CHAPTER - 1

INTRODUCTION

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1.1 GENERAL INTRODUCTION

Nature has devised several versatile and vital compounds without which our biological system would not operate, including the ~~very~~ membrane that contains the living cell. Such compounds have led to many microheterogenous supramolecular systems that play an important role in many applications as exemplified by its numerous contributions to the field of science. In ~~these~~ This class of compounds the one that ~~are~~ is used in diverse research areas, from basic chemical kinetics to membrane mimetics in biological sciences is the so-called "Surfactant".

Surfactants or SURFACE ACTIVE AGENTS as the name indicates are substances that adsorb at the interfaces even when present in very low concentrations. They are found in many facets of civilized activity. Apart from our multifarous daily needs, they are highly exploited in innumerable commercial and industrial applications. The unique molecular structure and amphiphilic nature of these compounds have led to their uses in various fields.

Surfactants contribute to two main fundamental properties[1] that include (i) the adsorption at the interface giving rise to properties[1.] such as foaming, wetting, emulsification, dispersion of solids and detergency (ii) formation of "micelles" in solution leading to other properties such as solubilization and viscosity. Almost in all applications a combination of these properties are generally involved.

The first group of surfactants for general application that was traditionally classified as synthetic were developed in Germany during World War I in an attempt to overcome the shortage of animal and vegetable fats. Thereafter, till date many new surfactants have emerged and have 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, as for example, mixtures of surfactants. In most of the commercial and industrial applications single surfactants are seldom used and mixed surfactants forming mixed micelles are generally preferred[2,3]. 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

Surfactants are amphiphilic substances consisting of a long chain hydrophobic hydrocarbon "tail" and a hydrophilic / polar "head" which may be ionic or nonionic. Based on the charge on the polar head group and its molecular structure they can be classified as follows :

Ionic Surfactants :

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

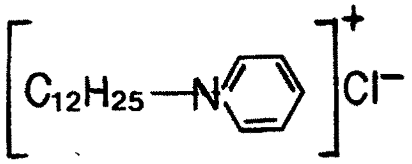
Sodium dodecyl sulfate (SDS) : $C_{12}H_{25}SO^-_4\ Na^+$

Potassium laurate : $CH_3(CH_2)_{10}\ COO^-\ K^+$

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

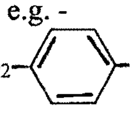
e.g. cetyl trimethylammonium bromide (CTAB) : $C_{16}\ H_{33}\ \overset{+}{N}\ (CH_3)_3\ Br^-$

Dodecyl pyridinium chloride



Nonionic Surfactants :

The surface active portion bears no apparent charge e.g. -

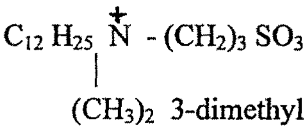
Triton X 100 (TX 100) : $CH_3\ C(CH_3)_2\ CH_2\ C(CH_3)_2$-  -O-$(CH_2CH_2O)_{9\,5}\ H$

Brij 35 : $CH_3\ (CH_2)_{11}\ (OCH_2\ CH_2)_{23}\ OH$

Zwitterionic Surfactants :

The surface active portion bearing both positive and negative charges e.g.

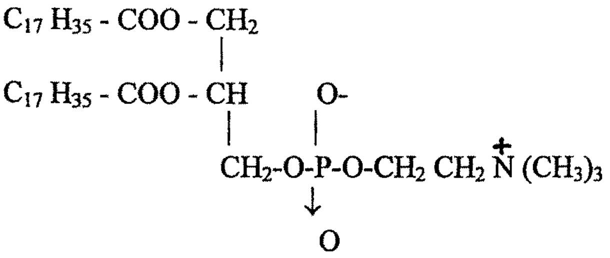
Betaines :



$C_{12}H_{25}\underset{(CH_3)_2}{\overset{+}{N}}-(CH_2)_3SO_3$

3-dimethyl dodecyl propane sulfonate

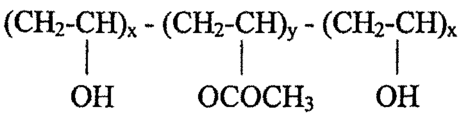
Lecithin (a triglyceride)



$$\begin{array}{l} C_{17}H_{35}-COO-CH_2 \\ \qquad\qquad\qquad\;\; | \\ C_{17}H_{35}-COO-CH \qquad O- \\ \qquad\qquad\qquad\;\; | \qquad\quad | \\ \qquad\qquad\qquad\; CH_2-O-\underset{\underset{O}{\downarrow}}{P}-O-CH_2\,CH_2\,\overset{+}{N}(CH_3)_3 \end{array}$$

Polymeric Surfactants :

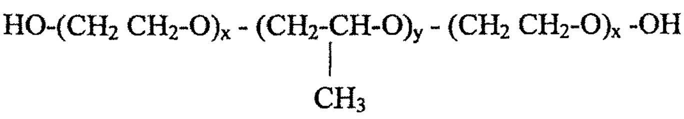
Partially hydrolyzed poly (vinyl acetate)



$(CH_2-\underset{OH}{CH})_x-(CH_2-\underset{OCOCH_3}{CH})_y-(CH_2-\underset{OH}{CH})_x$

Block polymers called pluronics

PEO - PPO - PEO

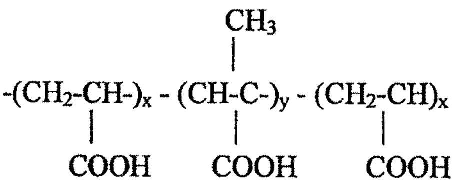


$HO-(CH_2\,CH_2-O)_x-(CH_2-\underset{CH_3}{CH}-O)_y-(CH_2\,CH_2-O)_x-OH$

Polyelectrolytes :

Lignosulfonates (anionic polyelectrolytes prepared by sulfonation by wood lignin)

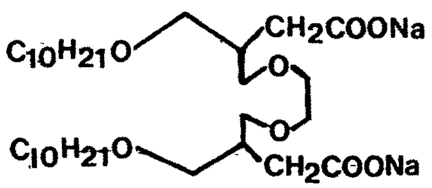
Polyacrylic acid and polyacrylic / polymethacrylic acid



$$-(CH_2-\underset{COOH}{CH}-)_x - (CH-\overset{CH_3}{\underset{COOH}{C}}-)_y - (CH_2-\underset{COOH}{CH})_x$$

Gemini Surfactants :

Two amphiphilic molecules connected together by small hydrophobic chain.



1.3 MICELLES

(a) Structure and Shape :

The presence of micelles was originally suggested by McBain[4]. He concluded that below the CMC most of the surfactant molecules are unassociated, whereas in the isotropic solutions just above the CMC, micelles and surfactants coexists with concentration of the latter changing very slightly as more surfactant is dissolved. The self association is strongly cooperative upto a certain micelle size for long chain amphiphile.

It was suggested by Adam[5] and Hartley[6] that micelles are spherical in shape. G.S.Hartley[6], 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 processes uncongenial**". A schematic representation of an ionic micelle is shown in Fig. 1.

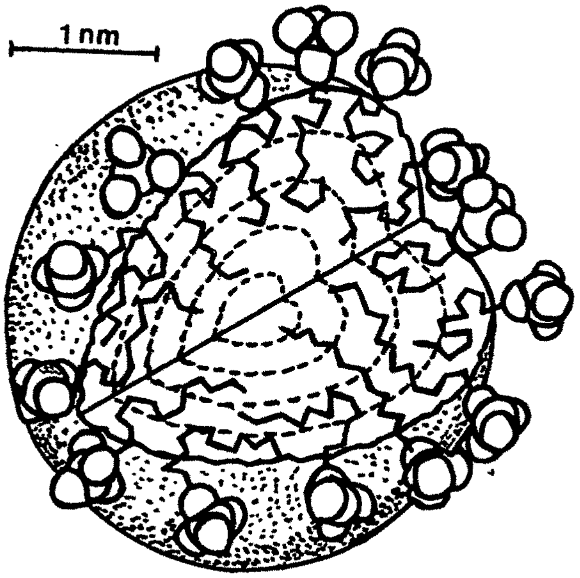


Fig. 1 : Three dimensional structure of a micelle containing 60 sodium dodecyl sulfate molecules. The hydrocarbon chains pack at liquid hydrocarbon density in the core and are almost as disordered as in the bulk liquid state (from ref. 193).

