
Chapter I

Introduction



1.1 Surfactants.

Nature has devised several versatile and vital compounds without which our biological system would not operate, including the cell membrane that contains the living cell. Such compounds have led to many micro heterogeneous supra-molecular systems that play an important role in many applications. In these classes of compounds, the one that are used in diverse research areas, from basic chemical kinetics to membrane mimetics in biological sciences are the so-called “Surface Active Agents” or “Surfactants”.

A surfactant or surface-active agent is a molecule that consists of a water-soluble (hydrophilic or polar) part and an oil-soluble (hydrophobic or non polar) part. The hydrophilic part is called the head group and the hydrophobic part is called the tail group. The two different hydrophilic and hydrophobic parts make the surfactant surface active in the sense that it adsorbs or accumulates at interfaces between polar and non-polar media, so that the head group is solvated in the polar medium and the tail group in the non-polar medium. Examples of such interfaces are those between water and air or between water and oil.

An interface between hydrophobic and hydrophilic media is always energetically unfavorable and a system is always trying to minimize the interfacial free energy. When a surfactant adsorbs at an interface, the free energy of that interface decreases (which is the reason for adsorption to occur) and therefore it becomes possible to have larger interfacial areas in the system. For example, if oil is mixed in water under constant stirring conditions, the formed droplets of oil in the water will be quite large. The droplets will eventually coalesce in to bigger droplets to lower the interfacial free energy and then they rise in general to surface due to lower density of the oil. However, if surfactant is present, it will adsorb at the water/oil interface, lower its surface energy so the droplets of oil will be much smaller and an emulsion is formed. The emulsion can form a thermodynamically unstable macro emulsion, which eventually phase separates after some period of time, or a thermodynamically stable micro emulsion is formed. The surfactant's

ability to lower the interfacial energies is also important in the formation of foams and dispersions. Besides ability to lower surface energy, other properties of the adsorbed surfactant layer are of utmost importance. For example, the bending rigidity, the spontaneous curvature and the elasticity of the adsorbed layer.¹

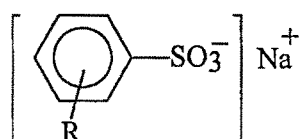
The importance of surfactants in enabling various aspects of interfacial science cannot be overstated. Surfactants are critical in many applications in agrochemicals, emulsion polymerization, metal cleaning, paper manufacturing, construction materials, oil recovery, fire fighting, textile manufacturing, plastics manufacturing, water treatment, drug delivery systems etc.² The first group of traditional or synthetic surfactants was developed in Germany during World War I in an attempt to overcome the shortage of animal and vegetable fats. Thereafter, till date synthesis of new classes of surfactants is being reported at an increasing rate and has made a major impact in the surfactant and detergent industry.

Many operations and processes in both domestic and industrial situations rely on the efficiency of surfactants. This led to many investigations to improve the performance properties of surfactants, e.g. mixture of surfactants. The surfactants used in a multitude of industrial products, processes and other practical applications, almost always consist of a mixture of surfactants. Thus the influence of the interaction between the components of a mixture on their physico-chemical properties, including the adsorption behaviour and micelle formation is of fundamental importance. Hence, a good deal of research is being carried out on various detailed mechanisms whereby surfactants function and about the ways in which mixtures of surfactants either reinforce or neutralize the efficiency of the single component.

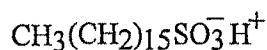
1.2 Classification of Surfactants.

Surfactants are usually classified according to the nature of their head group. Based on the charge on the polar head group and its molecular structure, they have been classified as follows,

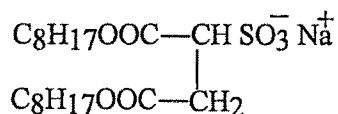
- I) Anionics: The surface-active portion of the molecule bears a negative charge.



e.g. Sodium dodecyl benzene sulphonate (SDBS)

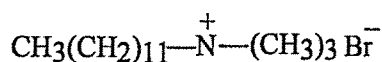


Hexadecyl sulphonic acid.

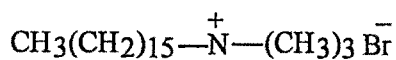


Sodium dioctyl sulpho succinate

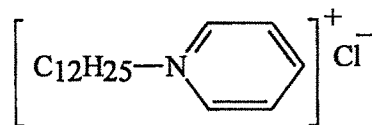
- II) Cationics: The surface-active portion bears a positive charge.



e.g Dodecyl trimethyl ammonium bromide (DTAB)

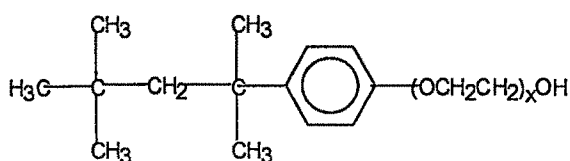


Hexadecyl trimethyl ammonium bromide (CTAB)



Dodecyl pyridinium chloride (DPC)

II) Nonionics: The surface-active portion bears no apparent charge.

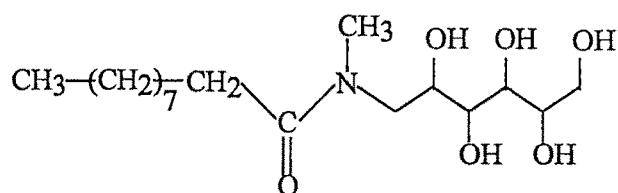


$x = 9-10$

e.g. Poly oxyethylene Tert-octyl phenyl ether (Triton X 100)

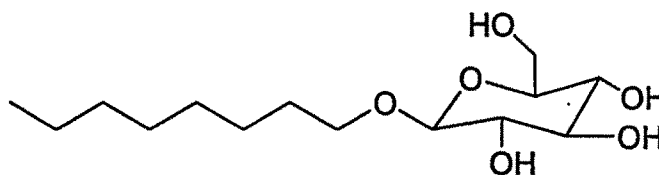


Brij 56



N-Decanoyl N-Methyl Glucamide (Mega 10)

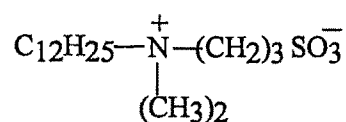
Alkyl Poly Glycoside



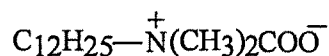
e.g. Octyl β -D glucoside

- IV) Zwitterionics: They are often referred as amphoteric. The surface-active portion bears both positive and negative charges.

e.g Betaines

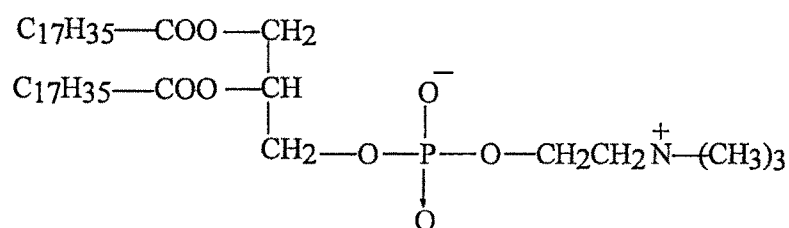


3-dimethyl dodecyl propane sulfonate

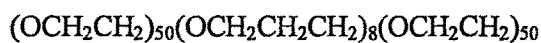


N-dodecyl-N,N-dimethyl betaine

Lecithin (a tryglyceride)

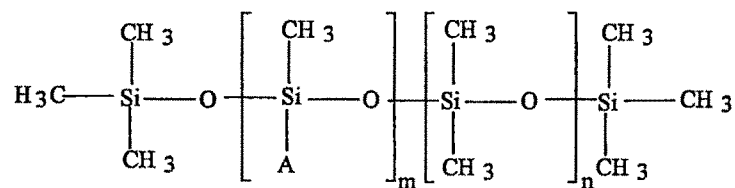


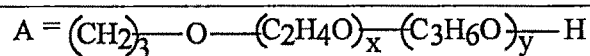
- V) Polymeric Surfactants: Block Polymers called Pluronics.



e.g Pluronic – 85

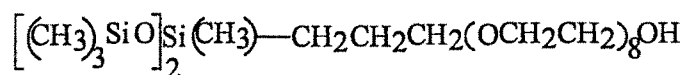
Silicone Surfactants. They consist of a per methylated siloxane hydrophobic group (poly dimethyl siloxane) coupled to one or more polar groups.^{3,4}





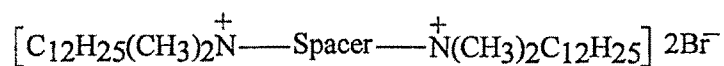
m = polyether modified siloxane,

x = ethylene oxide, y = propylene oxide



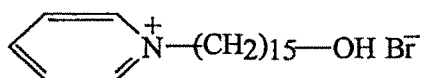
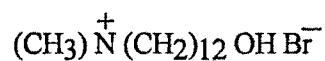
Methyl (propyl hydroxide, ethoxylate) bis (trimethyl siloxy) silane

- VI) Gemini Surfactants: These surfactants are made of two hydrophobic chains and two polar head groups covalently attached through a spacer group.^{5,6}

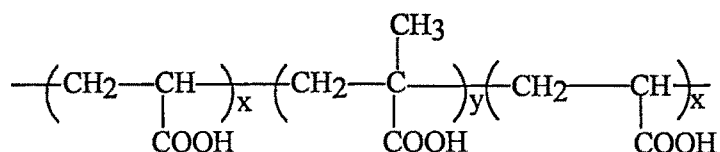


Spacer	Abbreviation
$-(\text{CH}_2)_2 - \text{O} - (\text{CH}_2)_2-$	12-EO-12
$-(\text{CH}_2)_6-$	12-6-12

- VII) Bolaform Surfactants: They have two identical hydrophilic groups separated by a hydrophobic spacer chain.⁷



VIII) Poly electrolytes: Ligno sulfonates (anionic poly electrolytes prepared by sulfonation of wood lignin).



Poly acrylic acid and poly acrylic/polymethacrylic acid.

1.3 Micelles.

The fundamental property of surfactants is their ability to form aggregates when mixed with water. Common type of aggregates are micelles and their presence was originally suggested by McBain.⁸ They begin to form at a specific concentration called the critical micelle concentration, cmc which is dependent on the surfactant structure. He concluded that below cmc, most of the surfactant molecules are unassociated whereas in isotropic solutions, just above the cmc, micelles and surfactants coexist with concentration of latter changing very slightly as more surfactant is dissolved.

The micelles consist of rather limited number of surfactant molecules, typically 50-150, forming a closed structure in order to minimize the contact between the surfactant's hydrophobic part and the water. The mechanism behind this is called the hydrophobic effect.^{9,10} The surfactant tail groups will constitute the liquid like hydrophobic interior of the aggregates, while the head groups form an outer hydrophilic layer towards the water phase. It was suggested by Adam¹¹ and Hartley¹² that micelles are spherical in shape. G. S. Hartley¹² one of the first to discuss the micelle structure, wrote in 1936, "The symmetrical asterisk form has no physical basis and is drawn for no other reason that the human mind is an organizing instrument and finds unorganized process uncongenial". It is generally assumed that micelles at concentrations close to cmc are spherical.^{15,16} Figures 1 and 2 illustrate, two-dimensional structure of ionic and nonionic micelle¹⁷ respectively.

