants used can contribute in reducing the load on the natural purification system, demand for high-performance surfactants is continuously increasing. Accordingly, novel surfactants have been successfully designed and developed [22-25]. In the following text a few important developmental trends within the surfactant field are discussed.

Polymeric Surfactants [26]

A macromolecule obviously needs to exhibit an amphiphilic structure. Asphaltenes, which are natural compounds found in crude oils, have polar and nonpolar groups. However, the location and segregation of these groups is often ill-defined, or at least less defined than in smaller molecules. There are two main configurations: ***"block"*** and ***"graft*"**, which are illustrated in the following scheme, where H and L represent hydrophilic and lipophilic monomer units, respectively.

Block type polymer H-H-H-H-H-H-H-H-L-L-L-L-L-L-L-L-L-L-L

Graft type polymer



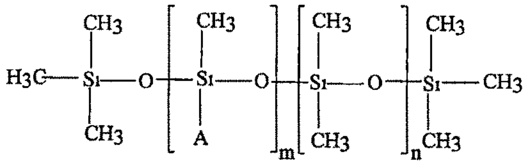
In the first case hydrophilic monomer units H are linked together to form an hydrophilic block, and lipophilic units L just do the same to form a lipophilic block. The result is a macromolecular surfactant with well defined and separated hydrophilic and lipophilic parts, which is just much bigger than a conventional surfactant molecule. The most used block polymer is the so-called copolymer of ethylene-oxide and propylene-oxide either with two or three blocks (as shown below). Although the hydrophilic and lipophilic parts are quite separated, the polymer polarity segregation is not that obvious since both groups are slightly polar, one (PolyEO) just barely more polar than the other (polyPO).

PEO-PPO-PEO: $HO\text{-}(CH_2CH_2\text{-}O)_x\text{-}(CH_2CHCH_3\text{-}O)_y\text{--}(CH_2CH_2\text{-}O)_x\text{-}OH$

These surfactants have many uses, in particular as colloid and nanoemulsion dispersants, wetting agents, detergents and even additive to dehydrate crude oils.

Silicone Surfactants [27]

The hydrophobic character of silicone oil, particularly dimethyl-polysiloxane is well known. The introduction of an organo-silicone group in a surfactant molecule tends to increase its hydrophobicity. Since Si is a heavier atom than C, a similar hydrophobicity is attained with less Si atoms than C atoms. Essentially all types of surfactants can be made with silicone based hydrophobic tail by replacing several C atoms by one Si atom or one dimethyl-siloxane group. Most of these surfactants can be crystallized in acetone to attain a high purity. Some of them are used in pharmacy as anti-flatulent surfactants since they are biologically inert. The general structure of silicone surfactant is as shown below



$A = (CH_2)_3—O—(C_2H_4O)_x—(C_3H_6O)_y—H$

m = number of polyether modified siloxane units, n = poly(dimethylsiloxane)units,
x = ethylene oxide, y = propylene oxide

Fluorinated Surfactants [19]

Hydrogen atoms of the surfactant hydrocarbon tail can be substituted by halogens, particularly fluorine (F) to produce fluorinated hydrophobes, which exhibit properties similar to polymerized tetrafluoroethylene (PTFE), known under the commercial brand name TEFLON. They exhibit high chemical inertia, mechanical and thermal resistance, low surface energy, and very high hydrophobicity. Unlike silicon compounds, the fluorinated tails sometimes won't mix with hydrocarbons. Hence, the polytetrafluorinated hydrophobe is also lipophobe with respect to hydrocarbons. Per fluorinated surfactants are prepared by polymerizing tetrafluoroethylene in the presence of methanol, so that the end product is an alcohol. The alcohol is then oxidized to produce a carboxylic acid or treated to synthesize another hydrophilic group: sulfate, amine or phosphate.

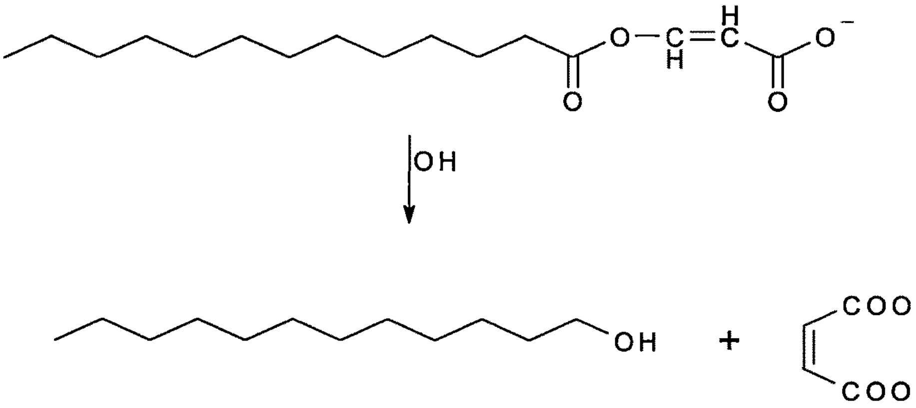
Example: $H(CF_2CF_2)_n\text{-}CH_2\text{-}OH$ $n = 2\text{-}4$

Sodium salt of perfluorinated acid in C_5 ($n = 2$) gives a good surfactant properties. This is perfectly consistent with the fact that its molecular weight (increased by 8 F atoms) becomes close to sodium palmitate MW. Salts of perfluorinated carboxylic acids are surfactants when they possess 5 to 9 carbon atoms. These salts dissociate much more than their hydrocarbon counterparts and tolerate high salinity and divalent cations. However, they are more expensive and their use is justified only in very special applications, as for instance in fire extinction foams, in which their thermal resistance is imperative. Perfluorinated carboxylates and sulfonates produce monolayer with less lateral interactions than their hydrocardon counterparts. They are able to turn a surface non-wettable to both water and organic solvents. They produce an interfacial tension down to 15 mN/m, i.e. twice as low as the value reachable with the best tension reducing hydrocarbon surfactants.

Hydrolysable surfactants [28]

Hdrolysable surfactants are surfactants in which a weak bond has been deliberately built in so that controlled breakdown will occur in acid, in alkali, by enzymatic catalysis or by other means. Acetal and ketal bonds are usually employed as acid-labile linkages. Esters are most commonly used to impart alkali sensitivity. There are several reasons behind the interest for hydrolysable surfactants. Firstly, surfactants with easily cleavable bonds can be expected to break down rapidly in the environment.

A second use of hydrolysable surfactants with limited stability is to have the cleavage product impart a new function. For instance, a surfactant used in personal care formulations may decompose on application to form products beneficial to the skin. Scheme1.1 illustrates another concept where a surfactant with good detergency properties breaks down under alkaline conditions to a hydrophobic fatty alcohol. Such a surfactant is of interest for combining cleaning and hydrophobization, e.g. in washing tents, rain clothes, etc. By controlling the pH of the formulation, the textiles will be washed and subsequently hydrophobized in a one-step process.

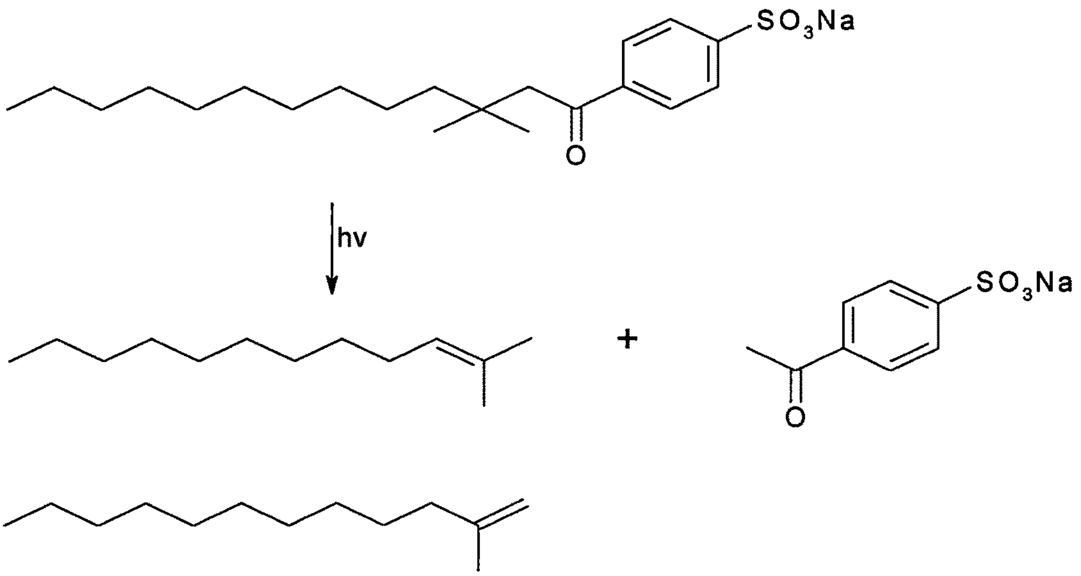


Scheme 1.1 Alkaline hydrolysis of an anionic hydrolysable surfactant into hydrophobic fatty alcohol and water soluble malate.

A third incentive for the development of cleavable surfactants is to avoid surfactant-related complications such as foaming or formation of unwanted, stable emulsions.

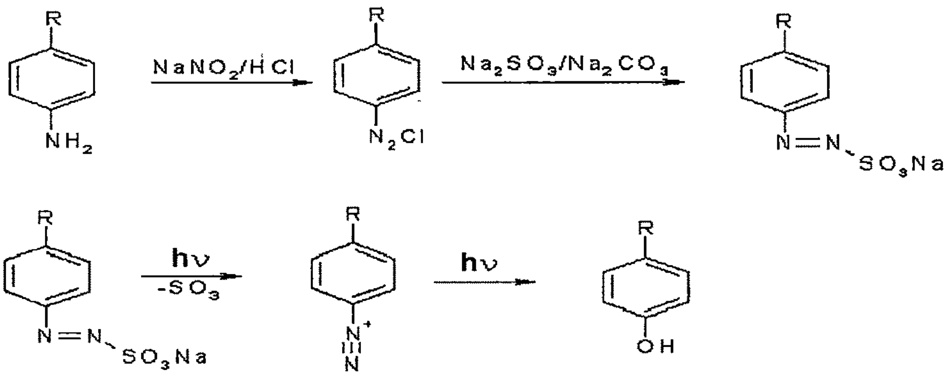
Light sensitive surfactants [29]

The concept of triggering cleavage of surfactant by UV light is attractive because it allows an extremely fast breakdown of the surfactant to occur. An alkylarylketone sulfonate, which bears some structural resemblance with alkylbenzene sulfonate surfactants, was synthesized by Epstein et al [30]. This compound is photocleaved into a water-soluble aryl sulfonate and a mixture of two methyl-branched olefins is formed, as shown in Scheme1.2. The surfactant is of interest for solubilization of proteins because the workup procedure is greatly facilitated by the instantaneous elimination of surfactant from the solution. The wavelength required for this type of photolysis, a so-called Norrish type II cleavage, is 300 nm and above. This low-energy radiation is generally harmless to proteins. In a series of studies Nuyken et al [31] prepared and investigated anionic surfactants containing the light-sensitive diazosulfonate group.



