Table 1. The abbreviations /symbols used throughout the study

NO.	Name	Abbreviation/Symbol
1	Sodium dodecylsulfate	SDS
2	Sodium dodecylbenzene sulfonate	SDBS
3	Sodium 1-dodecanesulfonate	SDST
4	α-sulfonato myristic acid methyl ester	MES
5	α-sulfonato palmitic acid methyl ester	PES
6	Tetra- n-butyl ammonium dodecyl sulphate	TBADS
7	Sodium deoxycholate	NaDC
8	1,4-bis(N-hexadecyl-N,N-dimethylammonium)butane dibromide	16-4-16
9	Cetyltrimethylammonium bromide	CTAB
10	Dodecyltrimethylammonium bromide	DTAB
11	Sodium Laurate	SL
12	Sodium dodecyltrioxyethylene sulfate	SDES
13	Cetylpyridinium bromide	CPyBr
14	Sodium Oleate	NaOA
15	Octyltrimethylammonium bromide	OTAB
16	Polyoxyethylenesorbitan monolaurate	Tween-20
17	Amitriptyline hydrochloride	AMT
18	Promazine hydrochloride	PMZ
19	Sodium Salicylate	NaSal
20	Ammonium bromide	NH_4Br
21	Sodium bromide	NaBr
22	Lithium bromide	LiBr
23	Cesium bromide	CsBr
24	Potassium Bromide	KBr
25	Sodium Chloride	NaCl
26	Anilinium hydrochloride	ANHC

27	*p*-toluidine hydrochloride	PTHC
28	Tetra-*n*-butylammonium bromide	TBAB
29	Tetra-*n*-pentylammonium bromide	TPeAB
30	Phenyltributylammonium bromide	PTAB
31	Hexanol	C_6OH
32	Critical micelle concentration	*Cmc*
33	Cloud point	CP
34	Poly-dispersity index	PDI
35	Optical density	OD
36	Non negatively constrained least squares	NNLS
37	Controlled environment vitrification system	CEVS
38	Small angle neutron scattering	SANS
39	Dynamic light scattering	DLS
40	Polarizing electron microscopy	POM
41	Transmission electron microscopy	TEM
42	Cryo -transmission electron microscopy	Cryo-TEM
43	Freeze fractured transmission electron microscopy	FF-TEM
44	Thin layer chromatography	TLC
45	Surfactant packing parameter	R_p
46	Volume of hydrocarbon chain	v
47	Effective area per head group	a_0
48	Length of the alkyl chain	l_c
49	Number of carbon atoms of hydrocarbon chain	n
50	Aggregation number	N
51	Interparticle structure factor	$S(Q)$
52	Particle form factor	$F(Q)$
53	Differential scattering cross-section	$\mathrm{d}\Sigma/\mathrm{d}\Omega$
54	Scattering vector	Q
55	Semimajor axis	a
56	Semiminor axis	b / c
57	Fractional charge / Degree of counterion binding	α

58	Hydrodynamic radius	R_{h}
59	Hydrodynamic diameter	D_{h}
60	Chemical shift	δ
61	Zero-shear viscosity	η_0

This piece of work is exclusively devoted to the solution behavior of surfactants or surface active agents with or without of additives. One of the original and predominant reasons for the ubiquitous deployment of surfactants is their remarkable ability to influence the properties of surfaces and interfaces, and thereby have an impact on industrial processes and products [1]. The useful and fascinating properties of surfactants are essentially a result of combining into one molecule certain groups that as separate molecules would be incompatible. These compounds are also known as amphiphiles, tensides or paraffin chain salts.

Surfactants have been widely used in both industrial and domestic fields since the first surface-active product was prepared commercially in 1930 [2]. The applications of surfactant in industry are quite diverse and have a great practical importance. Surfactants may be applied to advantage in the production and processing of foods, agrochemicals, pharmaceuticals, personal care / laundry products, petroleum, mineral ores, fuel additives and lubricants, paints, coatings and adhesives, photographic films, soil remediation among others [3-12].

Surfactant is a substance that when present at low concentration in a system has the property of adsorbing onto the surfaces or interfaces and subsequent alteration in surface or interfacial free energies [13,14]. They consist of a hydrophobic (usually a long hydrocarbon chain) and a hydrophilic (ionic or polar) groups (Figure 1).

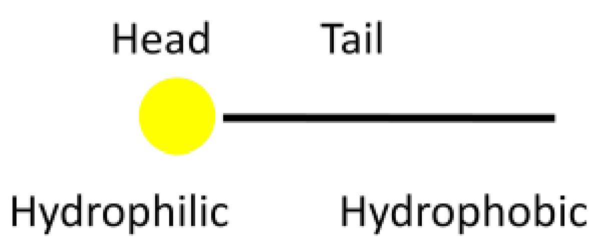


Figure 1. Schematic representation of a surfactant monomer.

Owing to the polarity of the distinct groups these substances have also been referred to as amphipathic, heteropolar or polar- nonpolar substances. The polar- nonpolar character is responsible for the unique properties shown by surfactant molecules in aqueous solution. When surfactant molecules are dissolved in a polar solvent (*e.g.*water), presence of the hydrophobic group in the interior of the water must cause distortion of the water structure, increasing the free energy of the system. In dissolved state, less work is needed to bring a surfactant molecule than a water molecule to the surface. Surfactant molecules, therefore, accumulate at the surface. Presence of surfactant monomers decrease the work needed to create unit area of surface. On the other hand, presence of the hydrophilic group prevents the surfactant molecule from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic group. The amphipathic structure of the surfactant, therefore, causes not only concentration of the surfactant molecules at the surface and reduction of the surface tension of water but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it. Depending upon the nature/charge of the hydrophilic headgroup, surfactants can be classified as cationic, anionic, zwitterionic or nonionic.

Anionic surfactants

They give rise to a negatively charged surfactant ion and a positively charged counter ion upon dissolution in water. Examples of anionic surfactant group include sulfonic-acid salts, alcohol sulfates, alkyl benzene sulfonates, phosphoric acid, esters and carboxylic acid salts. These are the most widely used surfactants in industrial applications [15-18] due to their relatively low cost of manufacture. Anionics are used in most detergent formulations and the best detergency is obtained by alkyl and alkyl aryl chains in the C_{12}–C_{18} range. Anionic surfactant tends to be good solubilizers and relatively non-toxic. A few anionic surfactants are shown in Scheme 1. SDS is a typical example of this class.