The spherical micelles have the following properties[7] (a) the association unit is spherical with radius approximately equal to the length of hydrocarbon chain (b) there are 50-100 monomers in micelle and increases as the hydrocarbon chain length increases (c) the counterions are bound to the micelles of ionic surfactants thus reducing its mobility compared to its nonionic counterpart (d) due to higher association number of surfactant micelles, 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.

Apart from spherical micelles the presence of different shapes was proposed[8,9]. Some of the major types of micelles are - (i) relatively small, spherical structures (aggregation number <100); (ii) elongated cylindrical rod like micelles with hemispherical ends (prolate, ellipsoids); (iii) large, flat lamellar micelles (disk like extended oblate spheroids) and (iv) vesicles almost spherical structures consisting lamellar vesicles arranged in one or more concentric spheres.

Ikeda et al.[9,10] have shown that in presence of low concentrations of sodium chloride, SDS form spherical micelles and associates itself into rod like micelles at high sodium chloride concentration. Many authors have discussed the size and shape of nonionic surfactants[11,12]. Their studies show that these micelles have disk like shape and that the polyoxyethylene chains in the outer mantle of the micelle must be in a randomly coiled conformation.

Many researchers have worked in the theory of micellar structure[13,14] based on their geometry of various micellar shapes and space occupied by the hydrophilic and hydrophobic groups of the surfactant molecule. The packing parameter $V_H/l_c a_o$ that they developed gives an idea of the shape of the micelle[15]. V_H, l_c and a_o are the volume occupied by the hydrophobic group in the micelle core i.e. $V_H = 27.4 + 26.9\ n_c\ \text{Å}^3$ 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. $l_c = 1.5 +$

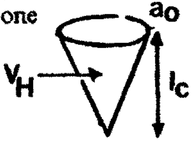
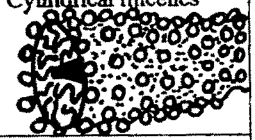
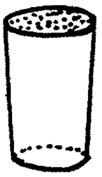
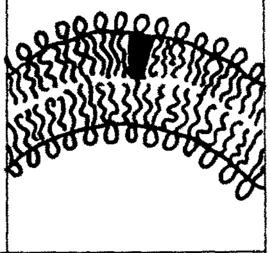
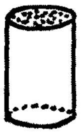
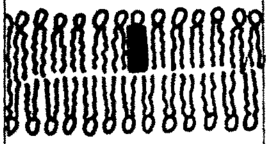
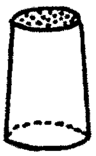
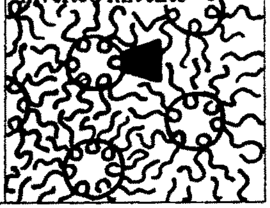
12.6 n_c Å and a_0 the area of cross section occupied by the hydrophilic group at micelle solvent interface. A schematic representation of different micelle structures are shown in Fig.2

Surfactants in a given solvent forms micelles, though the micelle formation depends on the type of the solvent[16]. 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 interior. Such micelle is termed as "normal micelle". In a non polar medium the lipophile attract the hydrophobic parts and forces the hydrophilic heads away, which then hold 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 micelles". Dimensionally reverse micelles are comparable with normal micelles and both are thermodynamically stable[16]. A diagramatic representation of normal and reverse micelle are shown in Fig. 3

(b) Critical Micelle Concentration (CMC) :

The colligative properties of surfactants in aqueous solution do vary in a simple way with concentration at lower concentration range as usually observed for solutions of conventional solutes. However, the physical properties of surface active agents differ from those of smaller or non-amphipathic molecules in one major aspect, namely the abrupt changes in their properties above a certain critical concentration[16]. This is shown in Fig. 4. The physical properties include equivalent conductivity, turbidity, surface tension, osmotic pressure, self diffusion, magnetic resonance, solubilization and microviscosity.

All these properties i.e. either interfacial or bulk show an abrupt change at a particular concentration which is consistent with the fact that at and above this concentration the surface active monomers associate to form larger units. These associated units are called "micelles" and the concentration at which this association phenomenon occurs

Lipid	**Critical packing parameter** $v/a_o l_o$	**Critical packing shape**	**Structures formed**
Single chained lipids (surfactants) with large head group areas **SDS** in low salt	< 1/3	Cone 	Spherical micelles 
Single chained lipids with small head group areas. **SDS and CTAB in high salt,** noionic lipids	1/3–1/2	Truncated cone 	Cylindrical micelles 
Double chained lipids with large head group areas, fluid chains. Phosphatidyl choline (lecithin) Phosphatidyl serine Phosphatidyl glycerol Phosphatidyl inositol Phosphatidic acid Sphingomyelin, **DGDG**[a] Dihexadecyl phosphate Dialkyl dimethyl ammonium salts	1-2/1	Truncated cone 	Flexible bilayers, vesicles 
Double chained lipids with small head groups areas, anionic lipids in high salt, saturated frozen chains phosphatidyl ethanolamine, phosphatidyl serine + Ca^{2+}	~1	Cylinder 	Planar bilayers 
Double chained lipids with small head groups areas, nonionic lipids, poly (cis) unsaturated chains, high T unsat phosphatidyl ethanoamine, cardiolipin + Ca^{2+}, phosphatidic acid + Ca^{2+}, cholesterol, MGDG[b]	> 1	Inverted truncated cone or wedge 	Inverted micelles 

[a] DGDG, digalactosyl diglyceride, diglucosyl diglyceride; [b] MGDG, monogalactosyl diglyceride, monoglucosyl diglyceride.

Fig.2 : Dependence of aggregate type and geometry on the packing requirements of surfactant head group and chains (from ref. 193)

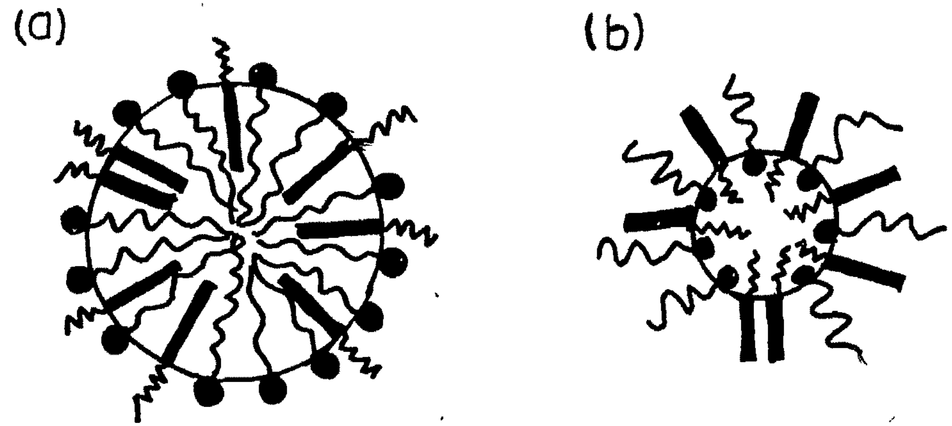


Fig. 3 : Schematic representation of mixed micelles (a) normal micelle (b) reverse micelle.