Scheme 1.2 Photocleavage of a surface-active alkyl aryl ketone

As can be seen from Scheme1.3, these surfactants are also similar in structure to the commonly used alkylbenzene sulfonates. A comparison of CMC values for the diazosulfonate and the normal sulfonate surfactants with the same 'R' substituent shows lower values for the former, indicating a contribution of hydrophobicity from the azo linkage.

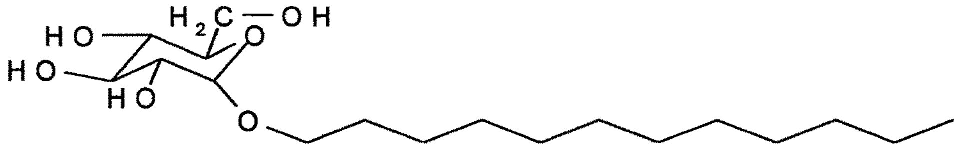


Scheme 1.3 Preparation and light-induced degradation of a diazosulfonate surfactant

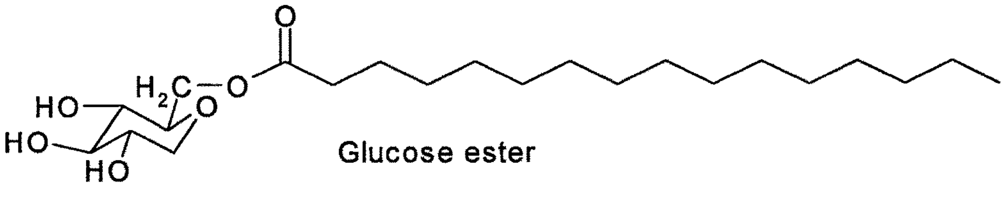
Photochemical cleavage yields sulfate ion and diazonium compound, which is further photolyzed in a second step. An interesting use of photolabile surfactants is as emulsifiers in emulsion polymerization [32, 33]. The use of a photolabile emulsifier opens the possibility to control the latex coagulation process simply by exposing the dispersion to UV irradiation. The ionic head group of the surfactant will be split off by photolysis leading to aggregation of the latex particles. Such latexes could be of interest for coatings.

Polyol surfactants [34, 35]

Polyol (Polyhydroxyl) surfactants are simple sugars, such as glucose or sucrose, cyclic polyols such as sorbitan, or acyclic compounds, such as polyglycerols (which may be regarded as a hybrid between polyhydroxyl and polyether). Hydroxyl groups are strongly hydrophilic, at the same time surfactants with long hydrocarbon chains are strongly hydrophobic. Therefore polyol surfactants have a high tendency to remain at the oil-water interface. Since aerobic, anaerobic biodegradation of these surfactants is fast they are rapidly biodegradable and show low aquatic toxicity. Structures of some representative polyol surfactants are



Alkyl glucoside



Glucose ester

Unlike ethoxylates the effect of temperature on solution behavior of polyol surfactants is small. Mixture of polyol surfactants (larger fraction) and ethoxylates (smaller fraction) can be formulated so that a non-ionic surfactant with phase behavior unaffected by temperature is obtained. Alkyl polyglucosides, *APGs,* are manufactured by direct reaction of glucose with fatty alcohol, using a large excess of alcohol in order to minimize sugar oligomerization. Sugar esters have traditionally been made by organic synthesis, yielding a complex mixture of esters. Glucose-based polyol surfactants having a disulfide linkage between the anomeric carbon of the sugar ring and the hydrophobic tail were synthesized and evaluated for use as solubilizing agent for membrane proteins. Cleavage into nonsurfactant products was performed by addition of dithioerythritol, which is known to split disulfide linkages under physiological conditions [36].

1.4 Physicochemical Properties and Performance of Surfactants

Most natural surfaces are negatively charged. Hence cationic surfactants will adsorb onto the surface with their positively charged hydrophilic head groups oriented towards the negatively charged surface and their hydrophobic tails oriented away from the surface making the surface water –repellent. Hence, if the surface is to be made hydrophilic (water-wettable), then cationic surfactant should be avoided and vice-versa.

Nonionics adsorb onto surface with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of the surface. If polar groups capable of H- bonding with the hydrophilic group of the surfactant are present on the surface, then the surfactant will probably be adsorbed with its hydrophilic group oriented toward the surface, making the surface more hydrophobic, if such groups are absent from the surface, then the surfactant will probably be oriented with its hydrophobic group toward the surface, making it more hydrophilic.

Table1.2 Applications of cationic surfactants based on their adsorption at surfaces.

Surface	Application as
Steel	Anticorrosion agent
Mineral ores	Floatation collector
Inorganic pigments	Dispersant
Plastics	Antistatic agent
Fibers	Antistatic agent, Fabric softener
Hair	Conditioner
Fertilizers	Anticacking agents
Bacterial cell walls	Bactericide

Since zwitterionics, carry both positive and negative charges, can adsorb on to both negatively charged and positively charged surfaces without changing the charge at the surface significantly. On the other hand, the adsorption of a cationic surfactant onto a negatively charged surface reduces the charge on the surface and may even reverse it to a positively charged. In similar fashion, the adsorption of an anionic surfactant on to a positively charged surface reduces its charge and may reverse it to a negatively charged. The adsorption of a nonionic onto a surface generally does not affect its charge significantly, although the effective charge density may be reduced if the adsorbed layer is thick.

The hydrophilic and lipophilic (or hydrophobic) moieties constituting surfactants are mainly responsible for it's being useful for a particular application. The hydrophilic and hydrophobic parts of a surfactant molecule have to be delicately balanced to result in formation of micelles. For example, short chain sodium alkanoates (C_1-C_5) are insufficiently hydrophobic and dissolve very easily in water due to the influence of the hydrated sodium ions and the hydrophilic character of polar carboxylate ions, and do not form micelles and behave like simple electrolytes. At the other extreme, longer chain sodium alkanoates ($>C_{18}$)

are almost insoluble in water due to hydrophobic long chain and ordinarily do not form micelles in water at room temperature. Alkanoates lying between these two extremes have been shown to be forming micelles in water. In order to make possible a more logical choice of surfactant for a particular system, Griffin has attempted to classify surfactants according to the strength and size of the hydrophilic and lipophilic portions of their molecules [37]. The balance of these two opposing groups is called the '**hydrophile-lipophile balance'** abbreviated as **HLB**. A surfactant where the lipophilic (hydrophobic) character is dominated has a low HLB value (below 9.0); one with dominant hydrophilic character has a high HLB value above 11.0, and that with moderately hydrophilic and moderately hydrophobic in the range of 9-11.

- When the hydrophilic group is in the middle of the surfactant molecular configuration, the wetting function is better than when it is at the end.
- When the hydrophilic group is at the end of the surfactant molecular configuration, the washing activity is better than when it is in the middle.
- If the surfactant structure remains chemically similar and has the same molecular size, the wetting and penetrant function of the surfactant is better with branched than nonbranched hydrophobic group configurations.
- As the surfactant molecular size becomes smaller, the wetting and penetrant function is better.
- As the hydrophobic group's branched configuration becomes larger, the washing and dispersion function of the surfactant is better.

General performance of a surfactant relative to molecular structure is given in the following series,

hydrophobic group strength decreasing as
aliphatic hydrocarbons > cyclanes > alicylic arenes > arenas

hydrophilic group strength decreasing as

sodium sulfates > potassium salt of organic acids > sodium salt of organic acids > -N (tertiary amine).

In general, in aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophobic tail increases to about 16. As a general rule for ionic surfactants with one hydrophilic group, the CMC is halved by the addition of one methylene (-CH_2) group. But for nonionic and zwitterionic surfactants, the magnitude of decrease in CMC is much larger. Chain branching and unsaturation of hydrophobic chain also has an influence on CMC. The CMC values increase with increase in the number of head groups of surfactant. If the chain length of hydrophobic group exceeds more than 18, the effect on CMC is limited as coiling of these long chains occur in water.

HLB and Use of Surfactants

Surfactants are characterized by the hydrophilic-lipophilic balance (HLB) ; a relative ratio of polar and nonpolar groups in the surfactant. Their use depends upon HLB. Some representative applications correlating to HLB are given here

HLB 1 to 3.5 : as antifoaming agents
HLB 3.5 to 8 : as emulsifiers for w/o system
HLB 7 to 9 : wetting and spreading agents
HLB 8 to 16 : as emulsifiers for o/w systems
HLB 13 to 16 : as detergents
HLB 15 to 40 : as solubilizers

1.5 Geminis: Surfactants of Next Generation

Another group of surfactants not discussed earlier is called as dimeric or gemini surfactants which are defined as surfactants made up of two identical amphiphilic moieties connected at the level of the head groups, or at the alkyl chains but still very close to the head groups, by a spacer which can be hydrophobic or hydrophilic, flexible or rigid [38-40]. A schematic representation of single chain, double chain and gemini surfactants is given in Figure 1.2.

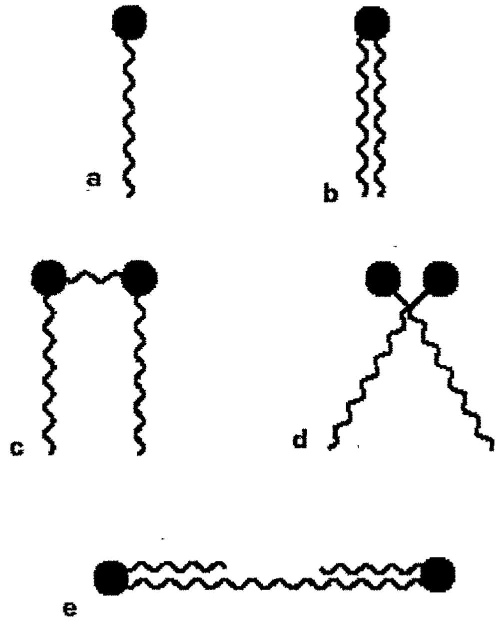


Figure 1.2 Schematic representation of different types of surfactants (a) single tailed, (b) double tailed, (c)&(d) gemini , (e) bolaform.