Cationic surfactants

They yield positively charged surfactant ion and a negatively charged counter ion upon dissolution in water. The prime use of cationic surfactants is their tendency to adsorb on negatively charged surfaces, *e.g.*, anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents, fabric softeners, hair conditioners, anticaking agent for fertilizers and as bactericides. Cationic surfactant first become important when commercial potential of their bacteriostatic properties is recognized. Examples of the cationic surfactants are given in Scheme 1. CTAB is a well known example of cationic surfactant.

Nonionic surfactants

They are characterized by hydrophilic head group that do not ionize in water. Nonionic surfactants are second to anionic surfactant in cleaning applications. An important group of nonionic surfactants includes those where the hydrophilic portion comprises a chain of ethoxy group and is known as ethoxylates [19]. The water–soluble moiety of this type contains hydroxyl group or a polyoxyethylene chain. Examples include polyethylenated alkylphenols, alcohols, ethoxylates, and alkyl phenols. Ethoxylated one is relatively non-toxic. They can be easily blended with other types of surfactant. Examples of the nonionic surfactants are summarized in Scheme 1. Tween-20 is an example of nonionic surfactant.

Zwitterionic surfactants

They contain two charged groups of opposite signs. The positive charge is almost invariably ammonium whereas source of negative charge may vary, although carboxylates is by far the most common. Zwitterionic surfactants [20] are often refer to as amphoteric; but the terms are not identical. Solution behavior of these surfactants depends strongly on the pH of the solution. Zwitterionic surfactants have excellent dermatological properties [21]. They exhibit low eye irritation and are frequently used in shampoos and other cosmetic products. Examples of the zwitterionic surfactants are provided in Scheme 1. Cocobetaineis a well known example of this class of surfactants.

Gemini surfactants

'Gemini surfactants' are made up of two amphiphilic monomers linked at the level of polar head group of each monomer by a spacer [21-25]. Because the polar head

groups are connected by a spacer in geminis, the distance between the polar heads within a dimeric unit depends both on the nature and the spacer length [26].

Unsymmetrical gemini surfactants have also been synthesized. They have either different hydrophobic tails or different types of polar head groups (heterogemini surfactants) or both.Among these gemini surfactants, cationic bis(alkyldimethylammonium)alkane dibromide type (represented as m-*s*-m, where m is the number of carbon atoms in alkyl chain and *s* is the number of carbon atoms in the spacer) has received more attention.The polar group can be positive (ammonium), negative (phosphate or carboxylate), or nonionic (polyether or sugar)**.** A great deal of variation exists in the nature of the spacer which can be short or long; rigid or flexible, and polar or nonpolar (Scheme 1)**.** Zana reported that the spacer length or hydrophobicity showed a pronounce effect on the aggregation behavior [24]. A schematic representation of a gemini surfactant is shown in Figure 2.

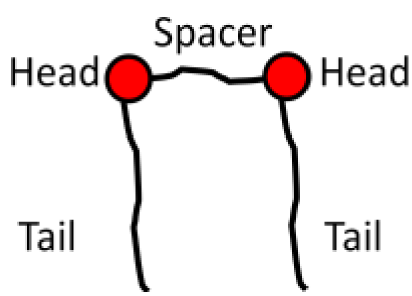


Figure 2. Schematic representation of a Gemini surfactant

Gemini surfactants were first synthesized and studied for their superior performance as catalyst in organic reactions [27]. Dimeric (so-called “gemini”) surfactants have attracted much attention by virtue of their appealing properties in comparison to classical “monomeric surfactants” [28-33]. They possess high surface activity and low cmc values, unusual viscosity changes with an increase in surfactant concentration, greater efficiency in lowering the interfacial tension, better wetting and solubilizing abilities and unusual micellar structure [34-39]. The better efficiency and effectiveness of geminis over conventional surfactants make them more versatile and cost-effective. For these reasons, gemini surfactants are now used in biochemical

[40], pharmaceutical [41], petroleum [42], gene therapy [43], corrosion [44], and catalysis [45-47]. Recently, dimeric surfactants have also found applications in the fields of crystal engineering [48,49], and supramolecular chemistry [50-54]. Gemini surfactants form vesicles, liquid crystalline phases and various other morphologies over broad concentration range, which can be exploited for a variety of potential applications.

Bolaform Surfactants

Bolaform surfactants or bolaamphiphiles (also known as *bolaphiles* or *alpha-omega-type surfactants*) are amphiphilic molecules which consist of two hydrophilic head groups, connected by a long linear polymethylene chain. Because, compared to single-headed amphiphiles, the introduction of a second head-group generally induces a higher solubility in water, an increase in the *cmc*, and a decrease in aggregation number. Bolaform surfactants are, in general, much less good surfactants than conventional ionic surfactants. However, bolaform surfactants often show biological activity [55], and some drugs are of bolaform nature. Some special bolaforms are capable giving rise to organized assemblies of peculiar structure [56].

Bio-surfactants

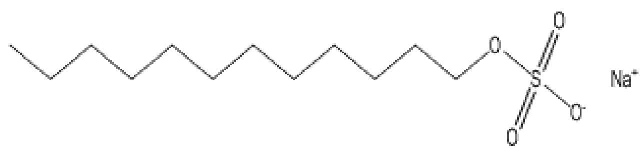
Bile salts are biosurfactants important in the digestion process of food. They are produced by the liver from cholesterol, stored in the gallbladder and occur in theorganism mainly as bile. Bile salts solubilize apolar material such as cholesterol, lipids, fatty acids, monoglycerides, and fat soluble vitamins. It has been reported by Martin et al. [57] that bile salts are metabolic together with phospholipids solubilize cholesterol-forming bile, which remains stored in the gall bladder to assist favorable absorption of fats. It has been shown that sparingly soluble cholesterol is solubilized in the mixed micelle of bile salts and phospholipids [58]. Conjugated bile salts have powerful detergent properties which are important in stabilizing the supersaturated state of bile and in promoting fat digestion / absorption.