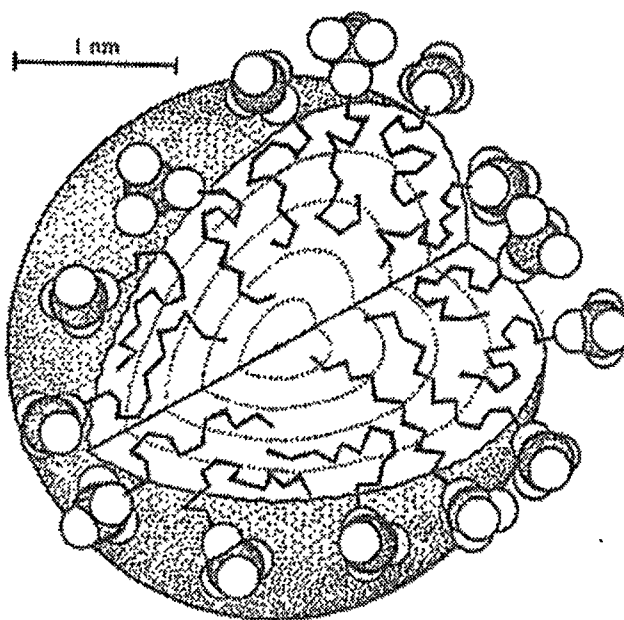


Figure 1. A spherical micelle of ionic surfactant emphasizing the liquid like character with a disordered hydrocarbon core (Ref. 17).

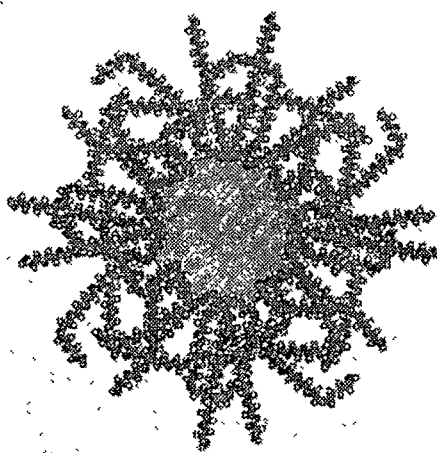


Figure 2. Schematic representation of a nonionic micelle (Ref. 17).

In aqueous medium, the surfactant molecule gets oriented in such a way that the polar heads are towards the solvent and the hydrocarbon groups away from it forming a part of micelle. Such micelle is termed as a “normal micelle”.

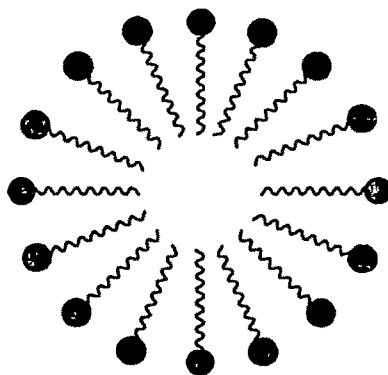


Figure 3. A Normal Micelle (In Aqueous Medium).

Whereas in non-polar/non-aqueous medium, the lipophile attracts the hydrophobic parts and forces the hydrophilic heads away, which then are held together by dipole-dipole interactions and lead to micelle core surrounded by hydrophobic groups in contact with the solvent, such micelles are termed as “reverse or inverted micelles”. Both types of micelles are thermodynamically stable and are comparable dimensionally. Diagrammatic representation of a normal and reverse micelle are shown in Figs. 3 & 4.

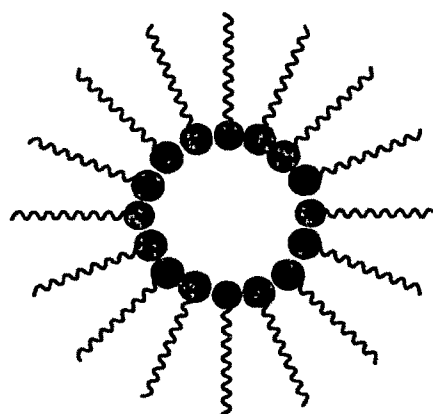


Figure 4. A Reverse Micelle (In Non-Aqueous Medium).

The shape of the micelle is dependent on the structure of the surfactant, typically the relative size of the head group and tail group. This is often described with the critical packing parameter, CPP, defined as,

$$CPP = \frac{V_H}{l_c a_0} \quad (1)$$

where V_H , l_c and a_0 are the volume occupied by the hydrophobic group in the micelle core i.e

$$V_H = 27.4 + 26.9 n_c \text{ \AA}^3 \quad (2)$$

where n_c is the number of carbon atoms in the hydrocarbon chain of the surfactant molecule. l_c is the length of the hydrophobic group in the core. i.e $l_c = 1.5 + 12.6 n_c \text{ \AA}$ and a_0 the area of cross section occupied by hydrophilic group at micelle solvent interface.¹ Spherical micelles will be formed if $CPP < 1/3$. As CPP increases, i.e as the relative size of the hydrophobic part increases, the curvature of the aggregates will decrease and disc-, tablet- and rod like micelles are formed. e.g. Hexagonal [$1/3 < CPP < 1/2$], lamellar [$CPP \approx 1$] and cubic [$CPP \geq 1$] phases are possible.¹⁸ A schematic representation of different kind of micellar structures and their dependence on the critical packing parameter is depicted in Fig. 5.

The spherical micelles have the following properties,⁹

- a) the association unit has radius approximately equal to the length of the hydrocarbon chain
- b) there are 50-100 monomers in micelle and this number increases as the hydrocarbon chain length increases
- c) the counter ions are bound to the micelles of ionic surfactants, thus reducing its mobility compared to its nonionic counter part
- d) due to higher association number of surfactant monomers, micellization occurs over a narrow range of concentration
- e) the micelle interior has essentially the properties of liquid hydrocarbon as a result of which it solubilizes water insoluble organic molecules.

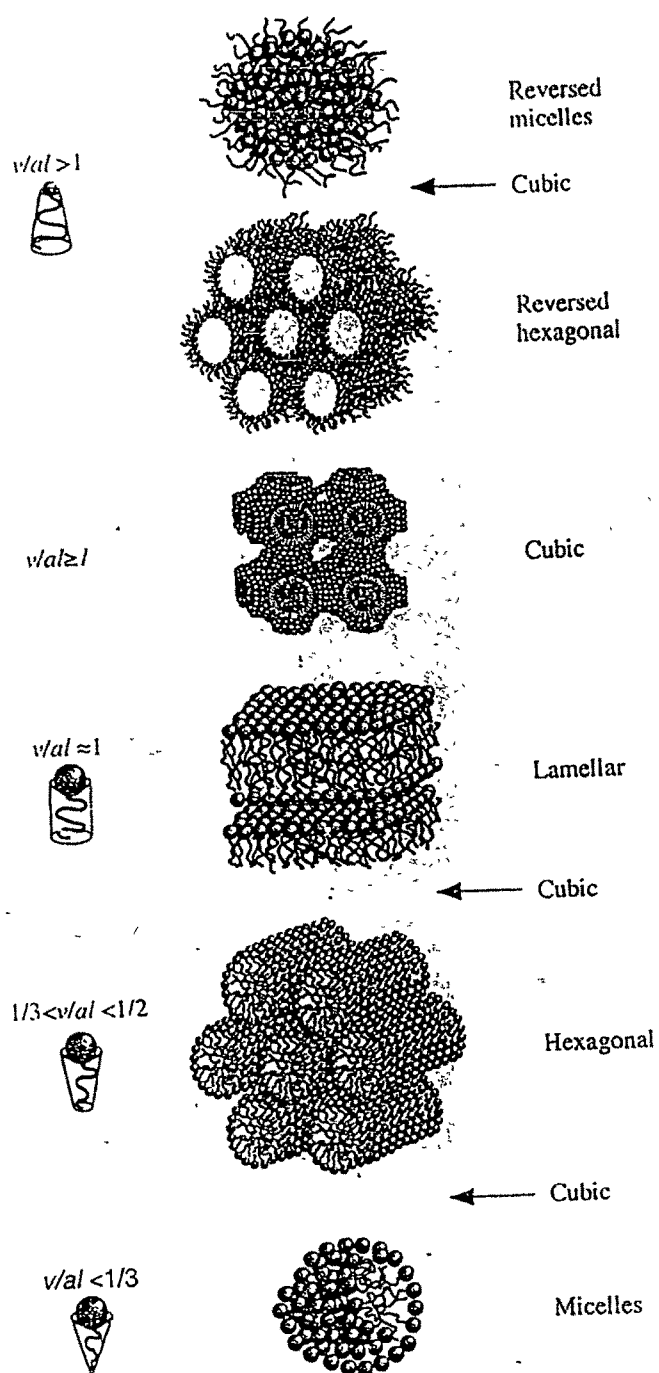


Figure 5. Critical Packing Parameters (CPP) of surfactant molecules and aggregate structures due to geometrical reason.

As mentioned earlier, apart from spherical micelles, different shapes of micelles are known they are; i) elongated cylindrical rod like micelles with hemispherical ends (prolate ellipsoids) ii) large, flat lamellar micelles (disc like extended oblate spheroids) and iii) vesicles, almost spherical structures consisting lamellar vesicles arranged in one or more concentric spheres.

Hayashi et al.¹⁹ have shown that in presence of low concentrations of sodium chloride, sodium dodecyl sulphate (SDS) form spherical micelles and associates itself into rod like micelles at high NaCl concentration. Hassan et al.^{20,21} have reported growth of SDS and CTAB micelles in presence of organic additives. Moreover, they have also reported existence of vesicles in aqueous solutions of cetyl trimethyl ammonium 3-hydroxy naphthalene 2-carboxylate (CTAHNC).^{22,23} More recently May et al.²⁴ have suggested a molecular level theory focusing on the early stages of micellar elongation (sphere to rod transition). They concluded that the interplay between inter head group and inter chain free energies play a crucial role in determining shapes packing free energies of the growing micelles.

1.4 Critical Micelle Concentration (cmc).

The physical properties of surface-active agents differ from those of smaller or non-amphiphilic molecules in one major aspect, namely the abrupt changes in their properties above a certain critical concentration²⁵ termed as the critical micelle concentration. The physical properties, which undergo abrupt changes and those, which are useful in determination of cmc, include, equivalent conductivity, surface tension, osmotic pressure, light scattering intensity, self-diffusion, solubilization and magnetic resonance. Each surfactant molecule has a characteristic value of cmc (really a very narrow range) at a given temperature and it is the simplest means of characterizing the colloid and surface behavior of a surfactant solute, which in turn determines its industrial usefulness and biological activity, and also gives a measure of the structurally interesting solute-solvent and solute-solute interactions.²⁶

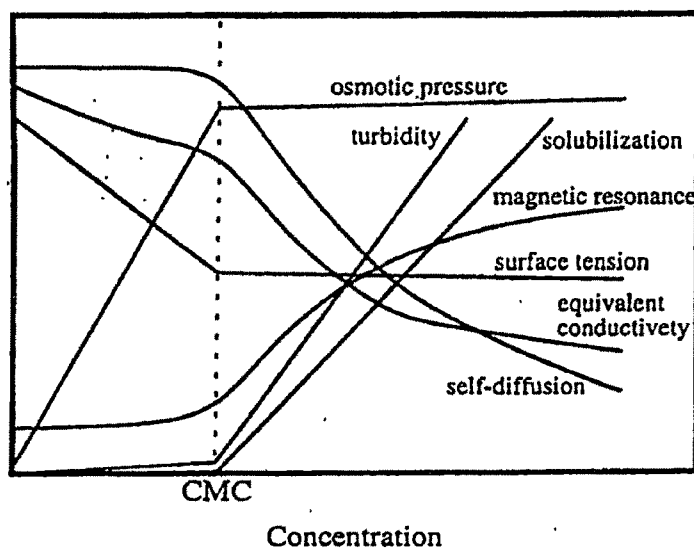


Figure 6. Schematic representation of concentration dependence of physico-chemical properties for solutions of surfactant.