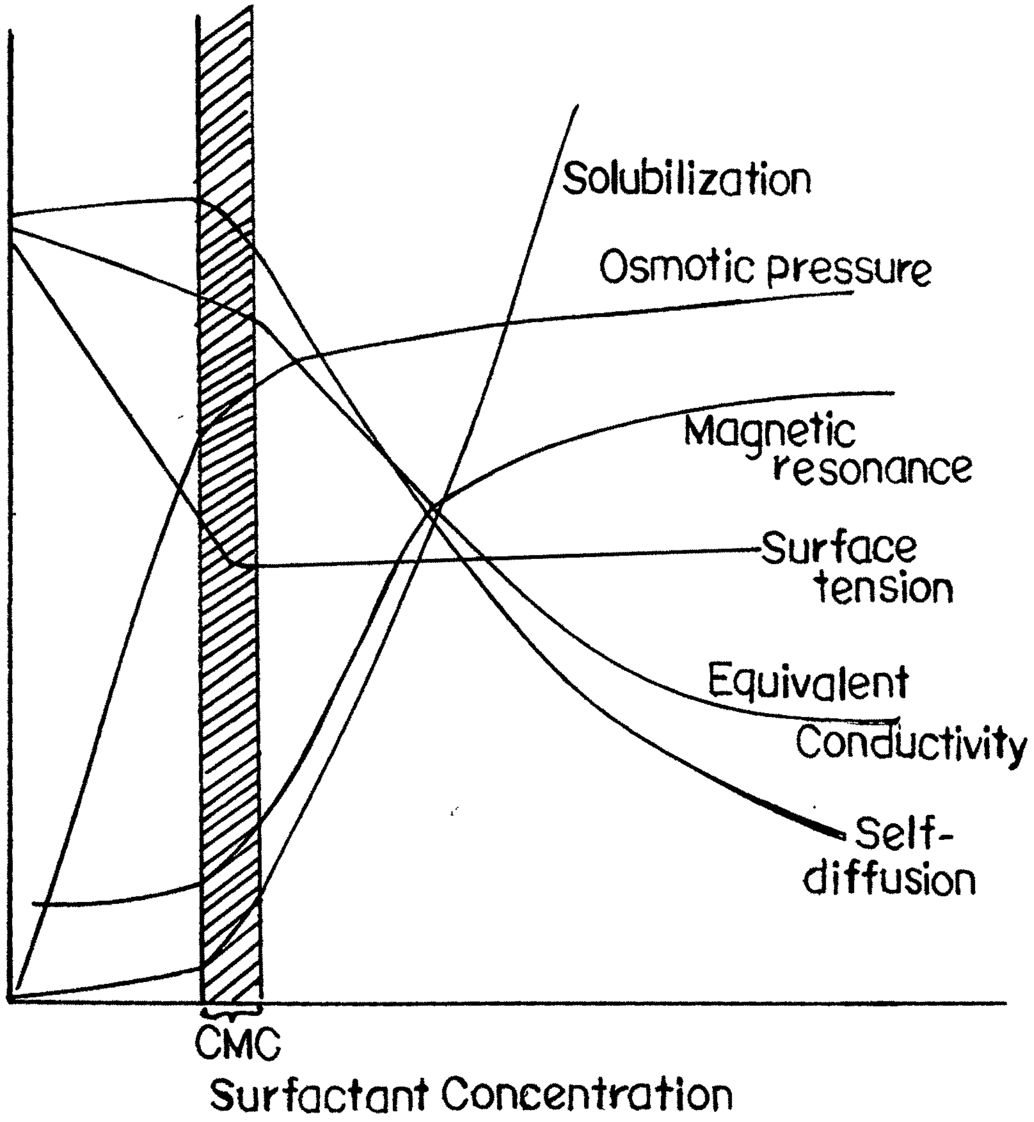


Fig. 4 : Changes in concentration dependence of a wide range of physicochemical quantities around the critical micelle concentration (CMC) of the surfactants.

is termed as the "critical micelle concentration" (CMC). Each surfactant molecule has a characteristic value of CMC at a given temperature. These micelles are important as models[17] of biological membranes.

1.4 FACTORS AFFECTING CMC

The critical micelle concentration (CMC) is characteristic of THE surfactant and depends upon various factors such as the hydrophobicity of the hydrocarbon chain[18], nature of the polar head group[19], counterion[20], temperature[21], pressure[22], pH[23], presence of electrolytes[24], polar[25] and nonpolar additives[26] etc.

(a) Surfactant Structure :

In aqueous medium, the CMC decreases as the number of carbon atoms in the hydrophobic tail increases to about 16[27]. As a general rule for ionic surfactants with one hydrophilic group, the CMC is halved by the addition of one methylene group[1]. But for nonionic and zwitterionic surfactants the magnitude of decrease in the CMC is much larger. However, as the chain length exceeds to more than 18 the effect on CMC is limited as coiling of these long chains occur in water[28].

Introduction of polar groups such as -OH in the hydrophobic chain too increases the CMC. Also, the surfactants with bulky hydrophobic / hydrophilic group delay the micelle formation due to steric factors. The fl~~ou~~uorocarbon based surfactants with same number of carbon atoms as the hydrocarbon based ones have a lower CMC[29].

In general, ionic surfactants have slightly higher CMC values compared to zwitterionics which is again much higher than nonionics for the same number of carbon atoms. Gemini surfactants have much lower CMC than longer chain surfactants[20]. If the ionic hydrophilic group is closer to the α-carbon atom of the hydrophobic group of the surfactant, the CMC increases[31]. In quaternary cations, e.g. $C_{12}H_{25}N^{+}(R)_{3}Br^{-}$ the CMC decreases as the length of R increases due to increasing hydrophobicity.

In case of polyoxyethylene nonionics of type C_nE_8 (n=9-15) as the number of carbon atoms increases the CMC decreases[32]. Rosen et al.[33] have reported the CMC values of $C_{12}Em$ (m=1-8) showing that the CMC increases with increasing hydrophilicity in the molecule. Similar studies were carried out by Crook and coworkers[34] for p-tert octylphenoxypoly (ethenoxyethanol) and reported an increase in the CMC.

In conventional ionic surfactants a change in counterion to one of ~~the~~ greater polarizibility or valence leads to decrease in the aggregation number. Sepulveda et al.[35] have reported the CMC values for hexadecyl and tetradecyltrimethyl ammonium micelles with various counterions.

(b) Effect of Additives :

The use of additives is a common method to alter the aggregation behavior of surfactants. The presence of a third component in the solution can modify the micellization process in two different ways[36-39] : (i) through specific interactions with the surfactant molecules or (ii) by changing the solvent nature. In this respect the aqueous solvent properties are modified by the addition of electrolytes and non-electrolytes.

The study of the influence of electrolytes is important in understanding the chemical environment of amphiphilic molecules. The electrolyte effect on the CMC is more pronounced for anionic and cationic surfactants where a depression in CMC is observed. Addition of electrolyte causes a reduction in the thickness of the ionic atmosphere surrounding the head group and consequently decreases the repulsion between them. Somasundaram et al.[40] have reported the CMC values for sodium dodecyl sulfate (SDS) in various electrolytes such as NaCl, Na_2SO_4, LiCl, CsCl, Cs_2SO_4, $MgCl_2$, $MgSO_4$ and $Na_3(PO_4)_2$. All these electrolytes decreased the CMC of SDS. Such studies of binding of cations on SDS micelles were reported earlier also by Mukherjee et al.[41].

Goddard[42] and coworkers studied the effect of alkali metal salts and some quaternary ammonium salts on the CMC of SDS solution. They found that the ability of alkali metal cations to decrease the CMC increases with the decrease in the size of the hydrated cation.

Hiroshi Maeda et al.[43] have determined the CMC of dodecyldimethyl amine oxide (DDAO) as a function of NaCl concentration. They discussed the nonlinear Corrin-Harkins relation in terms of the salting out contribution and/or micelle growth in addition to the contribution of the electric free energy of micelles.