Bile salts are amphiphilic molecules (also call facial amphiphile, most of these compounds are either anionic or neutral amphiphilic molecules) which do not have usual polar head and nonpolar aliphatic tail as in the case of classical surfactants [59]. Due to this specific facial structure, bile salt molecules lie flat at the aggregate surface. Bile salts from different species differ chemically in the structure of side chain, distribution, position and stereochemistry of the hydroxyl group attached [60]. The hydrophobic part of the molecule is based on long-chain fatty acids, hydroxy fatty acids or α-alkyl-β-hydroxy fatty acids. The hydrophilic portion can be a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid or alcohol. Depending on the number of hydroxyl groups present bile salts are named as hydrocholate, deoxycholate and cholate in which they have one, two and three hydroxyl groups, respectively. Examples of the bile salts are shown in Scheme 1.

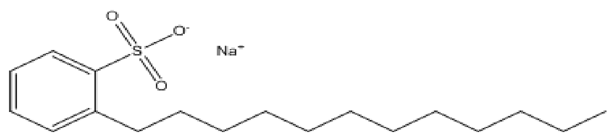
Structures of few typical surfactants

Anionic surfactant

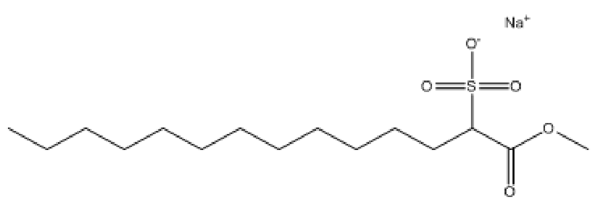
Sodium dodecyl sulfate



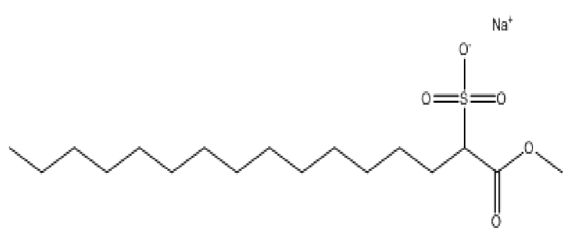
Sodium dodecylbenzene sulfonate



α-sulfonato myristic acid methyl ester



α-sulfonato palmitic acid methyl ester



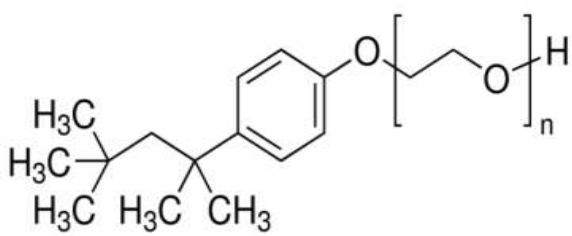
Cationic surfactant

Cetyltrimethylammonium bromide

Cetylpyridinium bromide

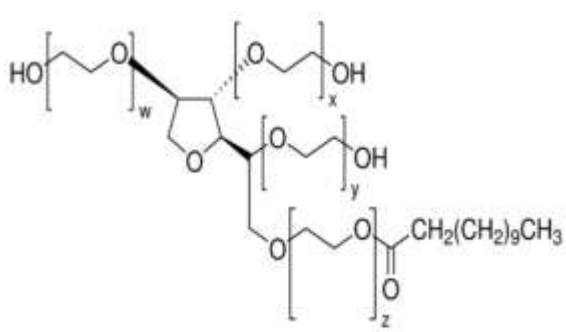
Nonionic surfactant

Polyoxyethylene t-octylphenyl ether (TX-100)



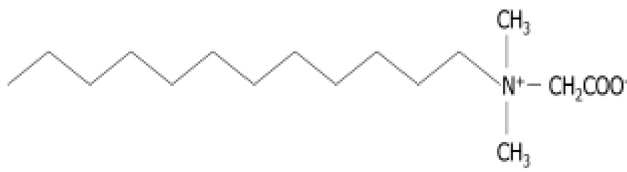
n=9-10

Polyoxyethylene sorbitan monolaurate(Tween-20)



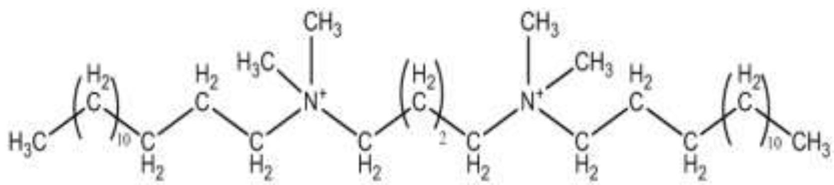
Zwitterionic surfactant

Cocobetaine (CB)

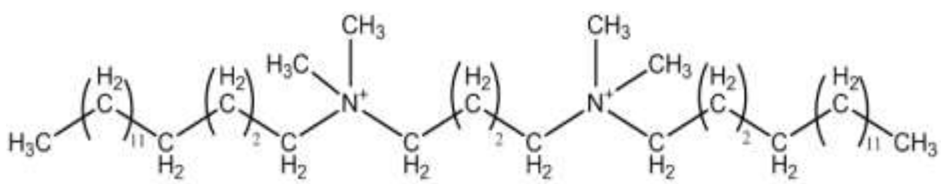


Gemini surfactant

1,4-bis(N-tetradecyl-N,N-dimethylammonium)butane dibromide (14-4-14)

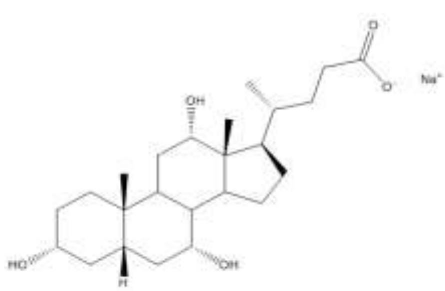


1,4-bis(N-hexadecyl-N,N-dimethylammonium)butane dibromide (16-4-16)

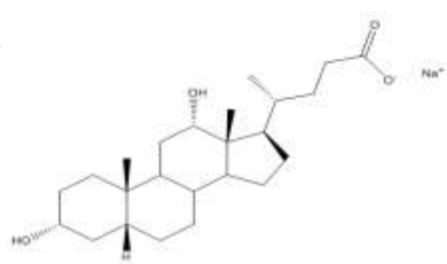


Bile salts

Sodim Cholate



Sodium deoxycholate



Scheme 1

Surfactant solution exhibits different properties *e.g.* micellization,clouding, solubilizationemulsification,adsorption, spreading. Among them, we have mainly focused on micellization,clouding, solubilization and microstructural transitions.