1.4.1 Factors affecting critical micelle concentration.

The physical properties of solutions of surface-active agents change markedly when micelle formation commences and therefore many investigations have been concerned with determining the values of critical micelle concentration in various surfactant systems. Moreover a great deal of attention has been there on elucidating the various factors that affect the cmc in aqueous solution, such as the hydrophobicity of the hydrocarbon chain,²⁷⁻³⁰ nature of the polar head group,^{28,29,31} counter ion,³²⁻³⁴ temperature,³⁵⁻³⁷ pressure,³⁸ pH,³⁹⁻⁴¹ presence of electrolytes,⁴²⁻⁴⁴ polar⁴⁵ and non-polar additives,⁴⁶ etc.

1.4.1 (a) Surfactant Structure:

The critical micelle concentration decreases as the number of carbon atoms in the hydrophobic tail increases to about 16.⁴⁷ For ionic surfactants with one hydrophilic group, the cmc is halved by the addition of one methylene ($-\text{CH}_2$) group.⁴⁸ But for nonionic and zwitterionic surfactants, the magnitude of decrease in cmc is much larger. Chain branching,

unsaturation of hydrophobic chain also has an influence on cmc.¹⁴ Recently Haldar et al.³¹ have reported the influence of introduction of multiple head groups in cationic surfactant on the micellar properties and it was observed that the cmc values increase with increase in the number of headgroups 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.⁴⁹ Moreover introduction of polar groups such as -O- or -OH in to the hydrophobic group causes a significant increase in cmc. The replacement of a hydrocarbon based hydrophobic group by a fluorocarbon based one with the same number of carbon atoms decreases the cmc.⁵⁰ However, exactly in contrast, the replacement of terminal methyl group of a hydrocarbon based hydrophobic group by a trifluoro methyl group causes the cmc to increase.

In general, ionic surfactants have higher cmc values compared to zwitterionics, which is again much higher than nonionic surfactants for the same number of carbon atoms. Dimeric or Gemini surfactants have much lower values of cmc than the conventional surfactants.⁵¹ Also, the cmc values of dimeric surfactants have been found to be dependent on the length, nature (hydrophilic, hydrophobic) and flexibility of spacer.⁵ For the series of quaternary ammonium surfactants $[C_{12}H_{25}N^+(R)_3Br^-]$, the cmc decreases as the length of alkyl chain (R) increases because of the corresponding increase in hydrophobicity.^{32,50}

For polyoxyethylene nonionics of type $C_{12}E_n$ ($n=4, 6, 8$), the cmc values increase as the ethylene oxide content increases,⁵² whereas for the surfactants of type C_nE_8 , ($n=9-15$) the cmc decreases as the number of carbon atoms increases.⁵³ Rosen⁵³ has also reported an increase in cmc with increase in hydrophilicity for C_nE_m ($m=1-8$) and p-tert octyl phenoxy poly(ethenoxy ethanol) respectively. For ionic surfactants in aqueous solution, the increased binding of the counter ions causes a decrease in cmc of the surfactant. Thus the counterion with higher polarizability decreases the cmc more. Recently Gandhi et al.³³ reported the influence of valence of counter ion on the mixed anionic-nonionic system and they observed that the counter ion with highest charge density and small size decreased the cmc more.

1.4.1 (b) Additives:

Numerous studies have been reported on the effect of additives on the micellar properties of surfactants. The presence of third component (additive) in the solution can modify the micellization process in two different ways;⁵⁴⁻⁵⁷ a) through specific interactions with the surfactant molecules or b) by changing the solvent nature. The modification of solvent properties by addition of electrolytes and non-electrolytes can either increase or decrease the cmc. Innumerable investigations on the study of the influence of electrolyte on the micellar properties of surfactants have been reported by several researchers.⁵⁷⁻⁶¹ The presence of electrolyte has more pronounced effect on the cmc of anionic and cationic surfactants. The presence of electrolyte reduces the thickness of the ionic atmosphere surrounding the polar head groups and consequently decreases the repulsion between them. Somasundaran et al.⁶¹ have reported the cmc values for sodium dodecyl sulphate (SDS) in various electrolytes viz. NaCl, Na₂SO₄, LiCl, CsCl, Cs₂SO₄, MgCl₂, MgSO₄ and Na₃(PO₄)₂. All these electrolytes decrease the cmc of SDS. Mukerjee et al.⁵⁷ have also reported similar studies concerned with the effect of electrolyte on micelle formation. Abe et al.⁵⁸ have reported the effect of different electrolytes (NaCl, NaOH and HCl) on the micelle formation of mixed amphoteric-anionic surfactant systems and they observed that the cmc values of mixed surfactant systems including HCl are much smaller than those of systems including NaCl. They concluded that the inorganic electrolytes affect the magnitude of hydrophobic-hydrophilic interactions between the constituent surfactant molecules in the mixed micelles. Goddard and coworkers⁶² studied the effect of alkali metal salts and some quaternary ammonium salts on the cmc of SDS and found that the ability of alkali metal cations to decrease the cmc increases with decrease in the size of the hydrate cation.

Engberts et al.⁶³ reported that the sodium salts decrease the cmc in the order $\text{Cl}^- < \text{Br}^- < \text{NO}_3^- < \text{I}^-$ for the surfactant 1-methyl 2-dodecyl pyridinium iodide. The order of decrease is in accordance with the lyotropic series of inorganic anions. The cmc decreases with increasing salt content followed the counterion concentration at cmc as given by Shinoda equation,⁶⁴

$$\log CMC = A - B \log(CMC + [NaX]) \quad (3)$$

where A & B are constants.

Attwood and coworkers⁴⁴ studied the influence of electrolyte on the micellization of phenothiazine, a drug molecule and concluded that addition of electrolyte promotes micelle formation in these type of molecules. Other than the electrolytes, organic additives are also known to influence the micellization behaviour of surfactants. Organic additives affect, either by being incorporated in to the micelle or by modifying solvent-solute interactions.⁵¹

The studies on effect of alcohols on micellar properties of surfactants were initiated by Ward⁶⁵ way back in 1940 and he found that the critical micelle concentration of SDS passes through a minimum on addition of ethanol. Such behaviour was confirmed later for the first three homologous alcohols in various micellar systems. It was found that long chain alcohols always decreased the value of cmc. Further contribution to the understanding of water-surfactant-alcohol systems were made by Shinoda,⁶⁶ Emerson and Holtzer,⁶⁷ Larsen and Tepley,⁶⁸ Miyagishi,⁶⁹ Hayashi and Hayano,⁷⁰ Manabe et al.,⁷¹ Guveli et al.⁷² and Christian et al.⁷³ Extensive studies on the effect of linear alcohols (ethanol to hexanol) on cmc, micellar molecular weight and degree of ionization of micelles of homologous alkyl trimethyl ammonium bromides have been reported by Zana and coworkers.⁷⁴⁻⁷⁹ Treiner and coworkers⁸⁰⁻⁸⁵ have extensively studied the partitioning of alcohols and other organic solutes in micellar solutions from cmc determinations. More recently, Gonzalez-Perez et al.⁸⁶ studied the cmc and degree of ionization of micelles of tetradecyldimethylbenzylammonium chloride (C₁₄BCl) and tetradecyltrimethylammonium bromide (C₁₄TBr) in aqueous solution of butanol and benzyl alcohol at different temperatures. They observed that benzyl alcohol influences the cmc values more strongly. The cmc values for both the surfactants decrease linearly with the molarity of the butanol, whereas in case of benzyl alcohol, peculiar breaks appear on both plots in C₁₄BCl.

Fendler and Fendler⁸⁷ have reported the cmc values for hexyl ammonium propionate surfactant in DMSO-water mixed solvent system. Similar studies were carried out recently by Chauhan et al.⁸⁸ on micellization of SDS in dilute aqueous electrolyte solutions. The effect of other organic solvents like glycerol, hydrazine, amines and esters has also been well studied.⁸⁹⁻⁹³

Urea and its derivatives are well known water structure breakers and protein denaturants.^{94,95} Since, Bruning and Holtzer⁹⁶ first demonstrated that urea disrupts micelles, many investigators reported that cmc of ionic and nonionic surfactants significantly increase with addition of urea in aqueous solutions.^{97,98} Two different mechanisms were proposed to explain urea action on aqueous solutions (a) urea acts as a water structure breaker (indirect mechanism) and (b) urea participates with the solvation of hydrocarbon chains in water by replacing water molecules in the hydration shell of the solute (direct mechanism). However, a computer simulation of urea action in aqueous solution showed negligible influence of urea on the water structure, rather it weakens the water/water interaction by replacing several water molecules from an apolar solvation shell.^{99,100} More recently, Asakawa et al.¹⁰¹ studied the influence of urea on micelle formation of fluorocarbon surfactants. Their results suggested significant differences in micellar characteristic between fluorocarbon and hydrocarbon surfactants and the cmcs of the fluorocarbon surfactants slightly decrease with the addition of urea.

Some other additives that markedly influence the aqueous solution properties are xylose, dextrose, fructose, sucrose and poly ethylene glycol; which are highly hydrophilic and water structure formers. Sulthana and coworkers¹⁰²⁻¹⁰⁵ have extensively studied the effect of poly ethylene glycol, acetamide, sucrose as well as urea on micellization of nonionic, anionic and anionic/nonionic mixed surfactant system. They observed that the cmc of SDBS & mixed anionic/nonionic (SDBS/C₁₂E₁₀) surfactant system increased in the presence of additives. However, it was found that the cmc of C₁₂E₁₀ as well as Myrj 45 decreased in the presence of additives.

1.4.1 (c) Temperature:

The effect of temperature on cmc of surfactants in aqueous medium is complex. The cmc value first decreases with temperature to some minimum and increases with further increase in temperature. The minimum in the curve for ionic surfactants occurs typically between 20 and 30°C. Whereas isolated examples exist of minima in cmc-temperature profile for nonionic surfactants. Such minima were observed at approximately 50°C for a series of octyl phenoxy ethoxy ethanols with oxyethylene chain lengths of between 6 and 10.¹¹²

The variation of cmc with temperature for ionic¹⁰⁷ and nonionic surfactant¹⁰⁸ is illustrated in Fig. 7. The decrease in cmc of ionic surfactants with temperature increase at lower temperatures is due to dehydration of the monomers, whilst further temperature increase causes disruption of structured water around the hydrophobic groups which hinders micellization.

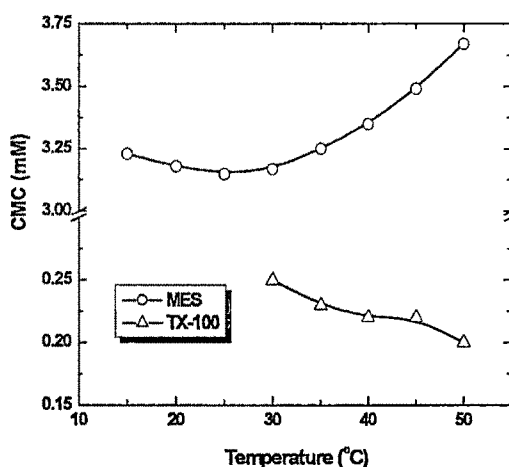


Figure 7. Temperature dependence of the cmc of ionic surfactant, α -sulfonato myristic acid methyl ester (MES) as well as nonionic surfactant - TX 100.