Engberts and Sudholter[44] reported that ~~the~~ sodium salts decreases the CMC in the order $Cl^- < Br^- < NO_3^- < I^- < Ois^-$ for the surfactant 1-methyl 2-dodecyl pyridinium iodide. The order of decrease is in parallel to the lyotropic series for the inorganic anions. The decrease of the CMC with increasing salt concentration followed the total counterion concentration at the CMC as given by Shinoda equation[45].

$\text{Log CMC} = A - B \log [\text{CMC} + (\text{Na X})]$ where A and B are constants.

A lowering of CMC of polyoxyethylenated nonionic surfactants following the addition of electrolyte has also been reported in literature[46], although the magnitude of lowering is less than for in ionic surfactants. Blankschtein[47] and coworkers have studied the effects of adding LiCl, KCl, NaCl, KBr and KI to aqueous solutions containing alkyl poly (ethylene oxide) ethers C_nE_m type nonionics i.e. $C_{12}E_6$, $C_{12}E_8$ and $C_{10}E_6$ through combined theoretical and experimental approach. The order of decreasing the CMC are, for anion ($Cl^- > Br^- > I^-$) and for cation ($Na^+ < K^+ < Li^+$)[48,49]. The measured log (CMC) varied with the salt concentration.

The effect of alkali metal ions on the CMC of crown ether type surfactant is also reported. Attwood[50] and coworkers studied the influence of electrolyte on the micellization of phenothiazone, a drug surfactant and concluded that the addition of electrolyte promotes the micelle formation in these type of molecules.

Mukherjee and Ray[51,52] have concluded that the "salting out" or "salting in" of the hydrophobic groups in the aqueous solvent system rather than the hydrophilic group of the surfactant is the main cause for the variation in the CMC of nonionic and zwitterionic surfactants.

Other than the electrolytes the organic additives lead to remarkable change in the CMC by modifying their interaction with water, surfactant molecule or with the micelle. In general the organic additives cause changes in the water structure, dielectric constant or cohesive energy density i.e. the solubility parameters[53].

Surfactants form micelles in the entire concentration range of ethylene glycol (in aqueous ethylene glycol as well as in pure ethylene glycol). Only few studies for micelle formation in water-ethylene glycol are reported[54]. Ahluwalia et al.[55] report an increase in the CMC values of Triton X100 as the concentration of (vol %) of ethylene glycol increases. The effect of aqueous ethylene glycol mixture on the CMC of cetyl pyridinium bromide is reported[56-58]. The CMC of the surfactant in the solvent mixture followed a logarithmic dependence i.e. $\log \mathrm{CMC}_{\mathrm{water}} = \log \mathrm{CMC}_{\mathrm{wate+EG}} + K\,[\mathrm{EG}]$. The increase in the CMC with ethylene glycol content has been explained on the basis of a decrease in the cohesive energy density and decrease in the dielectric constant of aqueous phase. Sjoberg et al.[59] employed surface tension and NMR measurements to examine the aggregation of cetyl trimethyl ammonium bromide (CTAB) in aquo-formamide and ethylene glycol mixtures. Such determinations of CMC in various aquo-formamide, ethylene glycol and dioxane for AOT was done by Moulik et al.[60].

Addition of 1,4 dioxane to aqueous SDS solution lowered its CMC whereas for DTAB and Triton X100 an increase in CMC was observed[61]. The heavy head groups in DTAB and Triton X100 hinder the transfer of dioxane molecules through the micellar surface thus causing a disruption of water structure around the hydrophobic group of these surfactant molecules.

Fendler and Fendler[62] reported the CMC values for hexylammonium propionate surfactant in presence of DMSO-water mixed solvent system. The effect of other organic solvents like glycerol, hydrazine, amines and esters have also been well studied[63-67].

The ability to depress the CMC of the surfactant in presence of alcohol depends upon the alcohol chain length, the extent of hydrocarbon solvent contact region and the free monomer concentration in solution. As the alcohol chain length increase the ability to depress the CMC increases. The effect of various alcohols on the CMC of potassium octanoate, decanoate, dodecanoate and tetradecanoate was reported by Shinoda[68]. He found that the CMC of fatty acid soaps is a linear function of alcohol concentration. The logarithm of the rate of change of CMC with the concentration of given alcohol is a linear function of the number of carbon atoms in the soap molecule.

Hamdiyyah et al.[69] have studied the effects of 1-propanol, 1-butanol, 1-hexanol and 1-octanol on the micellization parameters of SDS in heavy water and aqueous urea solutions. The micellar behavior of tetradecyl trimethyl ammonium bromide (TTAB), a cationic surfactant, in water-alkanol mixtures of different compositions were well studied. An initial decrease followed by an increase in the CMC values with increasing alkanol concentration was observed[70-71]. Similarly, the CMC values of potassium and silver dodecyl sulfates in lower alcohols and alcohol water mixtures were determined[72].

Zana and coworkers[73-78] have determined the effect of various linear alcohols on the micellization parameters of alkyl trimethyl ammonium bromide. Nishikido et al.[79] reported the CMC value of nonionic surfactants in aqueous solution in presence of various alcohols. They observed an increase and decrease in the values and discussed in terms of weakening of hydrophobic bonds and solubilization of alcohols in the micelle.

Some of the additives that markedly influences the aqueous solution properties are xylose, dextrose, fructose, sucrose polyethylene glycol which are water structure formers and urea and its derivative that are water structure breakers. These additives are highly hydrophilic and non-penetrating and form mixed micelles to very small extent. However, though urea is well studied, very limited studies, have been carried out on sugar derivatives.

Basumallick et al. have studied the effect of dextrose on SDS, CTAB and Triton X100[80]. The effect of sucrose and polyethylene glycol on the CMC of nonionic surfactants were studied and the results were discussed in terms of changes in solvent structure[81-86].

Urea and its derivatives are well known water structure breakers and protein denaturants[87,88]. It generally increases the CMC of ionic and nonionic surfactants, decreases the micelle size and increases the cloud point of Zwitterionic surfactants. The action of urea in aqueous solution is explained by different mechanisms[89-94].

A rise in the CMC of SDS, LiDS and DTAB in presence of urea at different temperatures was observed[95,96]. Recently, an ESR study of effect of urea on micelle formation and micro-environmental properties of SDBS micellar solutions has been investigated and an increase in CMC is reported[97]. A similar increase in the CMC for Triton X100 has been observed in presence of urea[98]. Blankschtein et al.[99] have presented results of a systematic experimental and theoretical investigation of the effect of urea on the micellization, micellar growth and phase separation of aqueous micellar solutions of nonionic n-dodecyl hexaethylene oxide ($C_{12}E_6$) surfactant.

Rehfeld[100] first proposed the solubilization of hydrocarbon into the micelle to the CMC of surfactant. He investigated the effect of a non-aqueous phase on the adsorption and micellization of an anionic surfactant SDS in hydrocarbon / water interfaces. Rosen et al.[101] also in a similar way carried out studies on zwitterionic surfactant in various hydrocarbon / water systems. Solubilization of the saturated hydrocarbons into the micellar core increases, the micelle becomes larger swollen sphere and the result is more room for the surfactant molecule and therefore the CMC decreases. Politi et al. studied the effect of urea on AOT reverse micelles[102].

(c) Effect of Temperature and Pressure :

The effect of temperature on the CMC for ionic and nonionic surfactants is generally attributed to the characteristic features of solubility - temperature relationships. The variation of CMC with temperature for ionic and nonionic surfactant is shown in Fig. 5.