Micellization

Surfactant in aqueous solution, at a minimum concentration, referred to as '*cmc*', associate dynamically to form spherical aggregates called micelles (Figure 3). Micelle, a Latin term, means "small bit" and was coined by J. W. McBain [61] in 1920 to describe colloidal sized particles of detergents and soaps.The number of surfactant monomers that aggregate to form a micelle is called aggregation number. Micelles do not exist at all concentrations and temperatures. For a typical surfactant at a given temperature, there is a narrow concentration range below which aggregation to micelles is absent and above which association leads to micelle formation. These micelles are also known as 'association colloids' in surface and colloid field.

The aggregation of surfactants/amphiphilic compounds can be demonstrated by measuring solution properties such as surface tension [62], dye solubilization [63], ^{1}H NMR [64,65], light scattering [66,67], fluorimetry [68,69], osmotic pressure [70], electrical conductivity [71,72], ultrasound velocity against the surfactant concentration.

Micelle formation, or micellization, is an important phenomenon not only because a number of interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in solution, but because it affects other interfacial phenomena, such as surface or interfacial tension reduction that do not directly involve micelles. The driving force behind micellization is the hydrophobic effect as proposed by G.S. Hartley in 1936 [73]. Of late, micelles have become a subject of great interest to the organic chemist and biochemist [74] to the former because of their unusual catalysis of organic reactions and to the letter because of their similarity to biological membranes and globular proteins [75]. Micelle catalyzed reactions, as models for electrostatic and hydrophobic interactions in biological systems, have been used to provide information regarding the mechanism of tuning of reactions occurring on biological surfaces. This is because that micelles are simpler and more easily modified. Therefore, a significant amount of systematic kinetic results have been reported on the effect of micelles on organic reactions [74,76-78].

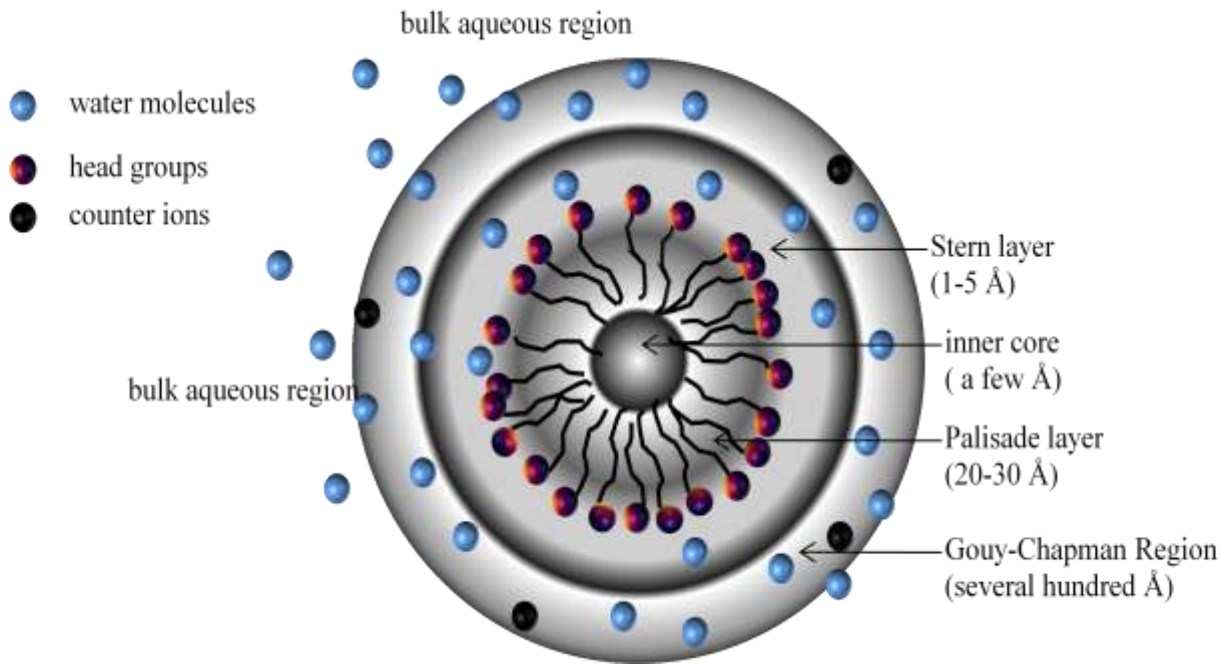


Figure 3. Spherical micelle

cmc is the most characteristic parameter of aqueous surfactant solution and physicochemical properties of the solution vary markedly above and below the *cmc* [73,79-82]. Many investigations have been concerned with determining values of the *cmc* in various systems, and a great deal of work has been done on elucidating the various factors that determine the concentration at which micelle formation becomes significant, especially in aqueous media. The factors known to affect the *cmc* in aqueous solution are: (i) structure of amphiphiles, (ii) the presence of various additives in the solution and (iii) experimental conditions such as temperature, pH, pressure, solvent, etc.

Types of micelles

Three types of micelles are formed in surfactant solutions. Micelles formed in polar solvents are called *normal micelles* and those formed in nonpolar solvents are called *reverse micelle*. Another type is *mixed micelle* which is formed upon mixing of two or more surfactants.The structure of reverse micelle is shown in Figure 4.

In nonpolar solvents, the surfactant molecules may associate due to dipole-dipole [83,84] interactions between the hydrophilic headgroups. This form of surfactant aggregates called *reverse micelle*. In reversed micelles the hydrocarbon tails are oriented outward into the bulk solvent while the hydrophilic head groups are oriented inward. Reverse micelle is more complex than normal micelles but can be used to solubilize polar solutes in non-polar solvent.

Surfactants can also solubilize materials into solvents other than water. The aggregation properties of surfactants in non-polar solvents are often changed markedly by the presence of traces of water or additives. The size and properties of reverse micelles vary with amount of water present [85- 87].Water in reverse micelles is expected to behave very differently from ordinary water because of extensive binding and orientation effects induced by polar heads forming the water core [88].