Whereas for nonionic surfactant, as the temperature increases the cmc value decreases. This is because the dehydration phenomenon is quite predominant with increase

in temperature resulting in increase in hydrophobicity. Different factors are responsible for the effect of temperature on cmc of nonionic surfactants, viz. i) the change in water structure around the ethylene oxide units (EO), ii) change in hydrogen bonding networks and iii) changes in the conformation of EO groups and iv) dehydration of hydrophilic groups.

The position of minimum in $\ln \text{cmc}$ - temperature profile has a thermodynamic significance i.e the minimum in the cmc represents the minimum in standard free energy of micelle formation¹⁰⁹⁻¹¹² that occurs at temperature at which $\Delta H_m^0 = 0$. Experimental evidence also suggests that the temperature at which minimum in cmc is observed is at which ΔH_m^0 is practically zero.¹¹³ For zwitterionic surfactants of type alkyl betaines, a steady decrease in the cmc is observed^{114,115} with increase in temperature in the range(6-60°C).

Zielinski and coworkers¹¹⁶ studied the effect of temperature (15-55°C) on micelle formation of aqueous solutions of alkyl trimethyl ammonium bromides having octyl, decyl, dodecyl and tetradecyl chains. The value of cmc gives minima at 47, 28, 20 and ca 15°C for the octyl, decyl, dodecyl, and tetra decyl derivatives respectively. Sugihara et al.¹¹⁷ carried out similar studies on micelle formation of a series of homologous cationic surfactants having organic counterions (alkane sulfonates) with carbon number ranging from 1-4. They also observed a minimum in cmc-temperature curves around 30°C. del Rio et al.⁴¹ evaluated the cmc of N-octyl trimethyl ammonium bromide at different pH (3.2, 7.0 and 10.0) and different temperatures (15-35°C) and they also observed a minima around 25°C at all these pHs.

1.4.1 (d) Pressure:

The effect of pressure on cmc of a series of alkyl trimethyl ammonium bromides and on sodium dodecyl sulphates has been mainly studied by conductivity measurements.¹¹⁸⁻¹²¹ A cmc-pressure plot passes through a maximum. Fig. 8 depicts a representative illustration of change in cmc as a function of pressure. The increase in pressure initially retards micelle formation and later on favours it after a certain threshold value. Such behaviour has been

attributed to different factors viz. i) a pressure induced increase in dielectric constant of water, ii) solidification of the micellar interior and iii) breaking of water structure at higher pressures. Mesa¹¹⁴ studied the relation between the cmcs and temperature/applied pressure using an experimental data fit and explained it in terms of thermodynamic considerations. Sugihara et al.³⁸ studied effect of pressure on cmc of Nonyl methyl glucamide /Sodium perfluoro octanoate surfactant mixtures.

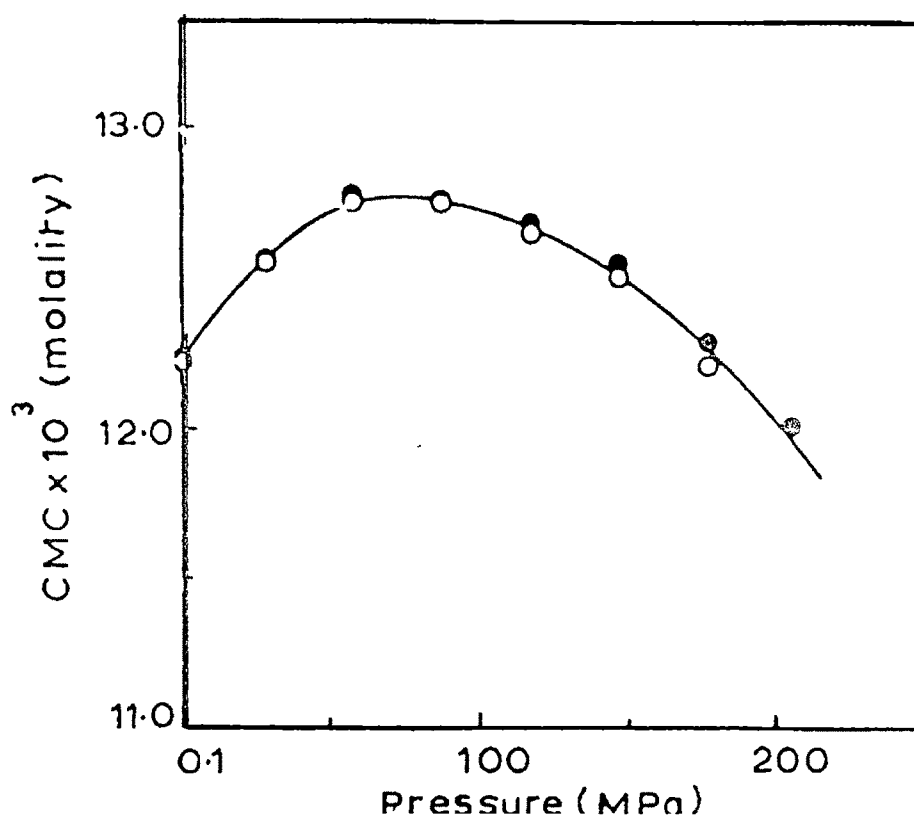


Figure 8. CMC of dodecyl pyridinium bromide as a function of pressure at 303 K.

1.5. Solubility-Temperature Relationship.

Solubility of surfactants is strongly temperature dependent and many important and intriguing temperature effects in surfactant self-assembly are known. One, which is of great practical significance is the dramatic temperature-dependent solubility displayed

notably by ionic surfactants. The solubility is low at low temperatures and then suddenly increases by orders of magnitude in a relatively narrow range of temperature. The phenomenon is designated as the Krafft point and the temperature for the onset of strongly increasing solubility is known as Krafft temperature. The temperature dependence of surfactant solubility in the region of Krafft point is illustrated in Figure 9.

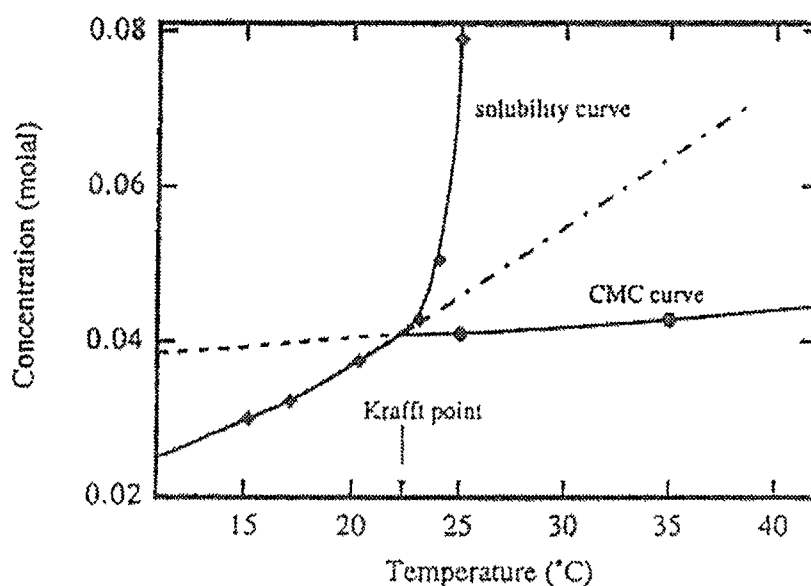


Figure 9. Temperature dependence of surfactant solubility in the region of Krafft temperature.

At Krafft temperature, the solid hydrated surfactant and micelles are in equilibrium with unimers.¹²² Krafft point may vary dramatically with subtle changes in surfactant chemical structure. Following are some general remarks on the variation of Krafft point for alkyl chain surfactants;

- Krafft point increases strongly as the alkyl chain length increases. The increase is not regular but displays an odd-even effect,
- Krafft point is strongly dependent on the head group and the counter ion. Salt addition raises the Krafft point, whereas many other co-solutes decrease it.
- There is no general trend for the counterion dependence, For e.g. in case of alkali alkanoates, the Krafft point increases as the atomic number of counterion decreases, while the opposite trend is observed for alkali sulfonates or sulfates.

Whereas, for cationic surfactants, the Krafft point is typically higher for bromide than for chloride and is still higher for iodide. With divalent cations, the Krafft point is often much higher.

If the solubility of surfactant is low, it will not be effective and efficient in various applications. Hence development of surfactants with a lower Krafft point is essential. In case of Nonionic surfactants, a reverse behaviour is observed. A 1% (w/v) solution of a nonionic surfactant is isotropic at low temperatures and at higher temperatures a critical point is reached above which the solution becomes turbid. This temperature is referred to as the "Cloud Point" of the surfactant at a particular concentration. Although, there are many theories that explain the occurrence of cloud point, this phenomenon is assumed to occur because of the micellar growth and intermicellar interactions as well as dehydration of hydrophilic groups as temperature increases leading to the formation of larger aggregates and the solution becomes visibly turbid.

1.6 Thermodynamics of Micellization.

Almost all the physico-chemical processes are energetically controlled. Micelle formation or Micellization is an important characteristic of surfactant solution. Micellization i.e. surfactant self-assembly in general is some intermediate between phase separation and simple complex formation and is illustrated in the ways micellization has been modeled in thermodynamic analysis. A clear understanding of process of micellization is necessary for explanation of the effects of structural and environmental factors on value of cmc and also for predicting effects on it of new structural and environmental variations. Moreover, a thorough knowledge of driving force of micelle formation is very important and requires application of laws of thermodynamics to obtain the standard free energy, enthalpy and entropy of micellization. Two main approaches to the thermodynamic analysis of micellization process have gained wide acceptance, i) the pseudophase separation or phase separation model and ii) the mass action model.

1.6.1 Phase Separation Model:

In this model, micelle formation is considered as akin to phase separation, with micelles being the separated pseudo phase and cmc, the saturation concentration of surfactant in the unimeric state. For the calculation of thermodynamic parameters of micellization, the hypothetical standard state for the surfactant in the aqueous phase is taken to be the solvated monomer at unit mole fraction with the properties of infinitely dilute solution.²⁵ For the surfactant in the micellar state, the micellar state itself is considered to be the standard state. For the nonionic surfactant, the standard free energy of micellization is defined as,

$$\Delta G_m^\circ = RT \ln X_{cmc} \quad (3)$$

where X_{cmc} = cmc in mole fraction scale, and is defined as,

$$X_{cmc} = \frac{cmc(\text{molelit}^{-1})}{cmc(\text{molelit}^{-1}) + \text{Water}(\text{molelit}^{-1})} \quad (4)$$

ΔG_m° is the measure of the standard free energy change for the transfer of one mole of surfactant from solution to micellar phase. The corresponding entropy of micellization (ΔS_m°) and standard enthalpy (ΔH_m°) per mole of the monomer can be computed from the slope and intercept respectively of linear ΔG_m° vs Temperature plots or also by using the following well known thermodynamic relations,

$$\Delta H_m^\circ = -RT^2 \frac{d \ln cmc}{dT} \quad (5)$$

$$\Delta G_m^\circ = \Delta H_m^\circ - T\Delta S_m^\circ \quad (6)$$

An alternative method for the evaluation of ΔH_m° is to measure the heat of micelle formation directly using calorimetry.¹²³ However, this method becomes increasingly inaccurate as the cmc decreases.