In case of nonionic surfactants as the temperature decreases the CMC increases. Although, a minimum is observed at relatively higher temperatures e.g. octyl phenoxy ethoxyethanols with oxyethylene chain lengths between 6-10 at approximately 50°C. The well known dehydration phenomenon is quite predominant with increasing temperature for nonionics, in other words hydrophobicity increases with increasing temperature. Many factors contribute to the temperature effect on nonionic surfactants (i) the change in water structure around the ethylene oxide units (ii) change in the hydrogen bonding networks around the EO group (iii) changes in the conformation of EO groups[103,104].

However, in ionic surfactants an altogether different behavior is observed. The CMC-temperature relationship is complex. The CMC increases with increasing temperature passing through a minimum at lower temperature region. This decrease in the CMC at lower temperature region can be ascribed to the lowering of hydrophilicity. Further increase in the CMC with temperature is due to the disruption of water structure

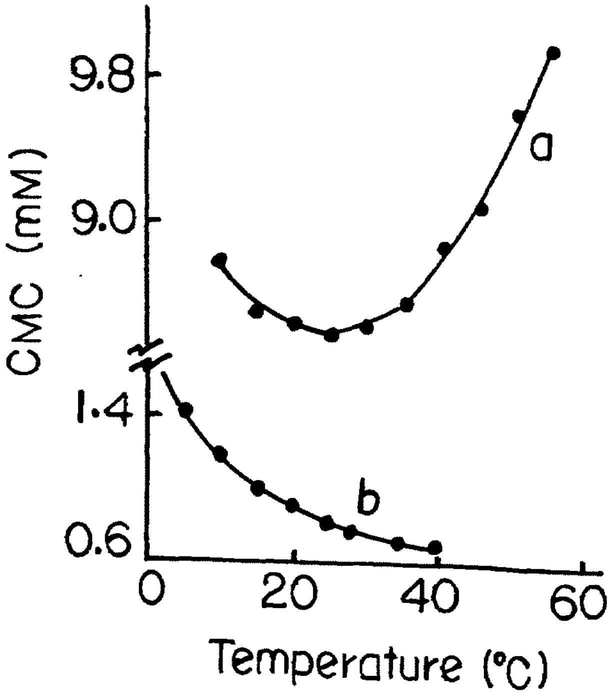


Fig. 5 : Variation of CMC with temperature for (a) sodium dodecyl sulphate; (b) $C_{10}E_5$ (taken from ref. 16).

around the hydrophobic portion of the surfactant molecule that opposes the micellization hence higher CMC[16]. The position of the minimum[105-108] has a thermodynamic significance i.e. the minimum in the CMC represents the minimum in standard free energy of micelle formation that occurs at temperature at which $\Delta H^{\circ}_{m} = 0$. Experimental evidence also showed that the temperature at which minimum in CMC is observed is at which ΔH°_{m} is practically zero[109].

Effect of Pressure :

The effect of pressure on self organization of surfactants has been studied[109].The CMC-pressure plot passes through a maximum. The increase in pressure initially retards micelle formation and later on favours after a certain threshold value of pressure is reached. The increase in CMC is due to the breaking of water structure at higher pressures. The release of surfactant monomers at lower pressures and their association at higher pressures together with changed dielectric constant of the solution with applied pressure also play vital roles in the self-organization[16].

The CMC of a series of alkyl trimethyl ammonium bromides and sodium dodecyl sulfates show a maxima in the CMC-pressure profile[88]. Further evidence for a maximum in CMC-pressure plot was presented by Nishikido et al.[110]. The overall effect of pressure on CMC of surfactants can be ascribed to (i) the solidification of micelle interior (ii) a pressure induced increase in the dielectric constant of water and (iii) the changes in the water structure.

Mesa[109] has analyzed the relations between the CMC's and temperature / applied pressure using an experimental data fit and discussed in terms of thermodynamic considerations. Measurements of CMC at high pressures were carried out by many workers. Sugihara et al.[111] have determined the CMC of sodium perfluorodecanoate aqueous solution at different pressures and temperatures. Similar studies of effect of pressure on the CMC of Nonyl N-methylglucamine / sodium perfluoro octanoate mixed systems were done by same workers[112,113].

(d) Solubility - Temperature Relationship :

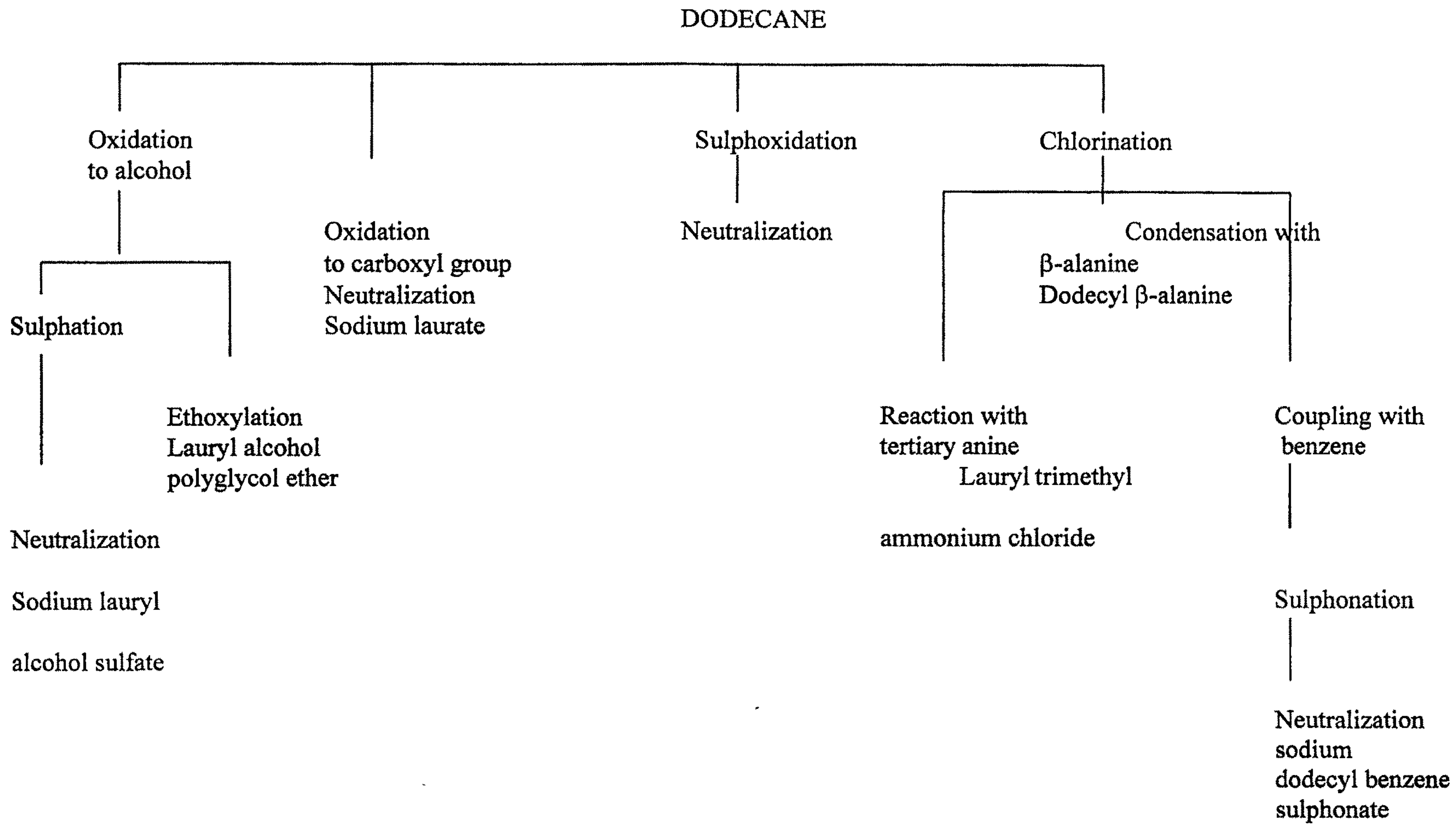
In ionic surfactants as temperature is raised its solubility increases gradually, then above a certain temperature there is a sudden increase of solubility with further increase in temperature. CMC of ionic surfactants too increase with temperature. At a certain temperature, the solubility becomes equal to the CMC i.e. the solubility curve intersect the CMC and the temperature just before the micelle formation is, termed as "Kraft point". At this temperature the solid hydrated surfactant and micelles are in equilibrium with the monomers[114].