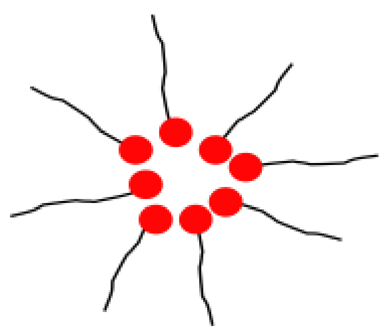


Figure 4. Reverse micelle

Mixed micelles

Mixing of two or more surfactants in an aqueous solution leads to the formation of mixed micelles. When more than one surfactants are added together in water, several physicochemical properties of the mixed system compared to those of the single surfactant are changed. The mixed system almost invariably yields enhanced interfacial properties (*e.g.* decreased *cmc*, higher surface activity) with respect to the individual surfactants, in what is termed *synergism*. The structure of mixed micelle is shown in Figure 5. However, it is the rich polymorphism in bulk that has, in recent years, attracted increasing interest in experimental investigations and theoretical modeling.

Mixed micellization is a special case of solubilization. Compared to pure micelles, mixed micelles have been shown to have considerable solubilization capabilities toward nonelectrolyte [89-90]. Mixed micelles have been used in the pharmaceutical field for solubilization of various hydrophobic drugs for the past two decades. Mixed micelles have been particularly employed for parenteral [91], oral [92], and dermal routes [93].

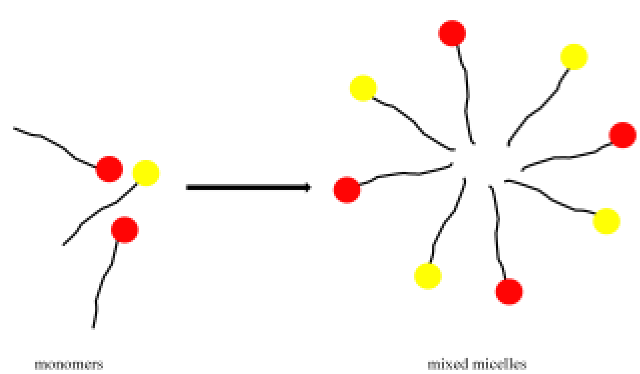


Figure 5. Schematic representation of formation of mixed micelle by the monomers.

Solubilization

Micellar solubilization is one of the most important properties of the surfactant solutions. The spontaneous dissolving of a substance (solid, liquid, or gas) by the reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution (with reduced thermodynamic activity of the solubilized material) is known as micellar solubilization.

Unlike homogeneous solvents, micelles possess different solubilization environments, ranging from the polar micelle-water interface to the relatively nonpolar hydrocarbon core of the micelle [94]. Micellar solutions have a general tendency to solubilize a certain amount of organic additives (hydrophobic or partly hydrophobic) [89, 95].
The overall water solubility of many hydrophobic molecules can be greatly increased by the presence of surfactant, due to formation of spontaneous aggregates. The capability of aqueous surfactant aggregates to incorporate solutes is the reason for the widespread use of such systems in industrial, biological, pharmaceutical (solubilize drugs in their hydrophobic cores), and synthetic chemical/catalytic applications [96, 97].Among others a relevant field of application is that of remediation of treatments of water and soil [98-101].

These applications are depending upon solubilization capacity of the micelles and nature of the solubilizate. Solubilization of organic compound in aqueous surfactant solutions is also useful in micellar-enhanced ultrafiltration [99, 102].

Small polar molecules in aqueous medium are generally solubilized close to the surface in the palisade layer or by adsorption at the micelle-water interface. Short – chain phenols, when solubilized in polyoxyethylenated nonionics, appear to be located between the polyoxyethylene chains. The emerging picture is that molecules with polar groups are mainly solubilized near the surface of the micelle [103].

Large polar molecules, such as long-chain alcohols or polar dyestuffs, are believed to be solubilized in aqueous medium, mainly between the monomers of surfactant in the palisade layer. Here, polar group of the molecules orientated toward the polar group of the surfactant and the nonpolar portions orientated toward the interior of the micelle. Depth of the penetration in the palisade layer depends on the ratio of polar to nonpolar structures in the solubilizate molecule. Longer-chain and less polar compounds penetrate more deeply than short-chain and more polar material.

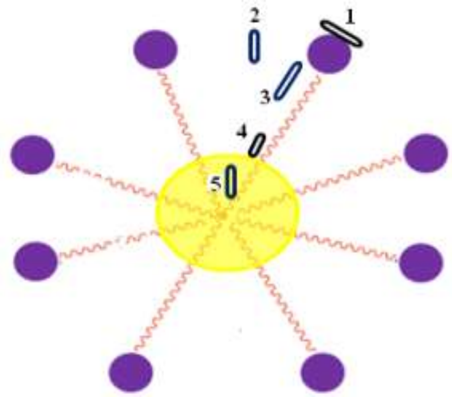


Figure 6: Various micelle solubilization sites: (1) micelle – water interface; (2) between the hydrophilic head groups; (3) palisade layer; (4) deeply in the palisade layer and (5) inner core of the micelle

Saturated aliphatic and alicyclic hydrocarbons and other types of molecules that are not polarized or not easily polarizable, are solubilized in aqueous medium in the inner core of the micelle between the ends of the hydrophobic groups of the surfactant molecules. It was reported by Reekmans and Lindemuththat aliphatic hydrocarbons are preferentially solubilized in the interior of the micelle [104,105]. Solutes of different structure types may solubilize in distinct regions in or around the micelle whilesolutes of similar hydrophobicitiesmay compete for the same site inside the micelle.

Many studies have been performed to determine the location of a solubilizate within a micelle and other related assemblies [106-108]. The location, distribution, and orientation of solubilized material in and around micelle are of fundamental importance in understanding the nature of the solubilization and its effect on the chemical and physical behavior of the resultant solution [109] and, therefore, consequence on micellar morphology [110-112].

The amount and the solubilization environment can play an important role in the final micellar shape. Mukerjee had proposed that an additive which is surface active to a hydrocarbon water interface will be mainly solubilized in the head group region and will promote micellar growth. It has been proposed by Kabir-ud-Din et al. that interfacial partitioning of organic additives causes micellar growth while interior solubilization produces swollen micelles [113-115]. These two types of micelles can impart different physico-chemical behavior to micellar solutions.