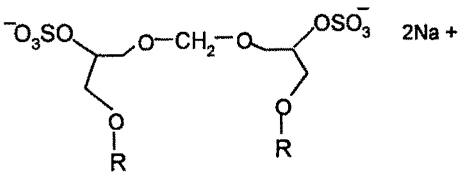
These surfactants have also been referred as “bipolar” or “bisquaternaryammonium” salts [41] in the case of cationic surfactants and even as “Siamese” [42] by analogy with siamese twins. These terms are all unsatisfactory because surfactants with two head groups and three alkyl chains and other surfactants featuring covalent binding of two or more than two amphiphilic moieties, not always identical are also synthesized. Nevertheless, the terms “dimeric” and “ gemini” are retained in this dissertation as most of the surfactants reviewed can be considered as made by covalently binding of two identical amhiphilic moieties, each comprising of one head group and one hydrophobic moiety, which may include more than one alkyl chains. It is essential that the spacer, whatever its nature, be located very close to the head groups. Indeed, when a fully hydrophobic spacer (polymethylene chain or aromatic group) connects the amphiphilic moieties far from the head groups, somewhere in the second half of the alkyl chains the dimeric surfactant is then simply a bolaform surfactant with a branched alkyl chain, characterized by a high critical micelle concentration (CMC) and poor performances [43].

Gemini surfactants can be further categorized depending on the charge on head groups as

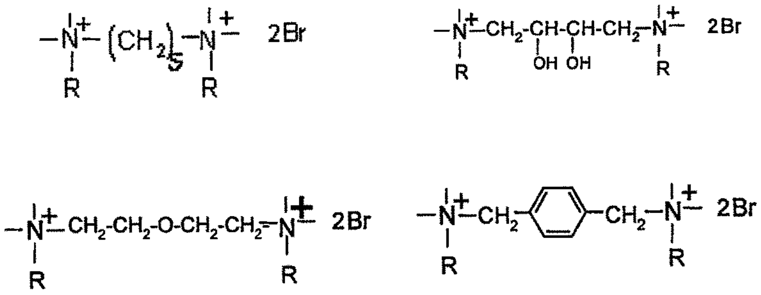
- Anionic surfactants
- Cationic surfactants
- Nonionic surfactants
- Zwitterionics surfactants and
- Hetero gemini surfactants.

Structures of some general representative gemini surfactants from all five categories are:

Anionic Gemini [44]

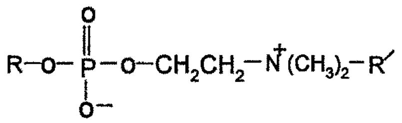


Cationic Gemini [45] bis (quaternary ammonium halide)



R is an alkyl chain where number of C atoms is 10-16. And in spacer, s is 2, 3, 4, 5, 6, 8, 10, 12, 16

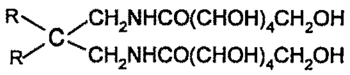
(iii) **Zwitterioinc Gemini** [46]



$$R-O-\underset{O^-}{\overset{O}{\overset{\|}{P}}}-O-CH_2CH_2-\overset{+}{N}(CH_3)_2-R'$$

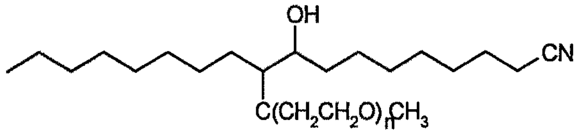
R and R ′ are an alkyl chains where number of C atoms is 6-14.

(iv) **Nonionic Gemini [47]** a di-sugar surfactant



R is an alkyl chain where number of C atoms is 6

(v) **Heterogemini Surfactant [48]**



where n is 8,12,16

Initial reports on dimeric surfactants concerned, mainly on use of bisquaternary ammonium halide surfactants as catalysts[49] and bioactive molecules [50]. Most studies, however, reported the surface tension measurements for CMC determination and an assessment of their capacity in reducing the surface tension of water. These studies did not arouse much interest among surface scientists in spite of the much lower values of the CMC and better biological activity compared to the corresponding monomeric conventional surfactants.

In early 90's after the synthesis of dimeric surfactants with a great variety of chemical structures, and their systematic studies revealed that such surfactants possess properties that make them superior to conventional monomeric surfactants [51-55]. Rosen [52] stated that these surfactants have "the potentials for being the next generation of surfactants -- surfactants for the nineties." He was much instrumental in the effort presently made in academic as well as industrial laboratories for a full understanding of the physicochemical properties of dimeric surfactants and for evaluating their performances in applications. The idea underlying the study of dimeric surfactants is that linking surfactants two by two (or three by three) may provide a newer way to control the shape of their aggregates (Figure 1.3) and thus some of their properties [55].

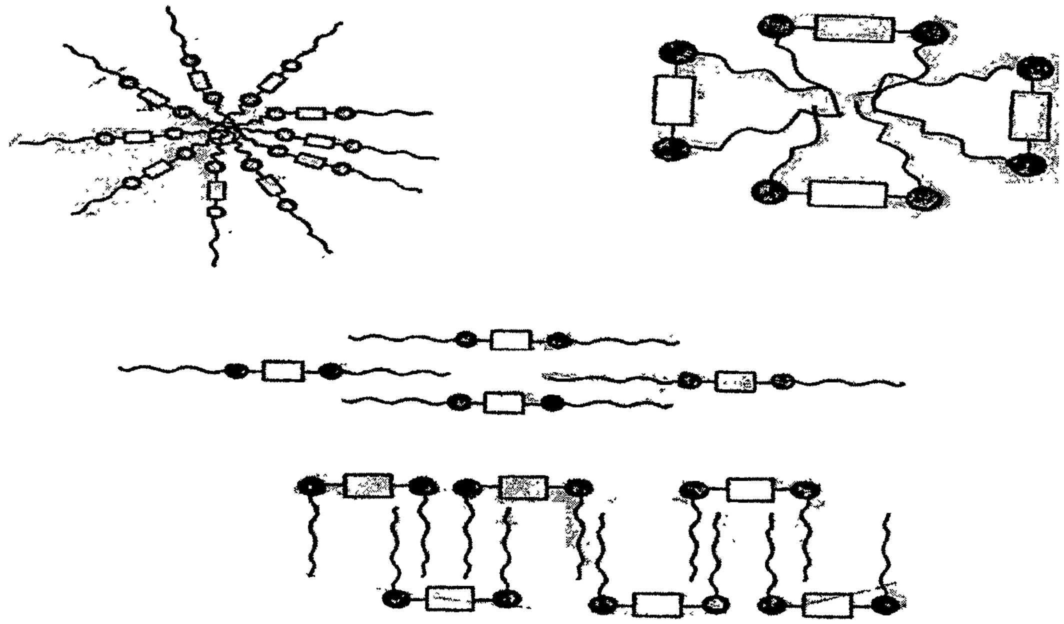


Figure 1.3 A schematic representation of possible "tunable" morphologies of gemini surfactant's micelles.

Moreover, they appear to have better solubilizing, wetting, foaming, and lime-soap dispersing properties than conventional surfactants [56]. These properties are commonly used to evaluate surfactant performances. Besides, the Krafft temperatures of dimeric surfactants with hydrophilic spacers are generally very low [53], giving these surfactants the capacity to be used in cold water. Some dimeric surfactants show remarkable rheological properties (viscoelasticity, gelification, shear thickening) at relatively low concentration, which are not observed with conventional surfactants having the same alkyl chain [57].

The alkanediyl-α,ω-bis(alkyldimethylammonium bromide) or bisquaternary ammonium bromides have been so far the most investigated dimeric surfactants[56]. These surfactants are designated by the abbreviation *m-s-m*, 2Br-, *s* and *m* being the carbon numbers of the alkanediyl group (spacer) and of the alkyl chain of the amphiphilic moieties.

1.6 Surfactant Solubility

In aqueous solution of surfactants, when all available interfaces are saturated, the overall surface energy reduction may continue through other mechanisms. Depending on the system composition, a surfactant molecule can play different roles in terms of aggregation (formation of micelles, liquid crystal phases, bilayers or vesicles, etc). The physical manifestation of one such mechanism is crystallisation or precipitation of surfactant from solution – that is, bulk-phase separation. While most common surfactants have a substantial solubility in water, this can change significantly with variations in hydrophobic tail length, head group nature, counterion valency, solution environment, and most importantly, temperature.

The Krafft temperature (k_T)

For most solutes in water, increasing temperature produces an increase in solubility. However, for ionic surfactants, which are initially insoluble, there is often a temperature at which the solubility suddenly increases very dramatically. This is known as the Krafft point or Krafft temperature, k_T, and is defined as the intersection of the solubility and the CMC curves, i.e., it is the temperature at which the solubility of the monomeric surfactant is equivalent to its CMC at the same temperature. This is illustrated in Figure 1.4. Below k_T, surfactant monomers only exist in equilibrium with the hydrated crystalline phase, and above k_T, micelles are formed providing much greater surfactant solubility. The Krafft point of ionic surfactants is found to vary with counterion and alkyl chain length [58]. Knowledge of the Krafft temperature is crucial in many applications since below k_T the surfactant will clearly not perform efficiently; hence typical characteristics such as maximum surface tension lowering and micelle formation can not be achieved. The development of surfactants with a lower Krafft point but still being very efficient at lowering surface tension is usually achieved by introducing chain branching, multiple bonds in the alkyl chain or bulkier hydrophilic groups, thereby reducing intermolecular interactions that would tend to promote crystallisation.

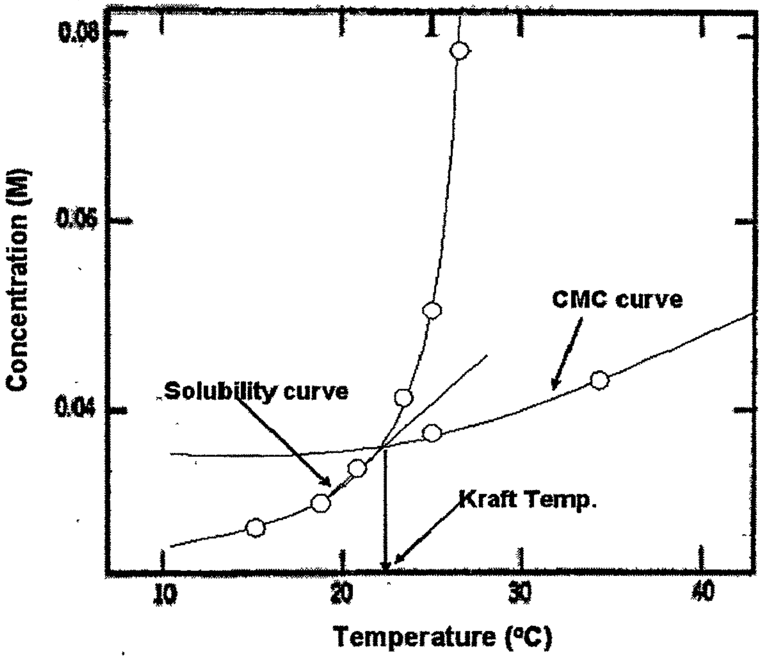


Figure 1.4 Surfactant solubility and the Krafft point.