For the evaluation of ΔG_m° for ionic surfactants, apart from the transfer of surfactant molecules from aqueous phase to micellar phase; the transfer of $(2 - \alpha)$ moles of

counter-ions is also to be considered and hence standard free energy of micellization of ionic surfactant is defined as,

$$\Delta G_m^\circ = (2 - \alpha)RT \ln X_{cmc} \quad (7)$$

where α is the degree of ionization of micelle; and is often computed from the ratio of the slopes of post micellar region to that of premicellization region of conductance – concentration profile.^{124,125}

The quantitative measure of the value of α is crucial in order to understand many aspects of the behaviour of micelles. The values of α is an important element in micelle stability in general¹²⁶ and in the growth of the spherical micelles in to rodlike structures,¹²⁷ which can lead to viscoelastic behaviour.¹²⁸ The fundamental importance of α accounts for the vast number of papers dedicated entirely or in part to its measurement using a wide variety of experimental techniques.¹³² Treiner and Makayassi¹²⁹ evaluated α by taking a constant ‘n’ value, where n is the aggregation number of a micelle. Evans¹³⁰ also suggested a similar method for determination of α , if aggregation of micelle was known. Barney Bales¹³¹ also suggested a similar definition of α on the basis of the aggregation number of micelle, with an attempt to define α in a way that it is independent of any particular experimental method. Very recently Bales et al.¹³² again defined the degree of ionization of micelle - α , but the method used was based on Krafft temperature measurements. This method is valid for α measurements of cationic and anionic surfactants.

1.6. 2. Mass Action Model:

This method assumes that the micelle and the undissociated surfactant ions are in the association dissociation equilibrium and law of mass action can be applied. Micellization is thus considered as a stepwise process and the micelles are not monodisperse, but there is a distribution of aggregation numbers of micelles or micelles are polydisperse. This model was originally applied mainly to ionic surfactants but later on Corkill et al.¹³³ applied it to nonionic surfactants too. According to this model, the standard free energy of micellization per mole of the monomeric surfactant is defined as,

$$\Delta G_m^\circ = RT \ln X_{cmc} \quad (\text{for nonionics}) \quad (8)$$

whereas for ionic surfactants,

$$\Delta G_m^\circ = \left(2 - \frac{P}{n}\right) RT \ln X_{cmc} \quad (9)$$

where $\alpha = \frac{P}{n}$. The equations for the free energy of micellization by phase separation and mass action model are similar, but the two equations differ slightly because of differences in the way in which the mole fractions are calculated. In phase separation model, the total number of moles present at cmc is equal to the sum of the number of moles of water and surfactants, whereas the total number of moles in the mass action model is equal to the moles of water, surfactant ions, micelles and free counterions.

Apart from the phase separation model and mass action model, Hill¹³⁴ applied small system thermodynamics to micellar systems. The distinguishing feature of small systems/multiple equilibrium approach is that it yields expressions that describe the changes of monomer and micelle concentration with total surfactant concentration. This model treats the aggregation number as a thermodynamic variable. Also, this model enables us to carry out the calculations of thermodynamic quantities of single micelle rather than ensemble of micelles. Hall and Pethica¹³⁵ applied this model to non-ionized non-interacting surfactant systems. Tanford¹³⁶ proposed a model for micelle formation based on the geometrical considerations of a micelle. The equations were proposed, which relate the micelle size and cmc to a size dependent free energy of micellization. This model has been further developed by Ruckenstein and Nagarajan¹³⁷ and was applied for the prediction of the properties of sodium octanoate micellar solutions.¹³⁸

Model of Evans and Ninham¹³⁰ has also been used for the computation of thermodynamic parameters of micellization. The free energy of micellization is defined as,

$$\Delta G_m^\circ = RT \ln X_{cmc} = \Delta G_{HP}^\circ + \Delta G_S^\circ \quad (10)$$

where ΔG_m° is the total Gibb's free energy per mole of surfactant associated with micelle formation. ΔG_{HP}° is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to the micelle interior. Whereas, ΔG_S° accounts for surface

contributions, which includes the energy associated with electrostatic interactions between the headgroup and counterions. Chandler et al.¹³⁹ have recently suggested a model based on law of mass action, to explain the driving force behind micelle formation. Theoretical predictions for temperature dependence and surfactant chain length dependence of cmcs for nonionic surfactants agree favourably with experimentally determined values.

The contributions of the hydrophobic and hydrophilic groups to the enthalpy change, for four different sodium alkyl sulfates bearing different alkyl chains i.e (C₈ – C₁₄) in the temperature range (10 – 55°C) were investigated by Moroi and co-workers.¹⁴⁰ Mosquera et al.^{30,40,41} have thoroughly investigated the thermodynamics of micellization of n-alkyl trimethyl ammonium bromides as well as N-octyltrimethylammonium bromide in different media. The thermodynamic parameters of micellization were evaluated by application of model of Evans and Ninham¹³⁰ in terms of hydrophobic and surface contributions which are pH dependent. Moreover, the enthalpy of micellization was observed to be strongly temperature dependent. Gonzalez-Perez et al.¹⁴¹ studied the micellar properties of tetradecyl and hexadecyl dimethyl benzyl ammonium chlorides in aqueous solution and observed a temperature dependence of ΔG_m° . Quintana et al.¹⁴² evaluated the thermodynamic parameters of micellization of block copolymers of polystyrene having different poly (ethylene/propylene) lengths, in n-octane & 5-methyl hexan-2-one. The characteristic of the copolymer and the block location in the micelle structure were found to influence the thermodynamics of micellization process. Micellization in various peptide molecules has also been thoroughly investigated.¹⁴³

Gaillon et al.¹⁴⁴ have developed a new thermodynamic model based on the electrochemical equilibrium of a dispersed phase (pseudophase) and have justified the existence of this condition for micellization or micellization product. Although, the micellization parameters can be evaluated in reasonable detail applying the phase separation or mass action model, in most cases, it systematically underestimates the experimental enthalpies.¹⁴⁵ Many studies of calorimetric heats of micelle formation of surfactants in aqueous medium have appeared in literature since the pioneering heat of

dilution studies by Goddard et al.¹⁴⁶ and heats of solution work by Benjamin¹⁴⁷. Olofsson et al.¹⁴⁸ carried out calorimetric measurements for n-octyl tetra oxyethylene glycol mono ether (C₈E₁₀) and TX 100 as a function of concentration at different temperatures. Enthalpies of solution of unimers at infinite dilutions and micelles at the cmc respectively were evaluated and enthalpies of micelle formation were computed. Moulik et al.¹⁴⁹ have thoroughly assessed the thermodynamics of micelle formation of ionic surfactants; viz. SDS, Cetyl Pyridinium Chloride and AOT using micro calorimetric measurements. They observed that ΔH_m° and ΔC_{pm}° values calculated by van't Hoff method and those directly determined by micro calorimetric measurements to be significantly different. Such difference results from the physico-chemical processes other than amphiphile aggregation contributing to the overall heat measured in the calorimeter. Sugihara et al.^{113,122,150-152} have also discussed in detail the thermodynamics of micelle formation of different surfactants which included α -sulfonato myristic acid alkyl esters, fluorocarbon surfactants & dodecyl ammonium alkane sulfonates. The thermodynamic parameters of micellization were evaluated taking the degree of counterion binding ' β ' in to consideration. de Lisi et al.¹⁵³ studied the thermodynamics of perfluoro octanoate/ Sodium dodecanoate mixtures and N-alkyl-N-methyl piperidinium chlorides¹⁵⁴ and octyl trimethyl ammonium chloride¹⁵⁵ in aqueous medium on the basis of pseudo phase separation model. Zielinski et al.¹⁵⁶ also applied pseudo phase separation model in order to evaluate the thermodynamic parameters of micellization for a series of alkyl trimethyl ammonium bromides having octyl, decyl, dodecyl and tetradecyl chains. However, they observed that though pseudo phase separation model of micelle formation was applicable to the decyl, dodecyl and tetradecyl derivatives, it could not be applied to the octyl derivatives. Other than the standard thermodynamic parameters of micelle formation, various other parameters like enthalpies of dilution, apparent and partial molar relative enthalpies, heat capacities, volume compressibilities and expansibilities were calculated.¹⁵⁷⁻¹⁶¹ Ahluwalia et al.¹⁶² determined calorimetrically the enthalpies of solution of some C₁₀E_n surfactants in monomeric and micellar states in presence of urea. Olofsson et al.¹⁶³ also evaluated enthalpy of micelle formation of C₁₂E_n (n = 5, 6 & 8) using microtitration calorimetric studies. Wang et al.¹⁶⁴ evaluated enthalpies of mixing for

three different binary systems; SDS:Water, CTAB:Water & TX-100:Water by microcalorimetry. Scamehorn et al.¹⁶⁵ used Isotherm calorimetry to determine the heat of micelle formation of binary surfactant mixtures. Blume et al.¹⁶⁶ investigated the lipid/detergent interaction thermodynamics as a function of molecular shape using isothermal titration calorimetry. They performed experiments on a series of $C_{12}E_n$ ($n = 3-8$) surfactants mixed with a phospholipid – POPC and evaluated the transfer enthalpies of the molecules between the various states (monomers, bilayers, micelles). Packing effects, controlling the hydration of the headgroups, the water exposure of the hydrocarbon core and the order of the hydrocarbon chains, determine the mixing effects. Recently Balcan and coworkers¹⁶⁷ used reversed phase liquid chromatography (RPLC) to investigate the thermodynamic properties of homogeneous ethoxylated nonyl phenols and their retention mechanism from methanol-water eluents. The enthalpy–entropy compensation effect behaviour was employed to investigate the mechanism of surfactant retention in the reversed phase system and their results reveal a similarity of interactions involved in RPLC with nonpolar stationary phases and aqueous eluents. Microcalorimetric studies were carried out to determine the apparent molar enthalpies for nonionic ethoxylated surfactant (C_6E_5) in aqueous solution at constant molality of ionic surfactant (C_6SNa) at 25°C by Ortona and his colleagues.¹⁶⁸ The microcalorimetric technique allowed computation of the enthalpic interaction parameter among unimers, the cmc and ΔH_m° for mixed micellar aggregates. The experimental ΔH_m° values are in quite good agreement with those predicted through ideal and regular solution approaches, provided that nonionic surfactant predominates in the surfactant mixture. However, there are deviations from ideal and/or regular solution behaviour when ionic surfactant content is more in mixed surfactant system and this has been attributed to the efficiency of electrostatic interactions among the sulfonic heads.

1.7 Adsorption at Interfaces.

Amphiphiles tend to accumulate at air/water or oil/water interfaces. The surface of a liquid is a boundary between two bulk phases viz. 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. Surfactant adsorption plays a critical role in many important industrial applications of surfactants such as wetting, adhesion, flotation, dispersion stability, detergency and thin-film formation. However in other application such as enhanced oil recovery processes, surfactant adsorption is a costly nuisance that is to be avoided.^{164,169} Thus the knowledge of surface area occupied by surfactant at an air/water interface is very important in surface science in order to optimize the conditions as per desired application.