Micellar morphology can also be triggered by solubilization.Hoffmann and Eriksson have reported that rodlike micelles solubilize large amount of organic additives. The solubilization of organic additives in different micellar region can be correlated with the structural organization of micellar aggregates and their mutual interactions [116-118]. The interior (core) solubilization of organic additives provides swelling to the already grown micelle and releases the requirement of the surfactant chain to reach the center of the core [105]. These factors may increase the smaller dimension of such anisotropic micelles with a resultant decrease in axial ratio (more spherical).

Microstructural Transitions in Aqueous Surfactant Solution

Surfactant aggregation is complex but reasonably well understood. Israelachvili et al. [79, 119] have developed a general theoretical frame work from which secondary structures (formed by a surfactant) may be deduced. It has been shown that many surfactants can be generalized into certain shape categories, which are likely to produce specific secondary aggregates in aqueous solution (Figure 7). R_p determines which aggregate the surfactant is most likely to form [120].

It is calculated by dividing the v by a_0 and l_c, so that the non–dimensional $R_p$is

$$R_p = v/l_c a_0$$

The tail and volume of the hydrocarbon chain of ncarbon atoms can be approximated by correlations of experimental data as:

$$l_c = (1.54 + 1.265n)\ \text{Å}$$

$$v = (27.4 + 26.9\ n)\text{Å}^3$$

Spherical micelles are formed when $R_p$is lower than 1/3; wormlike micelles are formed when R_p has a value in between 1/3 to 1/2; vesicles or bilayers are formed when 1/2 < R_p< 1. When the volume of the hydrocarbon part is large relative to the head–group area (R_p> 1), reverse micelles can be formed.

In aqueous media, surfactants with bulky or loosely packed hydrophilic groups and long hydrophobic groups tend to form spherical micelles because area occupied by them is large, while those with short, bulky hydrophobic groups and small, close-packed hydrophilic groups tend to form lamellar or cylindrical micelles. The essential consideration pertaining to the area occupied by the headgroups is the work necessary to overcome the electrical repulsion experienced by the like charges. A surfactant carrying a large charge on a relatively small charge –bearing atom will inherently be more apt to form spherical micelles due to the high energy needed to overcome the prohibitive charge density of the headgroup. A surfactant with a high degree of counterion binding may overcome headgroup repulsion by holding the oppositely charged counterion between headgroups of similar charge; headgroup repulsion is depressed and rod- or disk-shaped micelles become favored.

Surfactants with lesser head group areas tend to form larger, less curved, or even reversed structures. For ionic surfactants, the above area decreasing effect may be achieved by addition of a counterion (salt) or a suitable organic additive (cosurfactant).

Surfactants have long been of interest to the scientific community for their ability to form a rich array of aggregate morphologies in solution and their use in numerous industrial applications Single-tail surfactants usually form spherical micelles in aqueous solution above their *cmc*, which eventually grow to other shapes with increasing surfactant concentration.

Different types of assemblies can be transformed to one another depending on different factorssuch as the nature of the surfactant monomer, surfactant composition [121, 122], the ionic strength, the pH [123], the temperature, and/or the presence of additives in the solution [80, 125-131].

Micellar growth can result in micrometer long micelles, often referred to as ‘worm-like’, ‘thread-like’, or ‘giant’ micelles. Shear thinning and suppression of turbulent flow are related to flow induced changes in the structural orientations of wormlike micellar solutions. These flow properties are relevant in applications like thickners, and flow improvers in food, pharmaceutical and paint, cosmetics industry, fracturing fluids in oil production [132], enhanced oil recovery [133]. One of the practical applications of wormlike micellar solutions is their use as drag-reducing fluids [134], a promising technology for energy saving in heating/cooling systems. [135, 136].

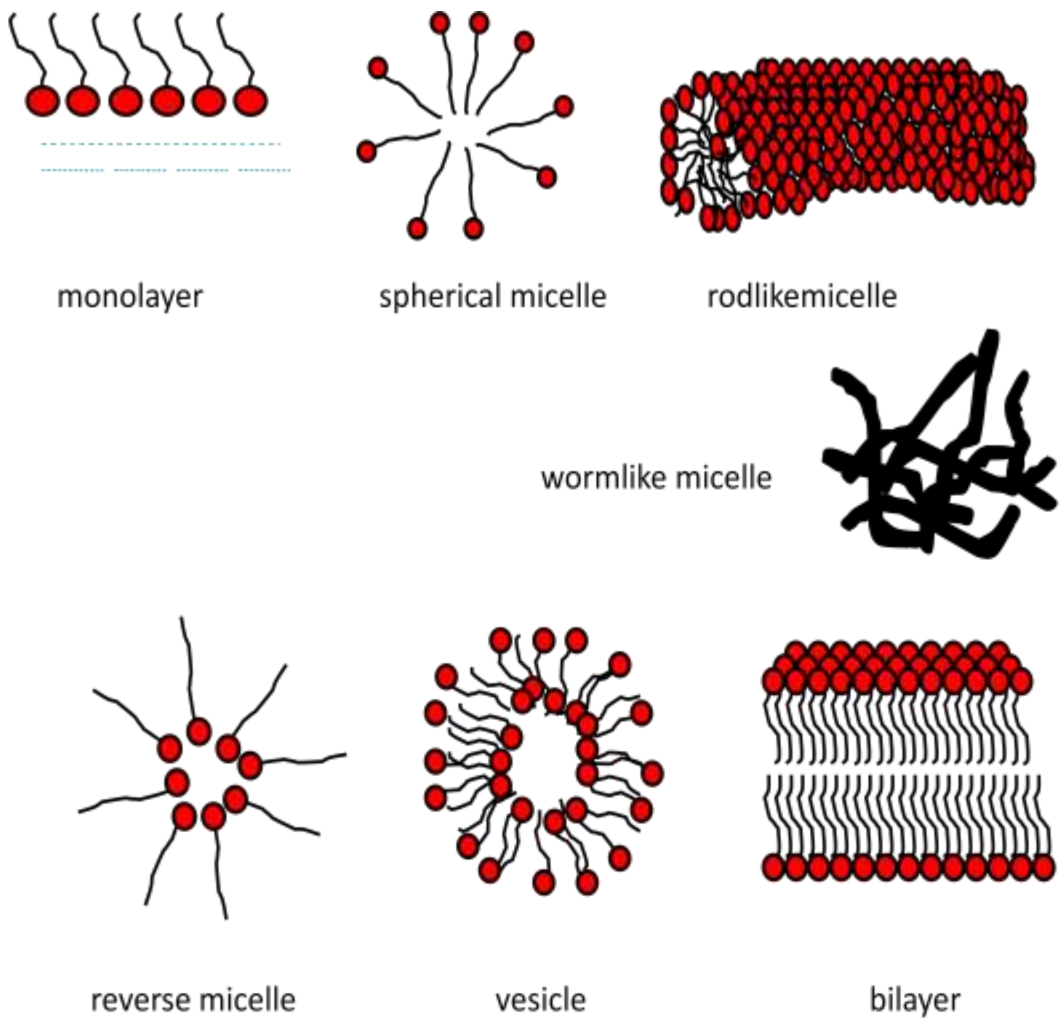


Figure 7. Examples of some of self-assembled structures formed by surfactant monomers.