The Cloud point (C_P)

For non-ionic surfactants, a common observation is that micellar solutions tend to become visibly turbid at a well-defined temperature. This is often referred to as the cloud point (Cp), above which the surfactant solution phases separate. Above the cloud point, the system consists of an almost micelle-free dilute solution at a concentration equal to its CMC at that temperature, and a surfactant-rich micellar phase (Figure 1.5). This separation is caused by a sharp increase in aggregation number and a decrease in intermicellar repulsions [59] that produces a difference in density of the micelle-rich and micelle-poor phases. Since much larger particles are formed, the solution becomes visibly turbid with large micelles efficiently scattering light. As like Krafft temperatures, the cloud point depends on chemical structure. For polyoxyethylene (PEO) non-ionics, the cloud point increases with increasing EO content for a given hydrophobic group, and at constant EO content it may be lowered by decreasing the hydrophobe size, broadening the PEO chain-length distribution, and branching in the hydrophobic group.

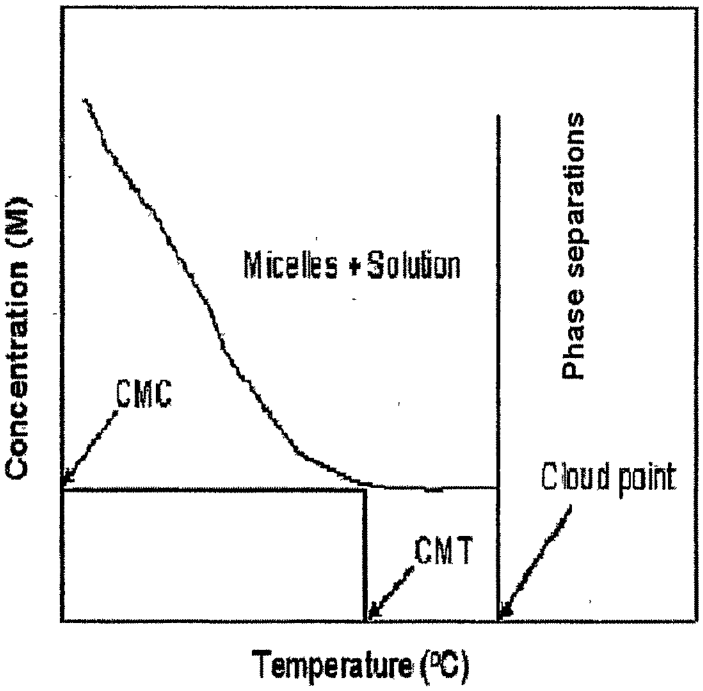


Figure 1.5 Surfactant solubility and the Cloud point

1.7 Critical Micelle Concentration (CMC)

It is well known that the physicochemical properties of surfactants vary markedly above and below a specific surfactant concentration, the CMC [60-62]. Below CMC, the physicochemical properties such as conductivity, electromotive force of ionic surfactants resemble to those of a strong electrolyte. Above CMC, these properties change dramatically, due to highly cooperative association of surfactant molecules. In fact, a large number of experimental observations can be summed up in a single statement; '**almost all physicochemical properties**

versus concentration plots for a given surfactant solvent system show an abrupt change in slope in a narrow concentration range (the CMC value)'. This is illustrated in Preston's [63] classical graph, illustrated in Figure 1.6.

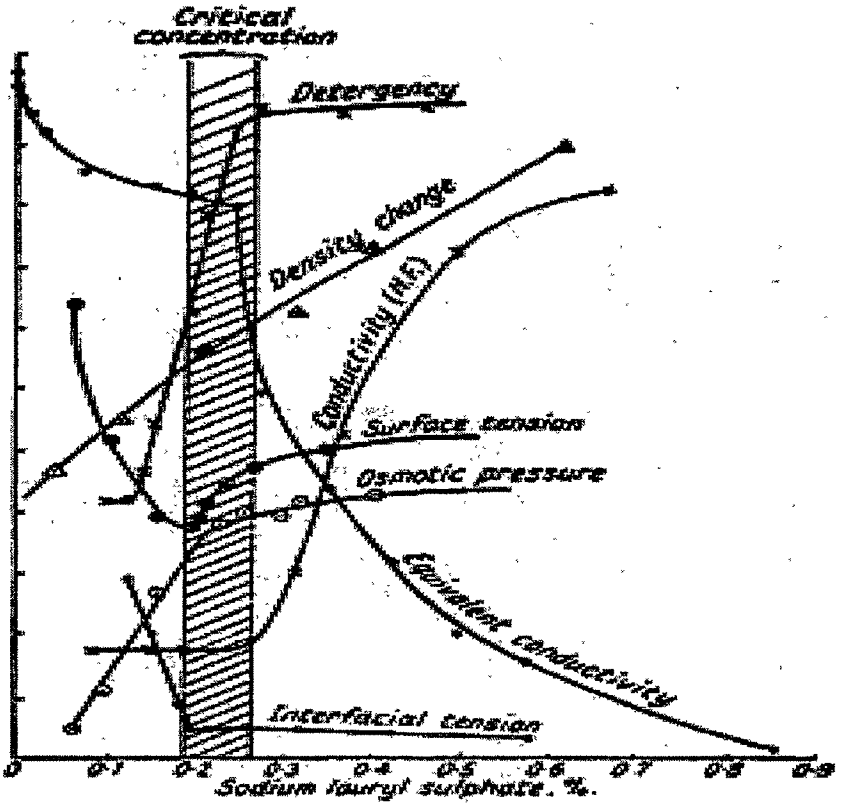


Figure 1.6 Schematic representation of concentration dependence of physicochemical properties for solutions of surfactant. The shading emphasizes the fact that the CMC is not necessarily sharply defined [Ref. 63]

In the pseudo-phase separation model micelles are treated as a separate phase and CMC is defined as the concentration of maximum solubility of the monomer in that particular solvent. The pseudo-phase model has a number of short-comings. However, the concept of CMC as is described in this model is very useful while discussing the association of surfactant into micelles. It is for this reason that the CMC value is perhaps, the most frequently measured and discussed micellar parameter.

CMC Measurement

The general way of obtaining the CMC value of a surfactant is to plot some physicochemical properties of interest versus the surfactant concentration and observe break in the plot. Table 1.3 lists the most commonly used methods for CMC measurement. Many of these methods have been reviewed by Shinod [64] Mukerjee and Mysels [65]. It should be noted that different experimental techniques may give slightly different values for the CMC of a particular surfactant. The nature and limits of applicability of specific methods for determining CMC vary widely.

Table 1.3 Some commonly used methods for CMC determination [66-68].

- UV/visible, IR spectroscopy
- Fluorescence spectroscopy
- Nuclear magnetic resonance spectroscopy
- Electrode potential/ Conductivity
- High resolution Ultrasonic Spectroscopy
- Scattering techniques
- Surface tension and foaming

The colligative properties of surfactants in aqueous solution do vary with concentration at lower concentration range as usually observed for solutions of conventional solutes. However, the physical properties of surfactants differ from those of smaller or non-amphiphilic molecules in one major aspect, namely the abrupt changes in their properties above a certain critical concentration. This is shown in Figure1.6. The physical properties include equivalent conductivity, turbidity, surface tension, osmotic pressure, self diffusion, magnetic resonance, solubilization, detergency, density change and micro viscosity.

All these surface or bulk properties show an abrupt change at a particular concentration which is consistent with the fact, that at and above this concentration the surfactant monomers associate to form larger units called "micelles" and the concentration at which this phenomenon (micellization) occurs is termed as the "critical micelle concentration" (Figure 1.7). Each surfactant has a characteristic value of CMC at a given temperature.

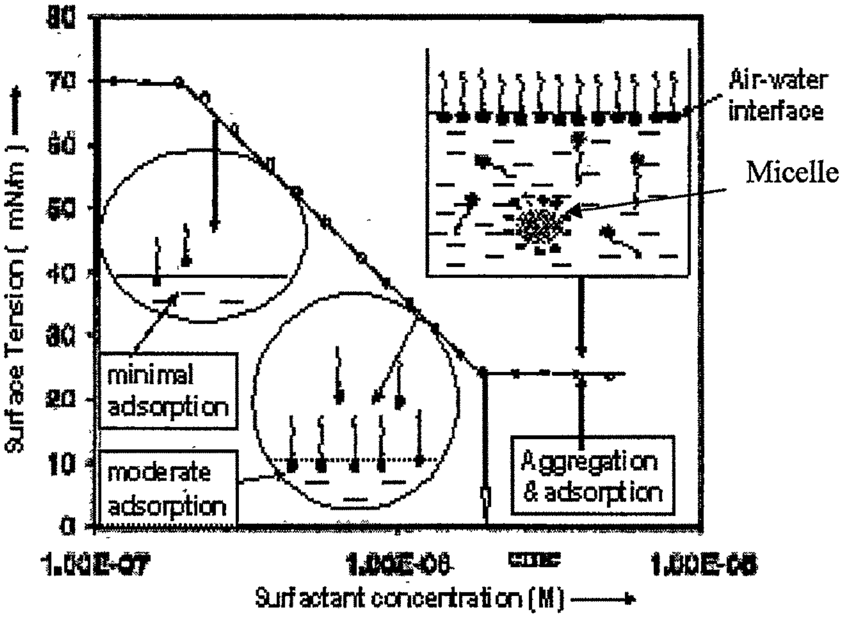


Figure 1.7 Surfactant adsorption and aggregation as a function of surfactant concentration and surface tension.

1.8 Factors Affecting CMC

The CMC is characteristics of surfactant and depends upon various factors such as hydrophobicity of hydrocarbon chain [70], nature of the head group [71], counterion [72], temperature[73], pressure[74], pH[75], presence of electrolytes[76], polar[77] and non-polar [78] additives etc.

In aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophobic tail increases to about 16 [79]. As a general rule for ionic surfactants with one hydrophilic group, the CMC is halved by the addition of one methylene group [80]. But for nonionic and zwitterionic surfactants the magnitude of decrease in the CMC is much larger. However, as the chain length exceeds to more than 18 carbon units the effect on CMC is limited as coiling of these long chains occurs in water [81].

Introduction of polar groups such as –OH in the hydrophobic chain increases the CMC. Also, the surfactants with bulky hydrophobic / hydrophilic group delay the micelle formation due to steric effects. The fluorocarbon based surfactants with same number of carbon atoms as the hydrocarbon based ones have lower CMC [82].

In general ionic surfactants have slightly higher CMC values compared to zwiterionics which have again much higher values than nonionics for the same number of carbon atoms. Gemini surfactants have much lower CMC than conventional monomeric surfactants [72]. If the ionic hydrophilic group is closer to the α-carbon atom of the hydrophobic group of the surfactant, the CMC increases[83] . In quaternary cations, for example $C_{12}H_{25}$ $N^{+}(R)_3$ Br^{-} the CMC decreases as the length of R increases due to increasing hydrophobicity.