The variation of surface tension (γ) with composition in case of solutions is one route to obtain information about surface concentration. J. W. Gibbs derived a relationship rooted in thermodynamics and well known as Gibbs adsorption isotherm,¹⁷⁰ in 1878 and has been cited as one of the pillars of colloid and interface science, comparable to Young-Laplace equation.¹⁷¹ 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,

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (11)$$

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,

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (12)$$

where subscripts 1 & 2 refer to solvent and solute respectively. Assuming Γ_1 – the excess concentration of the solvent to be equal to zero and for dilute solution,

$$\Gamma_2 = \frac{-1}{2.303nRT} \left(\frac{d\gamma}{d \log C} \right) \quad (13)$$

$$= \frac{-C}{2.303nRT} \left(\frac{d\gamma}{dC} \right) \quad (14)$$

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,

$$\Gamma_2 = \frac{-1}{2.303nRT} \left(\frac{d\gamma}{d \log C} \right) \text{ mol cm}^{-2} \quad (15)$$

where ' γ ' is in dyne/cm, concentration of surfactant in molarity, R in ergs mol⁻¹ K⁻¹ and the coefficient 'n' is equal to 2. The slope $d\gamma/d \log C$ is obtained from the linear portion of the surface tension- \log_{10} Concentration plot, which is quite often observed. Hua et al.¹⁷² derived an equation for calculating the value of coefficient 'n' for ionic surfactants in binary C₁₂SO₃Na/C₁₂E₈, C₁₂NBr/C₁₂E₈ and C₁₂SO₄Na/C₁₂E₈ mixtures. Value of 'n' for these systems in absence of electrolyte remains in the vicinity of 1, until the area per surfactant ion in the surface film reaches a value of about 1 nm². However, closer packing of surfactant ion in the film results in an increase of 'n' in to the range between 1 & 2.

The area per molecule of the surfactant at the air/water interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecules. From the surface excess, the minimum area per molecule of the surfactant at the air/water interface is computed as,

$$A_{\text{min.}} = \frac{10^{14}}{N_A \Gamma} \text{ nm}^2 \quad (16)$$

where N_A is Avogadro number and Γ is surface excess concentration of the solute 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. Rosen⁵⁰ has tabulated values of Γ_m for a wide variety of anionic, cationic, nonionic and zwitterionic surfactants. The length of the hydrophobic group has little effect on Γ_m except when it exceeds 16 carbon atoms; a significant decrease in Γ_m is observed, due to coiling of the chain. For poly oxyethylene nonionic surfactants of fixed oxyethylene chain length, the value of Γ_m remains almost unchanged with the length of hydrocarbon chain length.

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 has a very little effect on Γ_m . Increase in temperature, decreases Γ_m for ionic surfactants, whereas Γ_m increases with increase in temperature for nonionic surfactants.²⁵

Rosen et al.⁵³ have reported a decrease in surface excess concentration as the temperature as well as oxyethylene chain length of nonionic surfactant increases. However, the minimum area per molecule increases with increase in temperature due to increased thermal agitation of the molecules in the surface film. Jeong et al.¹⁷³ studied the effect of polydispersity of polyoxyethylene chain for dodecyl alcohol 7 ethoxylates ($C_{12}E_7$)

having different homologue distribution at the air/water interface. The headgroup areas deduced from Gibbs adsorption equation became small due to the preferential adsorption of short chain molecules on to the surface as the polydispersity increased. Murata et al.¹⁷⁴ also carried out investigation on effects of temperature (25-45°C) and chain length on the properties of long chain poly oxyethylene dodecyl ethers. They also observed that the area per molecule increases with elevating temperature and explained this on the basis of a scaling rule in polymer science, which suggested a coil-globule transition taking place between 35 and 45°C. Penfold and coworkers¹⁷⁵ calculated the surface excess concentrations of n-dodecyl N,N-dimethyl amino acetate at air/water interface. Owing to the importance of knowledge of surface area occupied by surfactant at an interface, Li et al.¹⁷⁶ attempted to solve the problem of value of 'n' by using the neutron reflectivity, which permits direct determination of surface excess Γ_m . Comparison of Γ_m value from neutron reflectivity to that of $(d\gamma/d\log C)/(RT)$ from surface tension data, enables to determine the value of 'n' at any surfactant concentration. The comparison yielded n=2 for the dimeric surfactants 12-2-12, 12-3-12 and 12-12-12.

Different authors have investigated^{164,169} the surface behavior of surfactant mixtures. Studies on anionic–nonionic mixed surfactant adsorption have been more extensive than those for mixtures of ionic surfactants.¹⁷⁷⁻¹⁸² The shielding of charged groups on ionic surfactants from each other due to presence of nonionic surfactant results in the reduction of electrostatic repulsion and is thus responsible for non-idealities in mixed surfactant adsorption.¹⁶⁷ Moreover, Zhao and Zhu¹⁸³ have reviewed single and mixed surfactant adsorption.

1.8. Thermodynamics of Adsorption.

Thermodynamic investigations of adsorption of surfactants can provide at least two important information about the adsorbed films i.e the Gibbs free energy of adsorption as a measure of surface activity of the surfactant and the enthalpy of adsorption of surface active homologues from aqueous solution at the air/water interface.¹⁸⁴ Since last two

decades, more detailed thermodynamic studies have dealt with the adsorption of surfactant mixtures.

The standard free energy of adsorption, ΔG_{ad}° is defined by the relation^{53,185}

$$\Delta G_{ad}^{\circ} = RT \ln cmc - N\Pi_{cmc}A_{cmc} \quad (17)$$

by considering the standard state here as a hypothetical monolayer at its minimum area per molecule at zero surface pressure. The second term in the above equation represents the surface work involved in going from zero surface pressure to the surface pressure at cmc (Π_{cmc}) at a constant minimum surface area per molecule ($=A_{cmc}$). When Π_{cmc} is in mNm^{-1} , A_{cmc} in nm^2 and R is in $\text{J mol}^{-1}\text{K}^{-1}$, with ΔG_{ad}° in kJmol^{-1} above equation becomes

$$\Delta G_{ad}^{\circ} = RT \ln cmc - 6.023 \times 10^{-1} \Pi_{cmc} A_{cmc} \quad (18)$$

The corresponding enthalpy (ΔH_{ad}°) and entropy of adsorption (ΔS_{ad}°) are computed from the well known thermodynamic relations. The standard free energy change upon adsorption determines the spontaneity of adsorption process as well as the magnitude of driving force. The standard enthalpy change upon adsorption indicates whether bond making/bond breaking predominates during adsorption. The extent of randomness is given by the standard entropy changes during adsorption.

Motomura et al.¹⁸⁶ investigated the thermodynamics of adsorption of surfactants at interfaces. Moulik and coworkers¹⁸⁷ reported the interfacial and micellization behaviour of binary and ternary mixtures of amphiphiles; Triton X 100, Tween 80 and CTAB. Moreover, the properties including standard free energy of adsorption have been studied for binary mixture of dodecyl ammonium chloride and caesium per fluoro octanoate at air/water interface.^{188,189} Sulthana et al.¹⁰²⁻¹⁰⁵ extensively studied the interfacial and thermodynamic properties of anionic, nonionic and anionic/nonionic surfactant mixture in absence as well as presence of different additives.

1.9. Mixed Surfactant Systems.

Surfactant systems used for practical applications consist of mixtures of surfactants, either because commercial surfactants are always mixtures due to the raw materials used and method of manufacture or because mixtures of surfactants often show better performance properties than individual surfactants.¹⁹⁰⁻¹⁹⁴ Because of this, there has been considerable research on the molecular interactions between different surfactants in their binary mixtures, particularly in relation to the existence of 'synergy' (a condition when properties of mixtures are better than the individual components, when surfactants are purposely mixed) between them.

Many theoretical approaches and various technological applications have progressed in the last few decades in the area of mixed surfactant systems. Several molecular thermodynamic theories have been developed recently by different investigators for predicting properties and interactions in binary surfactant systems.¹⁹⁵⁻²⁰⁰ Investigations on synergism in quantitative terms is a convenient method to study the molecular interaction between the surfactant molecules. Hua et al.²⁰¹ used non-ideal solution theory to derive equations for the conditions under which synergism can exist in aqueous binary mixtures of surfactants. Synergism in surface tension reduction efficiency, synergism in mixed micelle formation and synergism in surface tension reduction effectiveness were defined and the theoretical equations were applied to hypothetical and real systems. Depending upon the kind of surfactants, apart from 'synergistic effect', even 'antagonism' can be observed. Antagonism is observed when surfactants having similar headgroups and different hydrophobic groups; one being a conventional hydrophobic and other a perfluorinated one are mixed. Thus mixed surfactant systems have attracted attention of researchers due to pure scientific interest as well as from application point of view. Scamehorn,¹⁹⁴ Rubingh and Holland¹⁹⁰ and Ogino and Abe²⁰² have published books with a collection of review works in the field of mixed surfactant systems.

Clint²⁰³ proposed a phase separation model to describe the phenomenon of mixed micelle formation. This model treats the micelles as a separate phase from that of dissolved surfactant unimers and proposed that the mixed micelle is an ideal solution of two surfactants. It predicts the mixture cmc, micelle composition, and unimer concentration. Although it provides the description of nearly ideal mixing, it fails to predict either the cmc or monomer concentrations of surfactant mixtures differing in head groups. It was Corkill,²⁰⁴ who accounted for the non-ideal mixing and extended the Clint's ideal mixing model. He suggested that, since the micellar core is essentially hydrocarbon liquid like, then regular solution theory, which has been successful in treating non-ideal liquid mixtures, should also be useful for treating surfactant mixtures. This treatment takes into account the interaction between the surfactant molecules within the micelle core and thus provides better physical description for wider range of surfactant mixtures. All the effect arising due to changes in the charged state of mixed micelles containing ionic surfactants due to surfactant mixing are included in the activity coefficients of the regular solution approximation of Rubingh and Holland.^{205,206} This treatment takes in to consideration, the interaction between the surfactant molecules in the mixed micelles and has been expressed in terms of micellar interaction parameter, ' β^m '. Accordingly, when $\beta^m = 0$, the two surfactants form an ideal mixture, a negative β^m value suggests the interactions to be strongly attractive and mixed micelles are stabilized electro statically. A positive value of β^m indicates non-compatibility of constituent surfactant species and is thus a measure of antagonistic behaviour of surfactant mixture. The activity coefficients of two surfactants can also be estimated using this theory.