It is now well-understood that the addition of appropriate salt to aqueous surfactant solution reduces electrostatic repulsion between the headgroups and causes micellar growth, in which the spherical micelle undergo a transition to rodlike, larger cylindrical aggregates or flexible wormlike micelles and vesicles. Spherical micelles of quaternary ammonium halides grow gradually to rod-shaped on the addition of different counterions[137]. The counterion binding suppresses the micellar charge and a_o. This results in tighter packing, modifying the spontaneous curvature of the surfactant assemblies (Figure 7) and the solution properties [79, 138,139].

It is well-known that salts like KBr and NaSal induce pronounced growth of CTAB micelles [140, 141].The size and shape of the micelle are influenced by the counterion distribution or condensation on the micelle surface [142]. Weican et al. [143] have investigated the effect of KBr on the microstructure of CTAB micelles and showed that the hydrodynamic radius, R_h, of the CTAB micelles (0.01 M) increased from 3.5 to 43 nm with the addition of 0.6 M KBr.

Using Shear rheometry and cryo-TEM, Lin et al. have reported that addition aromatic acid to 0.02 M aqueous solutions of CTAB causes spherical micelles to undergo a transition to wormlike micelles [128]. The reported systems mainly include CPyX [144-149], CTAX [150, 149-155], or some other cationic surfactants [156-157].

Till date, different strategies have been used to grow the anionic micelle. Ikeda et al. [159] have shown that a transition of micelle shape from sphere to rod occurs in SDS solution when NaCl concentration was higher than 0.45 M. It was mentioned by Bertrand et al. that 3.5% aqueous solution of SDS can undergo transition from spherical to rod like in presence of 0.28 M NaCl [160].

Several reports indicate that change from Li^+ to Cs^+ as counterion induces micellar growth which can be related to hydration of specific counterion [161]. The formation of rod like micelles can be strongly enhanced in anionic surfactant solutions in presence of multivalent counterions (Ca^{2+}, Al^{3+}) [162,163]. Al^{3+} can bind together three surfactant head groups at the micelle surface thus causing a significant decrease of a_0 [162]. This induces a transition from spherical to cylindrical micelles.

Incremental calorimetric technique was used by Nguyen and Bertrand [164] to study the effect of low concentrations of alcohols on solutions of SDS with added electrolytes. These measurements reveal a discontinuity in the slope of partial molar enthalpy of solution versus concentration of alcohol curves. The authors assert that this break corresponds to the micellar sphere-to-rod transition. Upon continuous addition of Al $(NO_3)_3$, SDS solution passes through coagulation, redispersion, and an isotropic micellar L_1 phase where threadlike micelles were observed [165]. However, the viscoelasticity of SDS-$Al(NO_3)_3$ micellar solution is closely dependent on the high concentrations of SDS and $Al(NO_3)_3$, as well as temperature. Mu et al. [166] reported that 0.032 M SDES system shows the presence of spherical and some rodlike structureswith 0.8 M $AlCl_3$ using FF-TEM.

Kunz and coworkers [167-169] investigated an ion-specific micelle to vesicle transition with the addition of salts to catanionic surfactant constituted by DTAB/SL or DTAB/SDS with excess of anionic surfactant. However, an elongation of micelles is observed in the case of the DTAB/SLsystem with excess of DTAB.

Danino and coworkers [170] reported transition of spherical into linear wormlike micelles in the mixed catanionicsurfactant NaOA/OTAB. In oppositely chargedsurfactant solutions, the sphericalmicelles grow into linear wormlike micelles and these wormlikemicelles continue to elongate as one moves towards viscosity peak from either end.

Clouding phenomenon

Most nonionic surfactant aqueous solutions have characteristic to show clouding on heating, followed by a phase separation into two phases (surfactant rich and surfactant lean phases). The threshold temperature, at which clouding first appears in surfactant solutions, is known as CP [171-175] and the phenomenon is known as clouding phenomenon. Goyal et al. has suggested that an increase in temperature results in gradual removal of hydrated water from hydrophilic headgroups leading to van der Waals attraction between micelles to dominate and resulting into the clouding [173, 176].

Phase separation results from the competition between entropy, which favors miscibility of micelles in water, and enthalpy, which favors separation of dehydrated micelles from water [177]. In surfactant lean phase (the bulk aqueous phase) the surfactant concentration is approximately equal to its *cmc*, whereas, rest of the surfactant would remain in the rich phase. The phase separation is reversible when the system is cooled below the CP. To understand the clouding phenomenon, a variety of technique, including fluorescence spectroscopy [178], turbidimetry, [179-181], SANS, DLS [171, 182], and viscosimetry [171], have been used.

Clouding phenomenon is common with nonionic surfactants. However, it is comparatively less known with ionic surfactants [183-190]. It may be due to the large electrostatic repulsion between the aggregates of ionic surfactant.Hydration is another factor acting against the occurrence of the phenomenon [173, 183-186].

Recently, research activities have been focused on studying the relatively less common clouding phenomenon with anionic surfactants in combination with large hydrophobic cations, *e.g.*, SDS and quaternary ammonium bromides [191-199]. Sodium perfluorooctanoate and tetrapropyl ammonium bromide has shown the phenomenon while such behavior was absent in pure surfactant solution [200]. An acid-induced clouding with anionic surfactants was also reported [201].