However, in case of nonionic surfactants a reverse behavior is observed. An 1% (w/v) of nonionic surfactant solution 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[115-116] that explain the presence of cloud point, this phenomenon is assumed to occur because of the micellar growth and intermicellar attraction as temperature increases leading to the formation of larger aggregates and the solution becomes visibly turbid. Many researchers have investigated[117-119] and reported the cloud point of various nonionic surfactants in presence of charged and neutral solutes including the presence of an ionic surfactant.

1.5 LABS AND ALCOHOL ETHOXYLATES

Developments in new technology and the environmental issues continue to drive the detergent / surfactant scene. Although surfactants represent a large family of products of diverse nature and composition, there are two main products for volume and diffusion reasons - alcohol derivatives and alkylbenzene derivatives, where raw materials have an important influence[120].

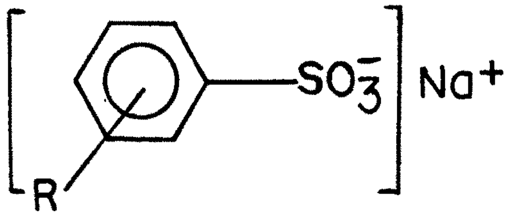
* Inspite of the growing number of environmental questions, linear alkylbenzene sulfonate (LABS) has been the choice over decades because of its cost



Illustrating low dodecane can be solubilized and converted into a detergent with varying quantities.

Ref : Davidson A., Mulwidsky B.M.. In : Synthetic detergents, 6th edn. Latimer Trend and Company Ltd. Plymouth, 1978, pp.12.

competitiveness, cleaning effectiveness and proven environmental safety. These alkyl aryl sulfonates are prepared[121,122] by the sulfonation of a number of alkyl substituted aromatic hydrocarbons starting from benzene naphthalene, toluene etc. The alkyl substituent in modern alkyl aryl sulfonates is a straight chain attached to the aromatic nucleus via Friedel Crafts reaction with $AlCl_3$ as catalyst. The sulfonation is generally accomplished with sulfuric acid and oleum or with SO_3. For optimal decisive properties the length of the alkyl chain rarely exceeds 12 carbon atoms e.g.

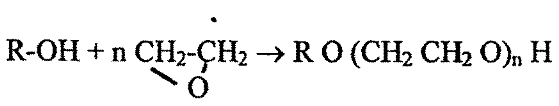


Sodium dodecyl benzene sulfonate $R = C_{12}H_{25}$

However, the laundry detergent reformulation gradually shifted from LABS to alcohol based surfactants, including alcohol ethoxylates (AE), alcohol ether sulfates (AES) accompanied by the growing usage of new sugar-based surfactants such as alkyl polyglucosides and N-alkyl glucosamides. Nonetheless, formulations of compact granules use three basic surfactant systems : LABS / AES / AE, LABS / AE and AE alone. Although the AE are primary surfactants in laundry detergents, they are still the second most used surfactant behind LABS, the "work horse" surfactant and is expected to remain so till the end of this century[123].

Polyoxy ethylenated alcohols, nonionic surfactants are more commonly called as the alcohol ethoxylate (AE)[124]. These compounds and many of their derivatives have been an integral part of formulations used in the consumer household, personal care, industrial and institutional markets for many years.

The chemistry of ethoxylation is simply defined by the following reaction[104].



$$R\text{-}OH + n\ \underset{\diagdown O \diagup}{CH_2\text{-}CH_2} \rightarrow R\ O\ (CH_2\ CH_2\ O)_n\ H$$

R = alcohol hydrophobe or lipophile
n = number of moles of ethylene oxides (EO)
(EO is hydrophilic)

These compounds have very low critical micelle concentration (CMC). Much lower than that of LABS and mixtures of these surfactants with LABS provides high detergency at low concentrations and favourable biodegradability. As detergent formulations become more complex mixing of surfactants especially with the nonionic surfactants will grow in importance and more importantly the multiple surfactants[125].

1.6 (a) Mixed Surfactants System :

Surfactants used for almost all industrial and commercial scales are invariably mixtures due to their economic and beneficial effects over individual surfactants. In the complex world of surfactant formulation today, the surfactant technologists needs to have a working knowledge of surfactant mixing principles as per the application desired for. This includes an understanding of mixed surfactant behavior both in the end use domain as well as in the formulation domain. Hence, in order to tailor the properties of the surfactant solution to best suit the desired application, one must be able to predict and manipulate (i) the tendency of surfactant solution to form micelles as reflected by the CMC (ii) the shape and size distribution of the micelles that form above the CMC (iii) the phase behavior of surfactant solution.

Indeed, the concentration of surfactant in solution which is used as a cleaning detergent, should exceed the CMC to ensure the presence of micelles in which the oily substances or dirt can be solubilized[126]. The size and shape of micelles directly control the viscosity and other rheological features of the micellar solutions which are important in many applications involving surfactants, for example in personal care products. Therefore, mixtures of surfactants offer a convenient way to optimize the micellar solution properties since by just changing the solution composition one can effectively find a range tuned to the desired features. Addition of nonionic surfactant to an ionic surfactant solution may significantly reduce the CMC and may also increase the size of the micelle. Clearly, a thorough understanding of the underlying physics and chemistry of mixed surfactant systems is highly desirable.

(b) Experimental Data and Various Proposed Theories :

Many theoretical approaches and various technological applications have rapidly progressed in the last few decades in the area of mixed surfactant system. In most of the cases when different types of surfactants are purposely mixed, "synergism", a condition when properties of mixtures are better than the individual components, is observed[126]. However, investigations of synergism in quantitative terms is a convenient method to study the molecular interaction between the surfactant molecules. Depending upon the kind of surfactants, apart from "~~S~~ynergistic" effect, even "antagonism" can be observed. s Lower case

"Synergism" is generally seen in mixtures of charged and an uncharged molecule which occur~~s~~ due to interaction between different head groups. On the other hand, "antagonism" can be reached by mixing surfactants having similar head groups and different hydrophobic groups ~~one being~~ for example a hydrophobic and other a perfluorinated one. As a result, studies on mixed surfactant systems have so far attracted much research of pure scientific interest. Scamehorn[3], Rubingh and Holland[127] and Ogino and Abe[2] have recently published books with a collection of review works in the field of mixed surfactant systems. These pertain to intermolecular interactions between the hydrophilic and hydrophobic groups, in addition to their applications.

Clint[128] proposed a phase separation model to describe the phenomenon of mixed micelle formation. This model treat~~s~~ the micellar material as a separate phase from that of dissolved surfactant monomers and proposed that the mixed micelle as an ideal solution of the two surfactants. It predicts the mixture CMC, micelle composition and monomer 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.

The expressions of Lange and Clint[128] for the nonionic mixture CMC has been experimentally verified for situations where ideal mixing is expected i.e. mixtures of n-octyl and n-decyl sulfoxides and mixtures of poly oxyethylenenonionics with varying chain length or head group. Also, Lange and Shinoda have predicted the CMC's of mixtures of soaps, mixtures of alkyl sulfates anionics and quarternary ammonium cationics.