In case of polyoxyethylene type nonionic surfactant C_nE_8 (n = 9-15), as the number of carbon atoms increases the CMC decreases [84]. Rosen et al [85] for

$C_{12}E_m$ (m = 1-8) and Crook et al [86] for p-tert octylphenoxypoly (ethenoxyethanol) have reported, increase in the CMC values with increasing hydrophilicity in the molecule.

In conventional ionic surfactants a change in counterion to one with the greater polarizibility or valency, leads to decrease in the aggregation number. Decrease in the CMC with increase in binding of counterion to micelles formed from hexadecyl and tetradecyltrimethyl ammonium salts with various counterions is reported by Sepulveda and Cortes [87].

The use of additives is a common method to alter the aggregation behavior of surfactants. The presence of a third component in the solution can modify the micellization process in two different ways [88-91]:

- Through specific interactions with the surfactant molecules
- By changing the solvent nature.

In this respect the aqueous solvent properties are modified by the addition of electrolytes and non-electrolytes.

The electrolyte effect on the CMC is more pronounced for anionic and cationic surfactants where a depression in CMC is observed. Addition of electrolyte causes a reduction in thickness of ionic atmosphere surrounding the head groups, consequently decreasing the repulsion between them. Maltesh, Somasundaram [92] and Mukerjee [93] have reported the CMC values for sodium dodecyl sulfate(SDS) in the presence of various electrolytes such as NaCl, Na_2SO_4, LiCl, CsCl, Cs_2SO_4, $MgCl_2$, $MgSO_4$ and $Na_3(PO_4)_2$. All these electrolytes showed decrease in the CMC of SDS.

The effect of temperature on the CMC of ionic and nonionic surfactants is generally attributed to the characteristics features of solubility- temperature relationships. The variation of CMC with temperature for ionic and nonionic surfactant is shown in Figure 1.8.

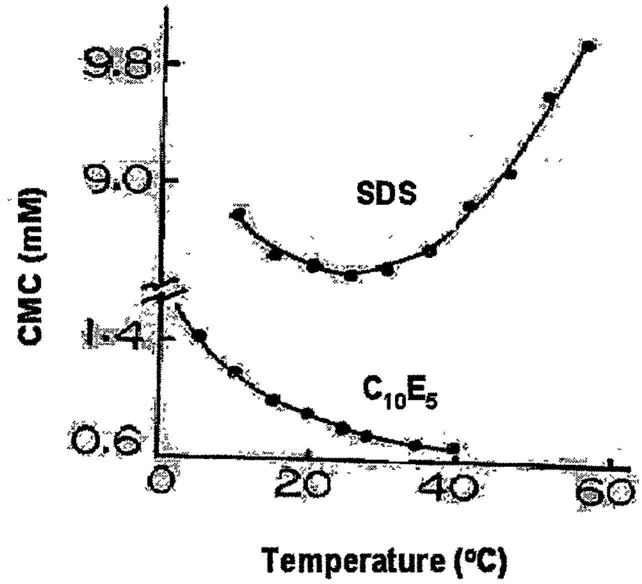


Figure 1.8 Variation of CMC with temperature for sodium dodecyl Sulphate(SDS) and $C_{10}E_5$

In case of nonionic surfactants as the temperature decreases the CMC increases. Although, a minimum is observed at relatively higher temperatures e.g. octyl phenoxy ethoxyethanols with oxyethylene chain lengths between 6-10 at approximately 50°C. The well known dehydration phenomenon is quite predominat with increasing temperature for nonionics. In other words hydrophobicity increases with increasing temperature. Many factors contribute to the temperature effect on nonionic surfactants e.g.

- The change in water structure around the ethylene oxide units
- Change in the hydrogen bonding networks around the EO groups
- Changes in the conformation of EO groups [86,94].

However, in ionic surfactants an altogether different behavior is observed. The CMC temperature relationship is complex. The CMC increases with increasing temperature passing through a minimum at lower temperature region. This decrease in the CMC at lower temperature region can be ascribed to the lowering of hydrophilicity. Further increase in the CMC with temperature is due to the disruption of water structure around the hydrophobic portion of the surfactant molecule that opposes the micellization hence higher CMC [95]. The position of the minimum [96, 97], has a thermodynamic significance i.e. the minimum in the CMC represents the minimum in standard free energy of micelle formation that occurs at temperature at which $\Delta H^{o}_{m} = 0$. Mesa [98] has given an experimental evidence to show that the temperature at which minimum in CMC is observed is the temperature at which ΔH^{o}_{m} is practically zero. He has also reported that the increase in pressure initially retards micelle formation and later on favors after a certain threshold value of pressure is reached. The increase in CMC is due to the breaking of water structure at higher pressure. According to Moulik [95] the release of surfactant monomers at lower pressures and their association at higher pressures together with changed dielectric constant of solution with applied pressure also play vital role in the self-organization.

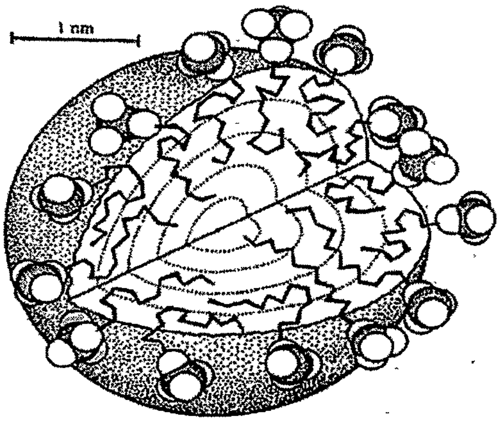
The CMCs of a series of alkyl trimethyl ammonium bromides and sodium dodecyl sulfates showed a maximum in the CMC-pressure profile [88]. Further evidence for a maximum in CMC-pressure plot was presented by Nishikido et al [99]. The overall effect of pressure on CMC of surfactants can be ascribed to

- The solidification of micelle interior
- A pressure induced increase in the dielectric constant of water and
- The changes in the water structure.

Measurements of CMC at high pressures were carried out by many workers. Sugihara and Mukerjee [100] have determined the CMC of aqueous solution of sodium perfluorodecanoate at different pressures and temperatures. Similar studies of effect of pressure on the CMC of nonyl N-methylglucamine / sodium perfluoro octanoate mixed systems was done by the same workers [74,101].

1.9 Aggregation Behavior of Surfactants

When surfactants are dissolved in water, the hydrophobic group disrupts the hydrogen bonded structure of water and therefore increases the free energy of the system. Surfactant molecules therefore concentrate at interface, so that their hydrophobic groups are directed away from the water and the free energy of the solution is minimized. The distortion of the water structure can also be decreased (and the free energy of the solution reduced) by the aggregation of surface-active molecules into clusters (micelles) with their hydrophobic groups directed towards the interior of the cluster and their hydrophilic groups directed towards the water [102]. When the surfactant molecules are packed close together at the interface, they undergo cooperative self-association in the bulk resulting in the formation of micelles and this process is termed as micellization. A schematic representation of an ionic micelle is shown in Figure 1.9.



Figures 1.9 Organization of surfactant molecules in a typical spherical micelle (three-dimensional structure)

As all chemical systems tend towards a state of minimum free energy; the aggregation of surfactant molecules to form micelles must result in a free energy decrease. The formation of micelles can be explained on the basis of the hydrophobic effect. In an aqueous solution of a surfactant, there is distortion of the water structure by the hydrophobic group of the surfactant, and the resulting increase in the free energy of the system, implies that less work is needed to bring a surfactant molecule compared to a water molecule to the surface. On the other hand hydrophilic group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The structure of the surfactant, therefore, causes not only adsorption of the surfactant at the surface and reduction of surface tension, but also orientation of the molecule at the surface, with hydrophilic group in the aqueous phase and hydrophobic group oriented away from it.

However, the surfactant molecules transferred from the bulk solution to the micelle may experience some loss of freedom from being confined to the micelle. In addition, they may experience an electrostatic repulsion from other similarly charged surfactant molecules in the case of ionic surfactants. These forces increase the free energy of the system and oppose micellization.

Aggregate morphology is mainly determined by a delicate balance between attractive hydrophobic interactions of surfactant alkyl tails and electrostatic repulsions of surfactant head groups [103]. In addition to repulsive interactions of electrostatic origin, repulsions due to hydration of the head groups must be taken into account. An opposing effect is exerted by the interfacial tension that tends to decrease the effective head group area. The molecular architecture of a given surfactant determines the type of aggregate into which a surfactant associates in aqueous solution. The relationship between the shape of the surfactant monomer and the aggregate morphology can be represented by the packing parameter approach [104].

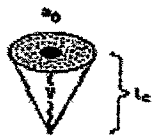
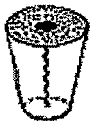
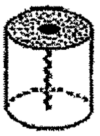
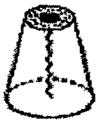
The packing parameter (P) is calculated using equation

$$P = V/a_0 l$$

where V is the volume of surfactant molecule, l is chain length of the extended alkyl tail, and a_0 the mean cross-sectional (effective) surface area of head group.

Surfactant molecules with packing parameter P < 1/3, form spherical micelles, with P in the range1/3-1/2, form ellipsoidal/cylindrical micelles and p in the range 1/2 – 1, form vesicles/bilayers. Inverted structures or reverse micelles are formed when P >1. The Table 1.4 shows the relationship of the architecture of surfactant monomer and aggregate morphology.

Table 1.4: Relationship between the shape of surfactant monomers and preferred aggregate morphology

Effective shape of the surfactant molecule		Packing parameter (P)	Aggregation morphology (Geometry of micelle)
	Cone	< 1/3	Spherical micelle
	Truncated cone	1/3-1/2	Ellipsoidal micelle
	Cylinder	1/2 – 1	Rod like, Vesicles, Bilayer micelle
	Inverted cone	>1	Reverse micelle

The architecture of a given surfactant monomer is important in determining the morphology of the aggregate into which surfactants self-assemble. Moreover, either addition of certain compounds or changing the conditions (e.g. temperature or surfactant concentration) can also influence the aggregate morphology.

Effect of surfactant concentration

An increase in surfactant concentration above CMC leads to the formation of more number of micelles [105], resulting into a decrease in the average distance between micelles and an increase in intermolecular repulsions. In order to accommodate the surfactants, spherical micelles may transform into wormlike micelles, where the distance between aggregates increases. The system thus rearranges into aggregates of higher order. Upon further increasing the surfactant concentration, lyotropic liquid crystals can be formed. Two commonly observed liquid crystalline phases are the normal hexagonal phase formed by infinite cylindrical aggregates packed in a two-dimensional array and the lamellar phase.