A few cationic surfactant solutions also show clouding behavior.Appell and Porte reported CP at high concentrations of sodium chlorate in aqueous solutions of either CTAB or CPyBr [187]. In a later study, Warr and co-workers showed that quarternary ammonium surfactants with tributyl headgroups exhibit cloud points in binary aqueous solution [188]. Cationic surfactants also show the behavior in the presence of hydrophobic anions, *e.g.*, erucyl-bis(hydroxyethyl)methyl ammonium chloride in the presence of tosylate or salicylates [202]. The CP appearance in these systems is explained in terms of increased hydrophobic interactions, the dehydration of the hydrophilic group [191] and the formation of large aggregates or clusters [185,195].

Warr et al. have reported that increased hydrophobicity near the headgroup region by an additional methylene group (going from tri-*n*- propyl- to tri-*n*-butylammonium) in a cationic surfactant results a departure (liquid-liquid phase separation) of the behavior of producing stable solutions at elevated temperatures [184]. This clearly shows that not only the temperature but also other equally important factors are responsible for producing the clouding in surfactant solutions.

It was reported by Yan et al. [203] that cationic polymer and anionic surfactants also show clouding phenomenon. They reported an unusual increase in the CP of such a mixed system (oppositely charged polymer and surfactant) with addition of salts, such as Na_2SO_4, NaCl, NaBr, and NaSCN.

Kim and Shah [204-206] have observed the clouding in AMT solutions (antidepressant drug) and have explored the effect of additives. It was observed that the CP decreases with increasing pH as well as concentration of electrolyte. This is due to a reduction in electrostatic repulsion between the AMT micelles. Kabir-ud-Din et al. [207-209] have also studied CP phenomenon in some amphiphilic drug solutions and reported the effect of different additives.

A number of applications are reported for the CP phenomenon in diverse fields[210-214] but the mechanism by which it occurs is not yet clear and still a source of controversy among different groups [202, 203, 215-218].

The Langer−Schwartz theory [218] predicts that the nucleated phase may appear as a cloud of small droplets that grow slowly beyond the critical droplet size or that it may form as an isolated droplet that rapidly grows to a very large size. The analogy can be drawn to surfactant solution in which liquid−liquid immiscibility occurs above the CP. Using a lattice gas theory, it has been shown that CP arises from a sudden increase in rotational entropy caused by rapid breaking of H-bonds between water and surfactant heads [217]. In ionic surfactantsolutions, above bonds are expected even stronger due to charged headgroup- water interactions.

Later on, phenomenon of clouding was explained on the basis of clustering of micellesdue to intermicellar interactions. In recent reports, it has been proposed that the formation of the connected micellar network [219], or strongly orientation dependent interactions [220], between water and micellar head groups could be responsible for the clouding phenomenon.

Some groups have explained CP phenomenon on the basis of micellar interaction and micellar growth. Corti et al. [171] interpreted the increase in turbidity as due to critical fluctuations of micellar concentrations and not to a temperature dependence of the micellar size. Glatter et al. [220] showed that there are micellar interaction and micellar growth in aqueous solutions of nonionic surfactants of the *n*-alkyl polyglycol ether type near the CP. They used SANS, depolarized light scattering and ultralow shear viscometry. On the contrary, Laughlin [221] suggested that micellar interaction and micellar growth have nothing to do with the CP because the phenomenon can also observed in non surfactant systems. Polar organic additives can decrease or increase CP in aqueous solutions [222]. Preferential adsorption of the additive at the micelle-water interface was found the main factor that determines the changes in the CP.

The CP phenomenon of surfactants has been utilized to design efficient extraction methods for the separation, preconcentration or purification of a variety of substances including metal ions and organic compounds [201, 223-229]. The cloud point extraction method offers a simple, rapid, sensitive, and inexpensive alternative to other separation or preconcentration techniques based on organic solvents.

Relevance of the Research Problem

For various applications, surfactants are required to be present simultaneously with different additives (another surfactant, salt, hydrocarbons, drugs etc.) to improve their performance through synergistic interactions.Studies on surfactants and their mixtures with a variety of additives in aqueou solutions are, therefore, of interest regarding their technical applications. The key question here is to understand the magnitude and nature of the additives as well as the mechanism involved so that suitably modified systems, having desired mode of action can be designed. Accordingly, a fundamental understanding of additive effect on the morphologies formed in aqueous surfactant solutions may lead to a more effective utilization of these systems in various practical applications (single or with other additives). The presence of grown micelles imparts high viscosity to solutions which might be of importance in industrial formulations as it enhances performance and customer appeal of the products. Control of viscosity of the formulations with additive can be achieved by varying the concentration and/or nature of additives. It is, therefore, of genuine interest to ascertain the effect of additive(s) (present singly or in combination of other one) on the solution behavior of surfactant. Further, effect of physico – chemical conditions (temperature, pH, concentration, etc.) on the solution behavior of surfactant is equally important factor to be considered in detail.

- The present thesis comprises of eight chapters (including **chapter 1** as general introduction). At the start of the **chapter 1**, various abbreviations and symbols (to be used throughout) are included in tabular form.
- Experimental details are provided in **chapter 2**.
- **Chapter 3** contains studies related to micellization and clouding phenomenon in various anionic surfactant solutions with and without TBAB. All these anionic surfactants have not shown any clouding phenomenon or phase separation in aqueous solution without TBAB.
- In **Chapter 4** we have synthesized an anionic surfactant (TBADS) on the basis of information collected in **chapter 3**. SANS studies were performed to

have an idea about the changes occurring in the TBADS solution when it is heated towards CP.

- **Chapter 5** has studies related to the clouding behavior of another anionic amphiphilic system (NaDC) having biological origin. To our surprise various additives (including TBAB) failed to produce clouding with NaDC solutions. However, NaDC solution shows clouding with AMT. Effect of various additives on the clouding behavior of NaDC + AMT system has also been checked in this chapter.

- The morphological transitions in anionic surfactants (SDS and SDST) with various additives (organic salts or drugs) are studied and included in **chapter 6.**

- Morphological transition studies were further extended with a cationic surfactant (CTAB) in presence of NaDC and work presented in **chapter 7**.

- Last **chapter 8** includes studies related to hexanol -triggered microstructural transitions in an aqueous cationic gemini surfactant (16-4-16) + KBr system using various physico-chemical and direct imaging technique**.**

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