According to this theory, the molecular interactions between two surfactants in micelles or at an interface are commonly measured by the so-called β parameters, which are conveniently obtained from critical micelle concentration data or from surface (or interfacial tension). The micellar interaction parameter is obtained by use of following equations,

$$\frac{(X_1^M)^2 \ln\left(\frac{\alpha_1 C_{12}^M}{X_1^M C_1^M}\right)}{(1-X_1^M)^2 \ln\left(\frac{(1-\alpha_2) C_{12}^M}{(1-X_1^M) C_2^M}\right)} = 1 \quad (19)$$

$$\beta^m = \ln\left(\frac{\left(\frac{\alpha_1 C_{12}^M}{X_1^M C_1^M}\right)}{(1-X_1^M)^2}\right) \quad (20)$$

where X_1 is the mole fraction of surfactant 1 in the total surfactant in the mixed micelle and C_1^M , C_2^M and C_{12}^M are the critical micelle concentrations (cms) for surfactant 1, surfactant 2 and their mixture respectively at the mole fraction α_1 . Equation 19 is solved iteratively using a computer programme for X_1 , which is then substituted in to Eq. 20 to evaluate β^m . Similarly the interaction parameter at the air/water interface is given by the relations,

$$\frac{(X_1)^2 \ln\left(\frac{\alpha_1 C_{12}}{X_1 C_1^0}\right)}{(1-X_1)^2 \ln\left(\frac{(1-\alpha_1) C_{12}}{(1-X_1) C_2^0}\right)} = 1 \quad (21)$$

$$\beta^\sigma = \ln\left(\frac{\left(\frac{\alpha_1 C_{12}}{X_1 C_1^0}\right)}{(1-X_1)^2}\right) \quad (22)$$

where X_1 is the mole fraction of surfactant 1 in the total mixed monolayer (on a surfactant only basis); C_1^0 , C_2^0 & C_{12} are the molar concentration in the solution phase of surfactant 1, surfactant 2 and their binary mixture respectively at a mole fraction α_1 of surfactant 1 required to produce a given surface tension, γ value (obtained from γ - $\log_{10}C$ plots). In this case also Equation 21 is solved iteratively for X_1 , which thus obtained is then substituted in Eq. 22 to evaluate β^σ . β^σ & β^m are quantitatively different but qualitatively similar.

According to Rubingh's approach,²⁰⁵ the micellar interaction parameter β^m should be constant over an entire range of composition. Such behaviour has been found to be valid in the case of anionic/nonionic surfactant mixtures of NaOL/C₁₀(EO)₆ and SDS/C₉PhE₁₀.²⁰⁷ Rubingh's regular solution theory is useful due to its simplicity and application to other phenomena. This non-ideal solution treatment has been used by many researchers all over the world for analysis of binary surfactant mixtures^{108, 208-212}

Although Rubingh's treatment has been extensively used, it has a few drawbacks,

I) the interaction parameter β^m is considered to be independent of temperature and micellar composition but it has been found to be substantially temperature and composition dependent.²¹³

II) Meaningful values of β^m have not been realized for some anionic/cationic surfactant mixtures.²⁰⁷ Contrary to expectations, positive β^m values have been obtained at all mole fractions of the anionic/cationic surfactant combination.

III) This theory cannot uniquely account for the interactional features of surfactants in the mixed micelles.^{108, 214, 215}

IV) If the regular solution theory is applicable to ionic/nonionic mixed micelles, the effective degree of counter-ion binding must be proportional to the mole fraction of ionic surfactant in the micelle, but this is contrary to the experimental observations.^{216, 217}

Motomura and coworkers²¹⁸ considered the micellization process to be similar to that of a macroscopic bulk phase and the energetic parameters associated with the process are expressed by excess thermodynamic quantities. They derived expressions for different combinations of surfactant solutions. This model is independent of the nature

of surfactants and their counter-ions and hence more suitable for studying the behaviour of binary surfactant mixtures. Asano et al.²¹⁹ successfully applied this treatment to sodium cholate/Octaethylene glycol n-decyl ether mixed surfactant system. The micellization behaviour of the binary mixed systems of sodium n-hexyl sulfate with sodium n-decyl-, n-dodecyl- and n-tetradecyl sulfate was studied by Sarmiento et al.²²⁰ and the micellar composition was determined by Motomura model.²¹⁹ However, the mutual interactions between the constituent surfactants in the mixed micelle were estimated from Holland and Rubingh's theory and the mixture was found to be non-ideal. Sugihara and coworkers^{221,222} also applied the Motomura theory²¹⁸ for the analysis of Nonyl-N-Methyl Glucamide (Mega-9)/Sodium per fluoro octanoate as well as Nonanonyl N-Methyl Glucamide (Mega-10)/Sodium deoxy cholate mixed surfactant system.

Sarmoria et al.^{196a} and Puvvada et al.^{196b} proposed a molecular thermodynamic model applicable to mixed binary solutions of non-ideal surfactant combinations on the basis of the cmcs of the individual surfactants and other solution conditions such as temperature, concentration, and type of salt present. They derived an expression for the mixture cmc identical to the expression derived by Rubingh.²⁰⁵ Various physicochemical quantities were evaluated from the knowledge of two molecular contributions; the free energy of mixed micelle formation ' g_{mic} .' Reflecting intramicellar interaction and the mean-field intermicellar interaction parameter. All the qualitative theoretical predictions reproduce very well the experimentally observed trends in aqueous solutions containing nonionic/nonionic, nonionic/ionic, zwitterionic/ionic and anionic/cationic surfactant mixtures.

Recently Blankschtein et al.²²³ developed a new computational approach on the basis of their molecular thermodynamic theory of mixed micellization to predict the critical micelle concentrations of commercial surfactants containing any number of surfactant components. This new computational approach was then implemented in the context of two user-friendly computer programs PREDICT and MIX 2,²²⁴ to predict the cmcs of several commercial surfactants of known chemical composition, including their

binary mixtures. Blankschtein et al.²²⁵ also presented a simplified working model to predict cmcs and synergism in binary surfactant mixtures, where one of the surfactant is Zwitterionic. The model takes in to consideration, the electrostatic interaction as a major contributor to synergism in mixed micelle formation and is applicable only to surfactants with linear hydrocarbon tails and neglects synergism due to packing of the surfactant tails in the micellar core.

Moulik and his group^{207, 226-228} have analyzed the behaviour of binary mixtures of aqueous surfactant solutions using Rubingh,²⁰⁵ Motomura²¹⁸ and the molecular thermodynamic theory of Puvvada^{196b} and Sarmoria et al.^{196a}. These theoretical approaches were successful in describing the mixed micellar properties of anionic/nonionic surfactant combination. They also discussed the scope and limitations of these treatments in describing as well as predicting the behaviours of different types of mixed micellar entities. Haque et al.²²⁶ and Ghosh et al.²²⁸ evaluated the composition, mutual synergism, component activity coefficients and cmc of mixed micelles with the help of propositions of Clint,²⁰³ Motomura,²¹⁸ Rubingh,²⁰⁵ and Rubingh & Holland.¹⁹¹

Rosen and his group^{27,28} have also been involved in the studies of mixed surfactant systems and their behaviour. They have investigated the interaction of cationic gemini surfactants with alkyl glucoside or maltoside surfactants as well as those of alkyl glucoside surfactants with conventional surfactants. The results were analyzed in the light of Rubingh's approach. It was observed that cationic gemini surfactants and their mixtures with either the alkyl maltoside or the alkyl glycoside show stronger interaction at the air/water interface than comparable conventional cationic surfactants. Whereas, maltosides interact weakly with conventional cationic, anionic and zwitterionic surfactants as compared to that of interaction of glycoside surfactant. Interaction was even more stronger when glycoside/maltoside surfactant mixture are interacted with the non-glycosidic surfactant.

Apart from all the theories that we have discussed till now, several other treatments for analysis of mixed micellization have emerged in the last decade from different researchers across the globe. This include the treatments by Khan and Marques,²²⁹ Bergstrom,^{198,230,231} Letellier,²³² Georgiev,²³³ and Maeda.²³⁴ Moreover, Hines et al.^{235a} and Rakshit et al.^{235b} have reviewed the work in the field of mixed surfactant systems, with an attempt to update the recent research trends in this field.

Letellier et al.²³⁴ discussed the mixed surfactant systems using thermodynamic cross differentiation relations. Georgiev²³⁵ has used what is known as the Markov chain model. It assumes that non-ideality arises due to interactions between the surfactants and an energy interaction parameter (β) was computed by introducing regular solution theory to the pseudo phase separation model. There are two different interaction parameters according to this theory, one arising due to the interaction of surfactants in the micelle and other due to the interaction at the air/water interface. These values are quantitatively different though qualitatively similar. Bergstrom¹⁹⁸ investigated synergism in mixed surfactant systems by analyzing the main contributions to the free energy of mixed surfactant aggregate; and introduced a novel expression for the free energy of mixing aggregated surfactant headgroups with surrounding solvent molecules. It was proposed that various entropy effects related to the surfactant headgroups, rather than specific interactions between them are mostly responsible for synergistic effects. Moreover the magnitude of synergistic effects increased with increasing asymmetry between the two surfactants. Bergstrom^{230,231} also investigated the synergistic effects in cationic/anionic surfactant mixtures. He derived an explicit expression for the critical micelle concentration as a function of the aggregate composition using Poisson-Boltzmann mean field theory and demonstrated that large synergistic effects that were experimentally observed can be rationalized in without the need of invoking any specific interactions between the surfactant headgroups. A simple relation, $\beta = -4e\ell/kT$ was derived i.e the interaction parameter ' β ' was directly related to the electrostatic free energy contribution ϵ_{el} for the pure surfactants. Recently Bergstrom²³¹ analyzed synergistic effects in mixtures of an ionic and nonionic surfactant by means of a novel model independent synergy

parameter. This model evaluation enables the comparison of experimental results with a theoretical model based on a Poisson–Boltzmann (PB) mean field theory for spherical, cylindrical and planar geometries. Moreover, the PB theory was found to better describe the synergistic behaviour than more conventional regular solution theory in the sense that the latter systematically underestimates synergism at low mole fractions and over estimates synergism at high mole fractions of ionic surfactant.

The micellar interaction parameter evaluated using Rubingh's theory²⁰⁵ accounts well for the headgroup/headgroup interactions. However Maeda²³⁵ suggested that besides the electrostatic interactions, the chain/chain interaction is also important and suggested a relationship by which chain/chain interaction can be computed. This chain/chain interaction becomes important in the mixed micelles when the hydrophobic group chain lengths are different. Maeda²³⁵ extracted a contribution, B_1 which accounts for the standard free energy change when a non-ionic pure micelle is replaced by an ionic monomer; in addition to another interaction parameter, B_2 (an analog of the familiar interaction parameter ' β ' in the regular solution approach) for mixed micelles.

According to this approach, the thermodynamic stability (ΔG_m) is defined as a function of mole fraction of ionic component (X_2) by

$$\Delta G_m = RT(B_0 + B_1X_2 + B_2X_2^2) \quad (23)$$

$$\text{where } B_0 = \ln C_1 \quad (24)$$

(C_1 is the cmc of the nonionic surfactant)

$$B_1 + B_2 = \ln \left(\frac{C_2}{C_1} \right) \quad (25)$$

(C_2 is the cmc of the ionic surfactant)

$$B_2 = -\beta^m \quad (26)$$

where all the quantities are on the unitary scale. Once can evaluate B_1 from above expressions and hence ΔG_m . Sharma et al.⁵¹ showed that for a mixed cationic Gemini

surfactant 1,4-butanediyl- α,ω -bis hexadecyl –dimethyl ammonium bromide (16-4-16) with $C_{12}E_6$, the free energy of micellization evaluated using phase separation model tally with the Maeda values. Whereas higher negative values of B_1 were obtained, indicating that chain/chain interactions are important for the stability of the mixed micelle. Ruiz et al. studied SDS/TX 100 mixed surfactant system²³⁶ and found an attractive interaction in this system. They also used Maeda's concept²³⁵ and found that the chain/chain interaction in this system was very low. Gandhi et al.³³ carried out tensiometric studies on several binary surfactant mixtures containing anionic surfactants viz. metal (lithium, sodium, potassium, copper, cobalt and magnesium) dodecyl sulfates and a nonionic surfactant TX 100. Marked interaction is observed with monovalent dodecyl sulfates. The influence of counterion valence on the formation of mixed micelles indicated that mixed systems with bivalent counterions in metal dodecyl sulfate resembled nonionic/nonionic surfactant systems, where weak/negligible interaction is observed. Salt addition revealed the weakening of interaction in the mixed systems, which is due to the head group charge neutralization and the dehydration of ethylene oxide units of the nonionic surfactants.