Effect of counterion

Counterions have a large influence on the morphology that surfactant aggregates adopt in aqueous solution [106]. Changing the counter ion of ionic surfactants for a more strongly bound one leads to a decrease in the effective head group area leading to micellar growth. Especially aromatic counterions like tosylate, benzoate, or salicylate are effective in inducing micellar growth [106-111]. In addition to a decrease in effective head group area (a_0), penetration of the aromatic ring of a counter ion between the surfactant molecules leads to an increase in the volume of the surfactant monomer. A combination of both effects results in an increase in P and consequently the surfactants self-assemble into a less curved aggregates. This case corresponds to a change from spherical to wormlike micelles. Upon growing, wormlike micelles may form a three dimensional network that shows viscoelasticity. The orientation of substituents on the aromatic ring appears to be extremely important for inducing viscoelasticity. For example, hexyltrimethylammonium o-hydroxybenzoate surfactants form a viscoelastic solution whereas this solution is not formed when the OH substituent is either in the meta or para position [112,113]. Molecular motions of threadlike micelles are fast and the aggregates are more dynamic [114,115].

Addition of oppositely charged surfactants

Aqueous solutions of mixed ionic surfactants (cationic and anionic) may have properties that differ considerably from aqueous solutions of the individual surfactants [116,117]. For example, aggregate morphologies are usually vesicular at low surfactant concentrations of the mixed systems whereas individual surfactants form spherical micelles at low concentration. The effective head group area decreases due to electrostatic interactions between the ionic head groups and due to release of water of hydration in case of mixed ionic systems. The volume of the alkyl tails remains the same. This result in a cylindrical shape for the cationic surfactant which will consequently self assemble to form vesicular structures in aqueous solution.

Effect of temperature

Change in temperature can have dramatic effect on the morphology of aggregates formed from nonionic surfactants. The main reason for these changes is the dependence of hydration of nonionic head groups on the temperature. Mixtures of nonionic oligo(ethylene oxide) dodecyl ether ($C_{12}EO_n$) surfactants and phosphatidyl cholines like dioleylphosphatidylcholine (DPPC) undergo a reversible micelle-to-vesicle transition upon increasing the temperature [118-122]. The hydration layer of the oxyethylene groups is reduced upon increasing the temperature leading to a decrease in the effective head group area of $C_{12}EO_n$. Moreover, the hydrocarbon chains of DPPC are in more compact cylindrical shape below the gel-to-liquid crystalline phase transition temperatures than above. A combination of both effects leads to a change in the shape of the $C_{12}EO_n$/DPPC surfactant combination from a cone to a cylinder upon increasing the temperature. Similar observations have been made with respect to aqueous mixtures of (nonionic) sugar based surfactants and phosphatidylcholine lipids [123]. In contrast, micelle-to-vesicle transitions in aqueous mixtures of phosphatidylcholine and octyl glucoside occur upon decreasing the temperature [124]. Most likely, this results from the temperature dependence of the CMC of octyl glucoside that decreases from 31 mM at 5°C to 16 mM at 40°C. In other words, the membrane solubilizing power of octyl glucoside decreases upon decreasing the temperature. Although hydration of ionic head groups is less sensitive to temperature changes than head group hydration of nonionic surfactants [125].

1.10 Mixed Surfactant System

Surfactants used for almost all industries and commercial scales are invariably mixtures due to their economic and beneficial effects over individual surfactants. In the complex world of surfactant formulation, the surfactant technologist needs to have working knowledge of principles involved in the mixing of surfactant as per the desired application. This includes an understanding of mixed surfactant behavior both in the end use domain as well as in the formulation domain. Hence, in order to tailor the properties of the surfactant solution to best suit the desired application, one must be able to predict and manipulate

- The tendency of surfactant solution to form micelles as reflected by the CMC
- The shape and size distribution of the micelles that form above the CMC
- The phase behavior of surfactant solution.

Mixed micellar systems could also arise due to the deliberate mixing of different surfactant types to exploit synergistic behavior in mixed systems or to have multiple qualities belonging to individual components in one mixture. Although, incorporation of solubilizates into surfactant micelles also results in the formation of mixed micelles, generally the term mixed micelle is used to represent a micelle that is composed of surfactants that are themselves capable of forming micelles. Mixed surfactants also micellize after critical micelle concentration like single surfactants. The tendency to aggregate is guided by their synergistic (attractive) and antagonistic (repulsive) interactions and this is reflected in their CMC values. Mixed surfactant systems, as is the case with single surfactant systems, exhibit preferential adsorption at interfaces at low concentration forming mixed monolayers leading to lowering of surface tension. At concentrations above CMC, surfactant molecules undergo co-operative self-association in the bulk to form mixed micelles. Different techniques have been used to collect structural information on mixed micelle formation, and to obtain their CMC [126-128].

During the formation of mixed micelles, both ideal and non-ideal mixing can occur. Since the hydrophobic effect, which drives the aggregation process, is not specific to surfactant head group, the formation of randomly mixed surfactant aggregates will be favored and this leads to the ideal component of mixing. But in the case of mixtures comprising of different surfactants, the electrostatic repulsion between the head groups lead to non-ideal mixing in the aggregate.

Mixing of dissimilar surfactants often leads to synergistic or anti-synergistic behavior due to the non-ideal interactions of the components. Synergistic results in substantially lower CMCs and interfacial tensions than the individual surfactant systems. This has lead to both theoretical and practical interest in the understanding of the behavior of mixed surfactant systems so that they could be exploited in fields such as detergency, enhanced oil recovery etc.

Mixed micellar systems involving a wide range of surfactants have been studied and include combinations of nonionic, anionic and cationic systems and their binary mixtures with zwitterionic surfactants [129-133].

1.11 Thermodynamics of Micellization

Almost all the physicochemical processes are energetically controlled. One of the most important characteristics of surfactant solutions is the micellization process. Hence a thorough knowledge of the driving force favoring micellization is highly important. This requires the detailed analysis of dynamic process (i.e kinetic aspects) whereby the laws of the thermodynamics may be applied to obtain the standard free energy, enthalpy and entropy of micellization. Two main approaches to the thermodynamics of micellization have gained wide acceptance

- The pseudo phase separation model and
- The mass action model.

Pseudo phase separation model considers the micelle as a separate phase at CMC and in the case of ionic surfactants also includes counter ions. In the calculation of thermodynamic parameters of micellization, the hypothetical standard state for the surfactant in aqueous phase is taken to be the solvated monomer at unit mole fraction with the properties of infinitely dilute solution. For nonionic surfactant the standard free energy of micellization is given by the equation

$$\Delta G^{o}_{m} = RT \ln X_{CMC}$$

Where X_{CMC} = CMC in mole fraction scale as defined by X_{CMC} = CMC (moles/lit) + H_2O (mole/lit). The ΔG^{o}_{m} measures the standard free energy change for the transfer of one mole of surfactant from solution to micellar phase. The corresponding standard enthalpy and entropy of micellization per mole of surfactant can be computed from well known relations

$$\Delta H^{o}_{m} = - RT^{2}(d\ln CMC/dT)$$

$$\Delta G^o{}_m = \Delta H^o{}_m - T\Delta S^o{}_m$$

In the computation of $\Delta G^o{}_m$ for ionic surfactants apart from the transfer of surfactant molecules from aqueous phase to micellar phase the transfer of (1- α) mole of counterions from its standard state to micelle is also to be considered, thus

$$\Delta G^o{}_m = (2-\alpha)\, RT \ln X_{CMC}$$

Where α is the average degree of ionization of micelles computed from the ratio of the slopes of the conductance vs concentration plot of post micellar region to pre micellar region [134]. Evans and Ninham[135] and Treiner and Makayassi [136] investigated another method for the evaluation of α if aggregation number is known.

The mass action model assumes that the micelle and the undessociated surfactant ions are in the association- dissociation equilibrium. This model was originally applied to ionic surfactants and later developed for nonionics too. The standard free energy of micellization per mole of surfactants is given by

$$\Delta G^o{}_m = RT \ln X_{CMC} \text{ (for nonionics)}$$

$$\Delta G^o{}_m = (2-\alpha)\, RT \ln X_{CMC} \text{ (for ionics)}$$

However, the equations differ only in the way by which the mole fractions are evaluated. In phase separation model the total number of moles present at CMC is equal to the sum of number of moles of water and surfactant whereas the total number of moles in the mass action model is equal to the moles of water, surfactant ions, surfactant in micelles and free counterions.

Also, few researchers have computed the thermodynamic parameters of micellization using the model of Evans and Ninham [135] given as

$$\triangle G^{o}_{m} = RT \ln CMC = \triangle G^{o}_{Hp} + \triangle G^{o}_{s}$$

Where $\triangle G^{o}_{m}$ is the total Gibb's energy per surfactant molecule associated with micelle formation, $\triangle G^{o}_{Hp}$ is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to micelle interior, $\triangle G^{o}_{s}$ explains the surface contributions that include the energy associated with electrostatic interactions between the head group and counterion.

Thermodynamic parameters for micellization of n-alkyl trimethyl ammonium bromides (n = 10,12,14) and thermodynamic properties of N-octyl trimethyl ammonium bromide in different media have been thoroughly investigated by Sarmiento et al [137].

Moroi et al. [138] have investigated the contribution of hydrophilic and hydrophobic groups to the enthalpy change for four kinds of sodium alkyl sulfates with different chain lengths of C_8 to C_{14} in the temperature range of 10 - 55^{0}C. Mukerjee et al. [139] have computed the thermodynamic parameters of micelle formation for sodium perfluorooctane. Micellization in various peptide molecules also has been thoroughly investigated by Mandal and Jayakumar[140]. Shen et al [141] have investigated the thermodynamics of block copolymer micellization in DMF/H_2O mixtures and discussed the various factors affecting the standard thermodynamic functions.

Although the micellization parameters can be evaluated in reasonable detail using phase separation or mass action model, in most cases it is under estimates the experimental enthalpies [142]. Van Os et al. [143] have determined the CMC's and enthalpies of micellization of model alkylarene sulfate and compared with the phase separation model. Many studies of calorimetric determination of heat of micelle formation in aqueous solution have appeared since the pioneering work by Goddard et al in 1957 [144] and heat of solution work by Benjamin in 1964[145]. A review of work prior to 1979 has appeared in 1980[146] which summarizes theoretically calculated and calorimetrically determined heat of micelle formation of anionic and cationic surfactants in water.

From the CMC of surfactant mixtures, the thermodynamic parameters of mixed micellization can be deduced. Moulik et al. [147] have computed the free energy, enthalpy and entropy of micellization for cationic surfactants and mixed states for sodium deoxycholate(NaDC) and TX-100. Recently Minato et al. [148] have done the thermodynamics and kinetic studies on phase behavior of binary mixtures of POP and PPO forming molecular compound systems. Carron et al [149] have investigated the effect of geometry of micelles on the thermodynamic properties of trialkylamine oxides in water.