It was Corkill[129] who accounted for the non-ideal mixing and extended the Clint's ideal mixing model. He suggested that since the micellar core is essentially liquid like then regular solution theory which has been found successful in treating non-ideal liquid mixtures should be useful for treating surfactant mixtures. This treatment differs from the ideal treatment in that the interaction between the surfactant molecules within the micelle can be included and therefore provides better physical description for wider range of surfactant mixtures.

All the effects from changes in the charged state of mixed micelles containing ionic surfactants due to surfactant mixing are included in the activity coefficients of regular solution approximation of Rubingh and Holland[130]. Their treatment considers the interaction between the surfactant molecules in mixed micelles. Accordingly, when $\beta=O$, the two surfactants form an ideal mixture, a negative β value indicates that the interactions are strongly attractive and mixed micelles are stabilized electrostatically. A positive β indicates incompatibility of the surfactant species and thus represents a measure of antagonistic behavior of surfactant combination.

According to Rubingh's approach the interaction parameter β is constant over an entire range of composition[130]. This is in general valid for anionic / nonionic mixtures of Na OL / C_{20} $(EO)_6$ and SDS/C_9PhE_{10}. Although Rubingh's regular solution

These need to be defined

treatment is useful due to its simplicity and application to other phenomena, it has a few drawbacks;

(i) the interaction parameter β is considered to be independent of temperature and micellar composition but has found to be substantially temperature and composition dependent[113].

(ii) Meaningful values have not been observed for anionic / cationic mixtures excepting a few like NaCDC / CTAB and NaTCDC / CTAB, contrarily β value were positive[130(b)].

Definition of these abbr ?

(iii) In case of TX100 and Tween 80 mixture negative β values were obtained indicating a probability of weak interaction. The interaction here has been ascribed to the compatibility of polyethylene oxide head groups of these surfactants[130(c)].

(iv) If the regular solution theory is applicable to ionic / nonionic mixed micelles, the effective degree of counterion binding must be proportional to the mole fraction of ionic surfactant in the micelle but this is contrary to the experimental observations[131,132].

Motomura and coworkers[133] have shown that the process of micelle formation can be treated from view point of thermodynamics. They considered the micellization to be similar to a macroscopic bulk phase and the energetic parameters associated with the process are expressed by excess thermodynamic quantities. They derived expressions for different surfactant combinations. This model does not depend upon the nature of surfactants and their counterions thus suitable for studying the behavior of binary surfactant mixtures. Asano et al.[134] have successfully applied this treatment to sodium cholate / octaethylene glycol n-decyl ether mixed system. Moulik et al.[135] have calculated the interaction parameter for NaDC / TX 100 mixtures using this model.

Very recently, Sarmoria et al.[136] and Puvvada et al.[137] have proposed a molecular thermodynamic model applicable to mixed binary solutions of non-ideal surfactant combination on the basis of the CMC's of the individual surfactants and other solution conditions such as temperature, concentration and type of salt present. They derived several equations to calculate the relevant physicochemical quantities. Unlike Rubingh's treatment the calculated activity coefficient values were very low, this indicates greater non-ideality of interaction. Very high values of β have been obtained for cationic-anionic combinations using this model.

The synergism exhibited in surfactant mixtures can be predicted from the CMC. In most of the cases the CMC of the mixture is always lower than the pure components. If the CMC values are intermediate between the pure components, the mixed micelles are ideal in nature.

Mixtures of alkylpolyglycol ethers $[C_nH_{2n+1}\ O(CH_2CH_2O)_mH]$ where n=12 and m=6 and also n=8 and m=6 showed ideal behavior. This suggests that amphiphiles having small difference in hydrophilic or hydrophobic structures may be considered to form ideal micelles. However, despite the apparent similarity in the mixtures of $C_9H_{19}COOH\ (OCH_2CH_2)CH_3$ and $C_{10}H_{12}COOH\ (OCH_2CH_2)CH_3$ the mixed micelles are nonideal which is due to the polydisperse ethoxylates[138]. The CMC of nonionic mixtures vary with electrolyte composition. The mixture of decylmethylsulfoxide ($C_{10}SO$) and decyldimethyl-phosphine oxide ($C_{10}PO$) was ideal in presence of 1 mM Na_2CO_3 and nonideal in its absence[139]. Aggregation number for mixtures of nonionic detergents showed substantial variation with the micellar composition.

The sodium salts of decyl benzene sulfonate ($3\phi\ C_{11}O$) and dodecyl benzene sulfonate ($4\phi\ C_{12}O$) in presence of 0.17M NaCl at 25°C[140] exhibited an ideality. Mixtures of alkyl sulfonates and that of cetyltrimethylammonium chloride / dodecyltrimethylammonium chloride showed nonideal behavior[141].

Ueno et al.[142] have shown that both sodium taurocholate and taurodeoxycholate with $C_{10}E_8$ formed nonionic rich micelles. The CMC values determined for CTAB with nonyl phenyl ethoxylates (NP-13, NP-20, NP-30) and Brij series were lower than their corresponding pure surfactants[143]. Kenjiro et al.[144] have reported a nonideal mixing behavior for betaine type zwitterionic and anionic surfactants. The same authors[145] have also shown a synergistic behavior in mixed micellar properties of SDS and α,ω, type cationic surfactants in presence of electrolyte. Synergism in binary mixtures of nonionic / cationic surfactant is also reported[146]. Ideal mixing of sugar based nonionic surfactant with anionic surfactant of tail length similar to sodium dodecyl sulfate has also been reported.

Negative deviations in the CMC for cetyl pyridinium chloride - tetradecyl trimethyl ammonium bromide mixtures is reported by Bakshi[147]. For mixtures of nonyl N-methylglucamine with sodium perfluorooctonoate a maximum in CMC is observed with respect to pure components. Non ideality in sodium dodecyl benzene sulfonate with polyoxyethylene octylphenols and tetradecyltrimethyl ammonium bromide was also reported by Graciaa and coworkers[148]. Similar behavior is observed for SDS/C_{12} maltoside. However, C_{12} maltoside / C_{12} betaine mixtures showed an ideal behavior[149].

In case of mixtures of ionic / nonionic amphiphiles the existence of minimum mixture CMC is not a rare occurrence. Ideal mixtures in general do not exhibit a minimum mixture CMC. Based on the average aggregation number of mixed micelles compared to pure components the CMC of the mixture will also be depressed and exhibits a minimum. This was observed for a mixture of decylbenzene sulfonate (3ϕ C_{10}) / nonylphenol ethoxylate (NPE-20) with average of 20 ethylene oxide units[151].

The fractional counterion binding decreases on the addition of nonionic surfactant because of the decrease in the surface charge density[152-156]. Hence, mixtures of anionic-nonionic surfactants are extensively studied. The reduction in the counterion binding is caused due to the shielding of surfactant ions by long polyether chain[157]. It was shown that the binding is different when nonionic surfactant is a dimethylphosphine or a dimethylamine as compared to ethoxylate. Mixing of two surfactant ions of opposite charges results in dramatic depression in the CMC as observed in the case of a mixture of anionic hexadecyl benzene sulfonate ($8\phi C_{16}$) and tetradecyl trimethyl ammonium bromide (TTAB)[158]. Such anionic / cationic interactions clearly produce a nonideal mixed micelle.

1.7 THERMODYNAMICS OF MICELLIZATION

Almost all the physicochemical processes are energetically controlled. One of the most important characteristics of surfactant solutions is the micellization process. Hence, a thorough knowledge of the driving force favouring micellization is highly important. This requires the detailed analysis of dynamics of process (i.e. kinetic aspect) whereby the laws of the thermodynamics may be applied to obtain the standard free energy, enthalpy and entropy of micellization.

Two main approaches to the thermodynamic analysis of micellization process have gained wide acceptance (i) the pseudophase separation model (ii) the mass action model.