1.10 Cloud Point and Performance Properties.

The aqueous solubility of nonionic surfactants is susceptible to temperature variation. Depending on their concentration and environment, they exhibit clouding after a threshold temperature causing a phase separation via dehydration of the polar groups in the molecules, followed by self association.^{237,238} Such a transition, called the cloud point is fairly sharp and rapid and can be normally monitored visually against an illuminated background. The point of clouding or CP has importance in the understanding of the thermodynamics of the stability/instability of the involved nonionic surfactants. It has an important role in many chemical processes where the clouding compounds are used alone or in a mixture for the purpose of active solubilization, reaction, separation and product formation.²³⁹⁻²⁴¹ The process of CP can be influenced by presence of additives. The additives modify surfactant-water interactions and thereby decrease or increase the CP.

Moreover, mixed ionic/nonionic surfactants are of prime importance in the area of enhanced oil recovery where such mixed surfactant systems might show advantageous solubility behaviour exhibiting cloud points higher than those of pure nonionic surfactant. Thus the mixed surfactants would be employed over a wide range of temperature, salinity and hardness conditions than individual surfactants.²⁴²

Performance Properties.

The interfacial and solution behaviour of surfactants leads to different key surface-active properties, viz. i) emulsification/demulsification, ii) wetting, iii) foaming/defoaming, iv) dispersion v) detergency and vi) solubilization.²⁴³ In almost all industrial applications, a combination of all these properties is generally preferred. Viscosity of surfactants is applicable to both handling of liquids in processing and also to the formulation of end use products in which a desired physical form is required. Surfactant solutions at very high concentration behave like Non-Newtonian liquids. In formulated products, the viscosity of surfactants in aqueous medium may be affected by the presence of electrolytes or other foreign substances that modify the water structure. Viscosity is thus important physicochemical property of surfactant solution. Some reports are there in literature on the viscosity of pure surfactant solution with or without electrolyte.^{244,245} Regardless of its importance, few studies on viscosity in the mixed system have been carried out in order to analyze the effect of mixing dissimilar surfactants.^{246,247}

Foam is a dispersion of a gas in liquid and is produced when air or gas is entrapped beneath the surface of liquids that expands to enclose the air within a thin film of liquid. The theoretical basis of foam has been extensively studied and its physicochemical principles are well addressed.²⁴⁸ The foaming efficiency and its stability shows significant variations with respect to presence of, i) additives, ii) chemical structure, iii) surfactant concentration and iv) temperature. Anionic surfactants are good foamers as compared that of nonionic surfactants. Thus in order to achieve an optimum condition, a mixture of anionic and nonionic surfactant would be an important tool to tune the surfactant mixture as per the desired application.

Detergency is a complex process involving interactions between surfactants, soil, textile and surface. The choice of surfactant is the key to success of the process. It has been observed that the soil removal efficiency of mixed surfactant systems is more as compared to that of pure surfactants.¹⁸ This is due to higher solubilizing power of mixed micelles. Thus knowledge of the influence of the mixed surfactant systems on the performance properties is essential in order to optimize the conditions, so as to formulate a detergent with desirable properties, as per the ultimate end use.

1.11 Ion Selective Electrodes.

Surfactants are involved in numerous industrial domains (emulsions for paints, pharmacology, detergents) where they are not only used in aqueous media but also in aquo-organic media. Handling of surfactants for use, formulation or production needs simple and reliable analytical techniques to determine their quantity in reaction media. With this aim, ion selective electrode for surfactants (ISE) have been developed in last three decades²⁴⁹⁻²⁵² and have been used, to study the physicochemical properties of surfactants in solution,²⁵³ determination of nonionic surfactant concentrations,²⁵⁴ determination of activity of surfactant/detergent in biological samples,²⁵⁵ study of adsorption of cationic surfactants on to clay minerals²⁵⁶ etc. We also developed a cation surfactant ion selective electrode in order to understand the behaviour of these polymeric membrane electrodes in aquo-organic medium and the role of solvent on surfactant self aggregation.

1.12 Polyoxyethylene Alkyl Ethers and α -Sulfonato Fatty Acid Methyl Esters.

Developments in new technology and the environmental issues continue to drive the detergent/surfactant arena. Because of low hard water stability and high skin irritation, traditional fatty acid soaps cause problems in many practical applications. To overcome this, numerous attempts have been made to develop more soluble and less corrosive soap derivatives. Thus substances derived from esters of monocarboxylic acids sulfonated in α -position are an important class of surfactants from economic and

ecological point of view.²⁵⁷ The general formula of α -sulfonato fatty acid esters or α -sulfonato carboxylic esters is,



(with R_1 and R_2 = alkyl groups, M = alkali metal).

α -sulfonato carboxylic acids are very important and will become more and more interesting in the future, as the raw materials for their preparations are fatty acids that can be obtained from oils and fats of renewable resources. They can be used as possible substitutes for surfactants based on petrochemicals. The main reason for growing importance of products from renewable raw materials is their superior digestibility in environment.

α -sulfonato fatty acid esters are practically useful and important, because they have

- i) Excellent primary and ultimate biodegradability²⁵⁸⁻²⁶⁰
- ii) Lower Krafft Point²⁶¹
- iii) Resistance to hydrolysis in hot acid or alkaline conditions²⁶²⁻²⁶⁴
- iv) Good hardness tolerance
- v) Higher ability of emulsification
- vi) Excellent detergency for fabrics
- vii) Lower cmc value compared to n-alkyl sulfates.

Most of the technically produced α -sulfonato fatty acid esters are prepared from unbranched saturated fatty acid esters that are derived from C_8 - C_{22} carboxylic acids and C_1 - C_3 alcohols. In particular, the C_{12} (lauric), C_{14} (myristic), C_{16} (palmitic) and C_{18} (stearic) acids are interesting because the ester sulfonates with these carbon chains have the

best properties for surfactant applications. Also, the methyl ester group in the α -sulfonato fatty acid esters can also be regarded as a short chain side group and this branching in the hydrophobic chains leads to a lowering of the Krafft point. The bulky sulfo group in the neighborhood of the carboxylate linkage is also responsible for resistance towards hydrolysis in hot acid or alkaline conditions. Moreover the esters of 15-17 carbon atoms are the best wetting agents in distilled and hard water.²⁶⁵ Also α -sulfonato fatty acid esters are mild to skin and thus being non-skin irritants makes them useful in cosmetics. Because of their good biodegradability and low phytotoxicity, α -sulfonato fatty acid esters are well suited as agrochemical additives and as their spreading properties are good even in hard water, they may be developed not only as additives for formulations but also as spreading agents in near future.²⁶⁶

Polyoxyethylene alkyl ethers, C_nE_m are nonionic surfactants comprising of an alkyl chain with methylene groups and a hydrophilic part with oxyethylene units. Nonionic polyoxyethylenated surfactants are used extensively in the chemical industry in areas like detergency, health and personal care, coatings and polymers.²⁶⁰ These materials are commercially produced by reaction of ethylene oxide with an active hydrogen-containing compound using a basic catalyst.



For commercially available surfactants, R represents either H (as for polyethylene glycols) or a hydrophobic group (usually C_1 to C_{20}) such as O, S or N. The number of moles of ethylene oxide (RXH) reacting need not be an integer and represent the average degree of polymerization of the ethylene oxide in the product.²⁶⁷ These compounds have very low values of cmc, much lower than that of α -sulfonato fatty acid esters. The mixtures of these two different class of surfactants will help in optimizing the physico-chemical properties as well as in formulating a detergent with low cmc values. Overall this will help in reducing

the total amount of surfactant usage for a particular application and thus less impact on ecology and economy.

1.13 Scope of the Present work.

The importance of surfactants in enabling various aspects of interfacial science cannot be overstated. Surfactants continue to be critical in many applications in agrochemicals, emulsion polymerization, metal cleaning, paper manufacturing, construction materials, oil recovery, fire fighting, textile manufacturing, plastics manufacturing, water treatment, drug delivery systems etc. The application potential of surfactants is due to their property of spontaneous self-aggregation resulting in micelle formation. Hence micellar properties of surfactants have been the subject of continuous research over a period of time.

However the majority of surfactants used in practice are not pure, but are mixtures of several surfactants. One important reason is that purification of surfactants is very expensive. Moreover, majority of important properties of surfactant are inferior to those of a mixed surfactant system. When surfactants of dissimilar charges are mixed together in water, several physico-chemical properties of the mixed system compared to that of single surfactant are changed owing to the fact that there is a net interaction between the constituent amphiphiles. Ionic and nonionic surfactant mixtures are commonly used in many practical applications as the solution behaviour of these surfactants can be complementary and also from the fundamental viewpoint, ionic/nonionic surfactant mixtures are important as they exhibit highly nonideal behaviour upon mixing. The addition of nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsions between the charged surfactant head groups and facilitate mixed micelle formation. The studies on mixed surfactant systems are thus helpful in adjusting the required properties.

Owing to the importance of mixed micellar systems composed of binary surfactant combinations from the fundamental, technological, pharmaceutical and biological consideration, we studied the interfacial, thermodynamic and performance

properties of ionic/nonionic surfactant mixtures. Also the surfactant mixture we have chosen includes nonionic surfactant of poly oxyethylene alkyl ether type (C_nE_m) type, which are widely used as emulsifiers, detergents and solubilizers. Whereas, anionic surfactant is of α -sulfonato fatty acid methyl ester type having superior detergency for fabrics, good tolerance against calcium ions and good biodegradability. Practically, the understanding of fundamentals of micellization as well as nature of interactions between these surfactants in mixed micelle can help in formulating an eco-friendly as well as consumer friendly detergent, which can also be used in hard water. Moreover, the knowledge of interaction between the constituent surfactants in the mixed micelle will be helpful in optimizing and tuning the performance properties viz. detergency, foaming and viscosity. This is important practically as all these performance properties are responsible in many technological processes involving surfactants.

V. A. Persegian²⁶⁸ wrote in 1973 the following sentences- “Despite enormous progress in understanding the genetics and biochemistry of molecular synthesis we still have only primitive ideas of how linearly synthesized molecules form the multi-molecular aggregates that are cellular structures. We assume that the physical forces acting between aggregates of molecules and between individual molecules should explain many of their associative properties; but available physical methods have been inadequate for measuring or computing these forces in solids or liquids”, in order to embrace and define a whole gray area of ‘self assembly of amphiphilic molecules’, that bridges chemistry, physics and biology, and which has been explored a lot in last five decades. Even though a lot of advancement has taken place in this field with development of newer instrumentation techniques and also due to efforts of researchers all over the world, still the knowledge on the understanding of the principles underlying micellization still seems to be little and thus his words seem to hold true even in present context after three decades. Still newer concepts are emerging and the area of micellization of amphiphilic molecules continues to grow at a brisk pace. The present thesis is one more attempt to shed light on the principles underlying the fundamentals of micellization/self assembly of pure as well as mixed amphiphiles.

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