Jha and Ahluwalia [150] have determined calorimetrically the enthalpies of solution of some $C_{10}E_n$ surfactants in monomeric and micellar states in the presence of urea. Enthalpy of micelle formation has been determined by calorimetric micro titration studies of $C_{12}E_n$ (n = 5,6 and 8) by Oloffson et al[151]. Enthalpies of mixing for three binary system SDS-water, CTAB-water and TX-100-water have been studied by micro calorimetric studies by Gu et al [152]. Rathman and Scamehorn [142] have used Isoperibol calorimetry for the determination of the heat of micelle formation in binary surfactant mixtures.

Fiscaro [153] has studied the thermodynamics of aqueous solution of biologically active bisquaternary ammonium chlorides. Verrall [154] has investigated the thermodynamic and aggregation behavior of mixed micellar systems of sodium dodecanoate and ethoxylated alcohols. The thermodynamic properties accompanying the micelle formation have been investigated for chlorhexidine digluconoate [147].

Other than the phase separation and mass action model small system thermodynamics was applied to micellar system by Fisher and Okaenfull [155]. The distinguishing feature of small system / multiple equilibrium approach is that it yields expressions that describe the changes of monomer and micelle concentration with total surfactant concentration. This variation in the monomer composition and concentration must be recognized to understand adsorption. Also, this system makes possible the calculation of thermodynamic quantities of single micelle rather than ensemble of micelles.

1.12 Surfactants at Interface

Amphiphile molecules tend to accumulate at air/water or oil/water interfaces. The surface of a liquid is a boundary between two bulk phases namely liquid and air. The ability of surfactants to adsorb at interfaces and lower the interfacial energies as well as their ability to form aggregates in water are the most important properties of surfactants.

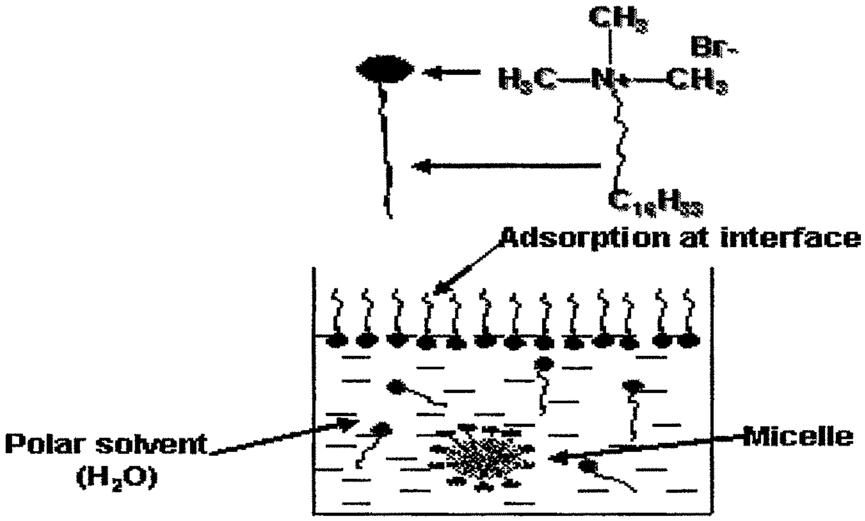


Figure 1.10: Adsorption, saturation and micellization of a typical surfactant in water.

Thus the knowledge of surface area occupied by surfactant at an air/water interface (A_{min}) and surface excess concentration (Γ_{max}) are very important in surface science in order to optimize the conditions as per desired application. The variation in surface tension (γ) with composition in case of solutions is one of the most important routes to obtain information about surface concentration. J. W. Gibbs derived a relationship rooted in thermodynamics and well known as Gibbs adsorption isotherm in 1878 [156,157]. The Gibbs equation expresses the equilibrium between the surfactant molecules at the surface or interface and those in the bulk solution. It is very useful as it provides a means by which the amount of surfactant adsorbed per unit area of the surface; "Surface Excess" may be calculated. The most general form of Gibbs equation is written as,

$$d\gamma = -\sum \Gamma_i d\mu_i$$

where $d\gamma$ is the change in surface or interfacial tension of the solvent; Γ_i is the surface excess concentration of the i^{th} component i.e it is the excess per unit area of surface of the i^{th} component present in the system over that present in a hypothetical system of same volume in which the bulk concentration in two phases remains constant up to an imaginary dividing surface; $d\mu_i$ is the change in chemical potential of the i^{th} component of the system. For a two component system at constant temperature,

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$

where subscripts 1 & 2 refer to solvent and solute respectively. Assuming $\Gamma_1 = 0$ i.e. the excess concentration of the solvent to be equal to zero and for dilute solution,

$$\Gamma_2 = \frac{-1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right) = \frac{-C}{2.303nRT}\left(\frac{d\gamma}{dC}\right)$$

where C is the concentration of surfactant. Above equation is applicable to the adsorption of non-dissociating solutes such as nonionic surfactants. For solutions containing a single surfactant, 'n' is the number of species whose interfacial concentration changes with change in the bulk phase concentration of the surfactant and thus the coefficient 'n' is equal to 1 in the case of nonionic surfactants. For ionic surfactants, in absence of any added electrolyte,

$$\Gamma_2 = \frac{-1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right)$$

where 'γ' is in dyne/cm, C is concentration of surfactant in molarity, R universal gas constant in ergs $\mathrm{mol^{-1}\,K^{-1}}$ and the coefficient 'n' is equal to 2. The $d\gamma/d\log C$ is obtained from the surface tension vs $\log_{10}$ concentration plot. From the surface excess, the minimum area per molecule ($A_{\mathrm{min.}}$) of the surfactant at the air/water interface can be computed which provides the information on the degree of packing and the orientation of the adsorbed surfactant molecules. The minimum area per molecule of the surfactant at the air/water interface is computed as,

$$A_{\mathrm{min}} = \frac{10^{14}}{N_A\Gamma}$$

where N_A is Avogadro number and Γ is surface excess concentration in mol /cm^2.

The surface excess concentration under the conditions of surface saturation Γ_m is generally used as a measure of the maximum extent of surfactant adsorption. There are several factors, which determine the maximum amount of surfactant adsorbed (Γ_m) at the air/water interface. Γ_m depends on surfactant structure, presence of electrolyte and temperature. Increase in the hydrophobic chain length of surfactant does not monotonically increases the adsorption but rather leveling off takes place [158].

The most pronounced effect of structure on Γ_m comes from the nature of the hydrophilic group or the size of the head group. Surface concentration decreases as the size of the head group of surfactant increases. Presence of electrolyte in solution increases the surface concentration for ionic surfactants due to decreased repulsion between the charged head groups.

Increase in temperature decreases Γ_m for ionic surfactants and increases for nonionic surfactants [159]. Rosen et al [85] have reported a decrease in the surface excess concentration as the oxyethylene chain length of nonionic surfactant increases. The evaluation behavior of fluorinated surfactants at air/water interface has been done by Guittard et al [160]. Hines et al [161] have calculated the surface excess concentrations of n-dodecyl N,N-dimethyl amino acetate at the air/water interface and compared the values obtained from neutron reflection studies. Schott [162] has determined the area per molecule for octoxynol-9 nonionic surfactant. Surface properties of ethoxylated nonionic surfactant were studied by Colin et al [163]. The surface behavior of mixtures of sodium dodecyl sulphate / TX-100 and dodecyl polyoxyethylene sulfate/ decyl methyl sulfoxide has been investigated by many authors [164,165]. Structure of mixed cationic –nonionic surfactant monolayer of hexadecyl trimethyl ammonium bromide and monodecyl hexaethylene glycol at air/water interface was also studied [132]. Neutron reflectivity has also been used to study the effect of temperature on the adsorption of nonionic surfactant mixtures like polyoxyethylene alcohols of $C_{12}E_n$ types i.e. $C_{12}EO_3/C_{12}EO_8$. The effect of temperature on the adsorption of dodecane onto nonionic and ionic surfactant monolayers at the air/water interface was reported by Aveyard et al.[166]. They also investigated the mixing of alkanes with surfactant at the air/water interface. The adsorption of ionic surfactants at the air/water interface of sodium n-alkyl sulfate and the influence of sorbitol on the adsorption of ionic surfactants is studied by Zajae et al [167]. Also, Zhao and Zhu [168] have reviewed single and mixed surfactants adsorption. Downes et al [169] have investigated the behavior of ammonium perfluorooctane at the air/water interface in the presence of salts.

The composition of mixed surfactants and cationic polymer/surfactant mixtures adsorbed at the air/water interface was recently investigated [170]. Soderberg et al [171] have reported the self assembly of nonionic sugar based surfactants at air/water interface.

1.13 Thermodynamics of Adsorption

Thermodynamics of adsorption of surfactants can provide important information about the adsorbed films i.e. Gibbs free energy of adsorption as a measure of surface activity of the surfactant at air/water interface. The standard free energy of adsorption, ΔG^{o}_{ad} is defined by the relation [172].

$$\Delta G^{o}_{ad} = RT\ ln_{CMC} - N_{A}\Pi_{CMC}A_{min}$$

The second term in the above equation is the surface work involved in going from zero surface pressure to surface pressure at CMC (Π_{CMC}), at constant minimum surface area/molecule A_{min}. The corresponding enthalpy and entropy of adsorption are computed from the well known thermodynamic relations.

The standard free energy change upon adsorption determines the spontaneity of the adsorption process and the magnitude of the driving force. The standard enthalpy change upon adsorption indicates weather bond making/ bond breaking is predominant during adsorption. The extent of randomness is given by the standard entropy changes during adsorption.

Recently thermodynamics of micellization and adsorption of Zwitterionic surfactants in aqueous media has been reported by Gad et al [173]. Motomura et al [174] and Bain and Robert [175] have studied the surface and thermodynamic properties of Cholines. Hassan et al. [132] have also investigated the micellization and adsorption properties of surfactant mixtures.

The interfacial and micellization behavior of binary and ternary mixtures of amphiphiles, Triton-X-100, Tween 80 and CTAB have been reported by Moulik and Ghosh[176]. Also, the properties including the standard free energy of adsorption have been studied for binary mixtures of decylammonium chloride and cesium perfloro octanoate at air/ water interface by different authors [177,178].

It is well known that mixing of surfactants often has interfacial properties that are more pronounced than those of their corresponding individual surfactants. Synergism in mixed monolayer has been related to various performance properties such as foaming, wetting, detergency, flotation, separation of minerals. Rosen [82] has applied the regular solution treatment to mixed monolayer formation at air/liquid interfaces in which the interaction between the surfactant molecules in the monolayer can be continuously deducted.

1.14 Performance Properties

The interfacial and solution behavior of surfactants lead to the following key surface active properties [179]

- Emulsification/de-emulsification
- Viscosity
- Wetting
- Foaming
- Dispersing
- Detergency
- Solublization

In almost all industrial applications a combination of these properties is generally preferred.

Surfactant plays a central role in emulsion and microemulsion system. Depending on chemical nature of surfactant and the relative constituent proportion, w/o or o/w microemulsion system can be obtained. Ionic surfactant is usually strongly hydrophilic hence ionic surfactant needs lipophilic cosurfactant for large solubilization. However, nonionic surfactants change their phase inversion temperature gradually with their oxyethylene chain length, so that a single optimum nonionic surfactant whose phase inversion temperature is close to a given temperature exhibits large solubilizing power. The phase inversion is the temperature at which the emulsifier shifts its preferential solubility from water to oil when the temperature is increased. But it is well established that nonionic surfactant may be a good solubilizer at optimum temperature; but only for a limited temperature range. On other hand, anionic surfactant is stable with temperature change but needs higher concentration [180]. If the size of the hydrophobic and lipophilic groups of the emulsifier increases, the CMC will decrease, the aggregation number will increases and the solubilizing power will be enhanced. So in order to increase the solubilization as well as the size of micelles, ionic or nonionic surfactant with long hydrocarbon chain lengths are used [181].

Viscosity of surfactants is applicable to both handling of liquids in processing and to the formulation of end use products in which a desired physical form is required. Surfactant solution at very high concentration behaves like non-Newtonian liquids as the viscosities of these solutions are affected by shear rate and the structure of surfactant aggregates, changes with temperature and pressure and shear history. In formulated products their viscosities measured in aqueous medium, may further be affected by the presence of additives, electrolytes that modify the water structure or the concentration of water with respect to surfactant. Viscosity of the liquid containing bulk surfactant is also known to play a significant role in defining the stability of formulated product. Foam stability affects the desired use profile of the product, while hydrolytic stability strongly affects shelf life. Hence, it is an important physicochemical property of surfactant solution.

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Wang [182] has studied the effect of inorganic salts of very high concentration on the viscosity behavior of sodium dodecyl benzene sulfonate. Edward [183] has determined the viscosity of SDBS solution. Kumar et al. [184] have reported the viscoelasticity of quaternary ammonium salt solutions in presence of sodium salicylate. Effect of alcohols, amines and aromatic hydrocarbons that cause structural changes in micellar systems have been extensively reported by Kabir-ud Din et al. [185]. Viscosity of various transition metal based surfactants in mixed benzene/ methanol system was reported by Kumar [186]. Asakawa et al [187] have studied the effect of salts on the viscosity of fluorocarbon/hydrocarbon mixed surfactants.

The effect of electrostatic charge on the viscous flow has been investigated as the electroviscous effect by Guveli et al [188]. From intrinsic viscosity dimension of micelle, volume of the hydrocarbon core, oxyethylene layer of the micelle were calculated, and correlated to intrinsic viscosity which depends upon the micelles, micelle solvent and micelle micelle interaction [189-192]. The relationship between the structure of micelle and its viscosity was correlated to the sharp increase in the viscosity of concentrated surfactant solution to the formation of rod like micelles that forms network in solution. The variation of the second virial coefficient described by Scatchard equation for micellar systems of SDS and DTAB as a function of added electrolyte was analyzed through various interactions such as micelle-micelle interactions [193].

Foam is produced when air or some other gas is entrapped beneath the surface of liquids that expands to enclose the gas with a film of liquid. Foaming is the property inherent to all surfactant solutions. The theoretical basis of foam has been extensively studied and its physicochemical principles are well documented [194]. Anionics are good foamer and nonionic are poor foamer [195]. Most of the work is reported only in anionics. The foaming power of detergent solution generally show significant variations with respect to

- Addition of small amount of additives
- Its chemical structure
- The surfactant concentration and temperature.

Although electrolytes do not influence significantly either the foaming power or foam stability of nonionic, they do show significant effect for ionic surfactants [196]. Electrolytes generally destabilize the foam by screening the repulsive forces between the ionic head groups that lead to reduced repulsion between surfactant layers or opposing film interfaces which in term lead top faster film drainage.

The effect of additives on the CMC of the surfactant is correlated to foam stabilization. Shick and Fowkes [197] have studied the interaction of additives and surfactant and concluded that the effective foam stabilizing additives are those that solubilize in the micelle palisade layer.

The foaming efficiency decreases as the cloud point of the nonionic surfactant is approached. Colin et al [163] have discussed the reduced foamability of dilute solutions of chemically modified ethoxylated nonionic surfactants. Also foaming studies have been used to estimate the changes in the composition of surfactant at air/water interface [198].

The addition of surfactants to water is well known method to improve the ability of aqueous solutions to wet and spread over solid surfaces. Janczuk et al [199] have studied the wetting efficiency of SDS on cassiterite. Enhancement in wetting properties of water insoluble surfactant by Draves cotton skin wetting test is reported by Rosen and Hua [200]. This test is commonly used technique for evaluating the textile wetting behavior of surfactants related to dynamic surface tension of the solution.

Addition of polyoxyethylenated nonionic to anionics generally increases the wetting power and decreases when added to a cationic surfactant [201]. Surfactants with centrally located hydrophilic groups are especially good textile wetting agents. Among the isomers of polyoxyethylenated straight chain amines the compounds with two OE groups of approximately equal oxyethylenes attached to nitrogen showed the best wetting property [202].

In detergency the micelles supply surfactant molecules to act on the dirt fabric interface for disloding the dirt which is finally dispersed in the aqueous medium by the incorporation in the micelle for removal by washing. Surfactants adsorb both on fibers and on soil particulates.

It was suggested that the solubilization behavior in hard water is an important factor in understanding the behavior of anionic detergents in soil removal. Literature survey indicates that detergency of LABS (linear alkyl benzene sulfonates) increase with decreasing water hardness. Maximum value of detergency is observed at 10^{-6} M Ca^{++} concentration [203].

Alcohol sulfates are known to be excellent detergents but very sensitive to water hardness and show less performance at low temperature [204]. Talaba et al [205] have studied the wetting, foaming and detergency efficiency of inclusion complexes of some nonionic surfactant with cyclodextrin. As mention, in detergency the solubilization of soil from fabric into detergent solution is one of the important event. Oh and Shah [206] have found from the rate of solubilization of orange OT from cotton into SDS solution that stable micelles are more efficient in detergency.

1.15 Methods of Investigation of Micellar Solution

Macroscopic Techniques

The macroscopic techniques such as surface tension, conductivity and viscosity are widely used to investigate the micellar solutions [207]. These techniques are very useful for the observation of transitions, as an abrupt change in the macroscopic properties investigated by these techniques [208]. The transition from spherical to rod-like micelles is accompanied by a significant increase in viscosity [209-211].

Scattering Techniques

The scattering techniques are the most direct techniques for the study of the structures of the micellar solutions. A scattering technique measures the scattered intensity I as a function of wave vector transfer Q(= $4\pi \sin\theta / \lambda$, where 2θ is scattering angle and λ is the wavelength of the incident radiation). Small angle neutron scattering (SANS), small angle X-ray scattering (SAXS) and light scattering (LS) are widely used to investigate the micellar solutions. Light scattering technique includes both static light scattering (SLS) and dynamic light scattering (DLS). In DLS, one measures the time correlations of the fluctuating intensity of light scattered from a system of colloidal particles undergoing Brownian motion. The scattering techniques are used not only to investigate the micellar structure but also for understanding the intermicellar interactions. Several reviews on the principles, methods and limitations of scattering methods used in micellar solution studies are available [212]. SANS, SAXS and DLS are the complementary techniques for the study of micellar solutions on a similar length scale of ~ 100 Å. For the structural study of micellar solutions, the use of SANS over SAXS is generally preferred as it is possible to obtain a very good contrast between the micelles and the solvent by preparing the solution in D_2O instead of H_2O. DLS is used to study the hydrodynamic properties of micellar solutions. The hydrodynamic radius (R_H) of the micelle is obtained by measuring the self-diffusion coefficient in the dilute solution; where the interaction between the micelles can be neglected [213]. In an ionic micelles, it is difficult to get a non interacting limit even at low concentration of surfactant molecule. Therefore measurement of R_H by this technique is subject to unknown errors. SANS is used to study both the dilute and concentrated micellar solution.

Spectroscopic Techniques

The formation of micelles will influence the local molecular interactions for the components. This in turn shows up a change in a number of spectroscopic parameters. Thus it is possible to probe several different aspects of the molecular organization in micellar solutions by spectroscopic techniques. The most general technique for the study of micellar solutions is nuclear magnetic resonance [214]. With the advent of Fourier transform techniques as well as high field superconducting magnets, NMR studies are feasible at submilimolar concentrations for many nuclei and thus highly appropriate for investigations of micelle formation. This technique has the highest spatial resolution. This obvious advantage has some drawbacks: lower resolution information such as particle size is difficult to extract from such information.

1.16 Scope of Present Work

Surfactants are among the most versatile materials of the chemical industry, appearing in divers products such as motor oils, pharmaceuticals, detergents and petroleum and flotation agents used in beneficiation of ores. The last decade has seen the extension of surfactants applications to high-technology areas such as electronics printing, magnetic recording, biotechnology, microelectronics and viral research. Surfactants are consumed worldwide in large quantities every day. This has led to the preparation of new generation surfactants such as dimeric surfactants which were later called as *Gemini surfactants*. These surfactants have wide range of applications such as anti-bacterials, liquid crystals, gene transfection agents, in road repair, for mineral floatation, for protection of metals from corrosion, as a phase transfer catalysts in regioselective addition reactions and in preparation of crystalline mesoporus materials. Many more detergent and oil based companies have to come forward to make newer cost effective geminis. So far over 1,000 international patents on gemini surfactants have been filed and investigations for newer products are in progress. In this way the field is very interesting and open to accept challenging contributions to enrich the science of physics and chemistry of interface. Hence, we have tried to synthesize a novel geminised surfactant series with different tail lengths, variable spacer lengths and different head group polarities. To our knowledge no systematic study is reported considering effect of head group polarity on the physicochemical properties of gemini surfactants. Hence we have undertaken it.

Objectives of the work

I. Synthesis of novel series of cationic gemini surfactants, such as 12-4-12 DMA/MEA/DEA, 12-s-12 MEA and 16-s-16 MEA (s = 4, 6, 8 and 10) and its monomeric counterparts C_{12}DMEAB and C_{16}DMEAB.

II. Characterization of synthesized surfactants by TLC, ^{1}H NMR, FTIR and C, H, N analysis.

III. To study the physicochemical properties of a series of gemini and its monomeric counterpart by conductance, surface tension, viscosity, UV-visible spectroscopy and SANS measurements.

IV. To study the role of gemini 12-4-12 MEA surfactant in mixed surfactant system composed of 12-4-12 MEA and C_{12} DMEAB.

V. To study the effect of sodium malate on aggregation behavior of 12-4-12 MEA and C_{12} DMEAB surfactants.

VI. To study the performance properties such as foamability, viscosity, and solubilization capacity for series of cationic gemini surfactants.

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