Phase separation model considers the micelle as a separate phase at CMC and in case of ionic surfactants the counterions are also included. In 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. For a nonionic surfactant the standard free energy of micellization is given by the equation -

$$\Delta G^\circ_m = RT \ln X_{CMC}$$

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

$$\Delta H^\circ_m = -RT^2 \, d\ln CMC / dT$$

$$\Delta G^\circ_m = \Delta H^\circ_m - T\Delta S^\circ_m$$

In the computation of ΔG°_m for ionic surfactants apart from the transfer of surfactant molecules from aqueous phase to micellar phase the transfer of (1-α) moles of counterions from its standard state to micelle is also to be considered, thus

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

α is the degree of ionization of micelles computed from the ratios of the slopes of the conductance-concentration plot of post micellar region to that of premicellar region[159]. Evans[160] suggested another method for the evaluation of α if aggregation number was known. Treiner and Mayakassi[161] recently evaluated α by taking a constant n value, where n is the aggregation number.

The mass action model assumes that the micelle and the undissociated surfactant ions are in the association - dissociation equilibrium. This model was originally applied to ionic surfactants and later developed for nonionics too.

The standard free energy of micellization per mole of the monomeric surfactants is given by -

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

$$\Delta G^\circ_m = (2-P/n) \, RT \ln X_{CMC} \text{ (for ionics)}$$

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

Also, few researchers have computed the thermodynamics parameters of micellization using the model of Evans and Ninham[160].

$$\Delta G^{\circ}_{m} = RT \ln X_{CMC} = \Delta G^{\circ}_{HP} + \Delta G^{\circ}_{s}$$

where ΔG°_{m} is the total Gibb's energy per surfactant mole associated with micelle formation, ΔG°_{HP} is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to micelle interior. ΔG°_{s} explains the surface contributions that includes the energy associated with electrostatic interactions between the head group and counterions and all other contributions arising from specific contributions.

Thermodynamic micellization parameters for n-alkyl trimethyl ammonium bromides (n=10,12,14) have been thoroughly investigated by Mosquera et al.[21,23]. Also, they have reported various thermodynamic properties of N-octyl trimethyl ammonium bromide in different media.

Moroi et al.[162] have investigated the contributions of hydrophilic and hydrophobic groups to the enthalpy change for four kinds of sodium alkyl sulfates with different chain length of C_8 to C_{14} in the temperature range of 10-55°C. Mukherjee et al.[163] have computed the thermodynamics of micelle formation of sodium perfluorooctanoate. Micellization in various peptide molecules also has been thoroughly investigated[164]. Eisenberg et al.[165] have investigated the thermodynamics of block copolymer micellization in DMF/H_2O mixtures and discussed the various factors affecting the standard thermodynamic functions.

Although the micellization parameters can be evaluated in reasonable detail using phase separation or mass action model, in most cases it systematically underestimates the experimental enthalpies[157]. Os et al.[166] have determined the CMC's and enthalpies of micellization of model alkylarene sulfonate and compared with the phase separation model. Many studies of calorimetric heats of micelle formation of surfactants in water or in aqueous solution have appeared since the pioneering heat of dilution studies by Goddard et al.[167] and heats of solution work by Benjamin[168]. A review of work prior to1979 is that by Stenius et al.[169] which summarizes calculated and calorimetric heats of micelle formation of anionic and cationic surfactants in water.

Olofsson et al.[170] have carried out calorimetric measurements for liquid n-octyltetra oxyethylene glycol monoether C_8E_{10} and Triton X100 as a function of concentration at different temperatures. Enthalpies of solution of monomers at infinite dilution and micelles at the CMC respectively were calculated and enthalpies of micelle formation was derived.

From the CMC of surfactant mixtures, the thermodynamic micellization parameters can be deduced. Moulik et al.[171] have computed the free energy, enthalpy and entropy of micellization for cationic surfactants and mixed states also for sodium * deoxycholate (NaDC) and TX100. Recently, Sato et al.[172] have done the thermodynamic and kinetic study on phase behavior of binary mixtures of POP and PPO forming molecular compound systems. Desnoyers et al.[173] have investigated the effect of geometry on the thermodynamic properties oftrialkylamine oxides in water. ✗ define

Other than the standard thermodynamic parameters ~~on~~ of micelle formation various other parameters like enthalpies of dilution, apparent and partial molar relative enthalpies, heat capacities, volume compressibilities and expansibilities were calculated[174-176].

Ahluwalia et al.[177] have determined calorimetrically the enthalpies of solution of some $C_{10}E_n$ surfactants in monomeric and micellar states in presence of urea. Enthalpy of micelle formation have been determined by microtitration calorimetric study of $C_{12}E_n$ (n=5,6 and 8) by Oloffson[178]. Enthalpies of mixing for three binary systems, SDS water, CTAB-water and TX 100-water have been studied by microcalorimetery[179]. Scamehorn et al.[180] have used Isoperibol calorimetry for the determination of the heat of micelle formation in binary surfactant mixtures. Costas et al.[181] have determined the heat capacity for various alcohol + AOT mixtures. Attwood and coworkers[182] have determined the apparent molar enthalpies by heat conduction calorimetry for aqueous solutions of drug surfactants in presence of electrolytes.

Fiscaro et al.[183,184] have studied the thermodynamics of aqueous solutions of biologically active bisquarternary ammonium chlorides. Verrall and workers[185,186] have investigated the thermodynamic and aggregation behavior of mixed micellar systems of sodium dodecanoate and ethoxylated alcohols. The thermodynamic properties accompanying the micelle formation have been investigated for chlorhexidine digluconoate[171].

De Lisi et al.[187-189] have thoroughly investigated the partial molar volumes, densities, heat capacities osmotic coefficient and enthalpies of dilution for number of surfactant systems. Thermodynamic studies on N,N,N octyl octyldimethyl ammonium chloride in water-urea mixtures is also reported[177]. Roux et al.[190] have investigated the thermodynamics in micellar solutions between PEG-SDS mixtures. Recently De Lisi and coworkers have reported the excess free energy, enthalpy, entropy of binary mixtures of sodium dodecyl sulfate and dodecyl dimethylamine oxide.

Other than the phase separation and mass action model small system thermodynamics was applied to micellar systems by Hill[191]. The distinguishing feature of small systems / multiple equilibrium approach is that it yields expressions that describes the changes of monomer and micelle concentration with total surfactant concentration. This variation in the monomer composition and concentration must be recognized to understand adsorption. Also, this system makes possible the calculation of thermodynamic quantities of single micelle rather than ensemble of micelles.

1.8 ADSORPTION AT INTERFACES

a) Factors Affecting Adsorption :

Amphiphiles tend to accumulate at the air / water and oil / water interfaces. The surface of a liquid is a boundary between two bulk phases namely liquid and air (Fig. 6). The variation of the surface tension γ with composition in case of solutions is one of the most important routes to obtain information about surface concentration.

A relationship rooted in thermodynamics and well known as Gibb's adsorption isotherm was derived in 1878 by J.W.Gibbs[192]. This relation has been cited as one of the pillars of colloid science, comparable to Young-Laplace equation.

The most general form of Gibb's equation can be written as[193] -

$$d\gamma = \Sigma \Gamma_i \, d\mu_i$$

where $d\gamma$ is the change in surface / interfacial tension of the liquid, Γ_i is the surface excess concentration of the ith component i.e. it is the excess per unit area of the surface of the ith 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 upto the imaginary dividing surface. $d\mu_i$ is the change in chemical potential of ith component of the system.

For a two component system at constant temperature

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

1 and 2 are the subscripts referring to solvent and solute respectively. Assuming Γ_1 = 0 i.e. the excess concentration of the solvent (the dividing line can be assumed to meet that condition) and for dilute solution -

$$\Gamma_2 = \frac{-1}{2.303\, RT} \frac{d\gamma}{d \log C} = \frac{-C}{2.303\, RT} \frac{d\gamma}{dC}$$

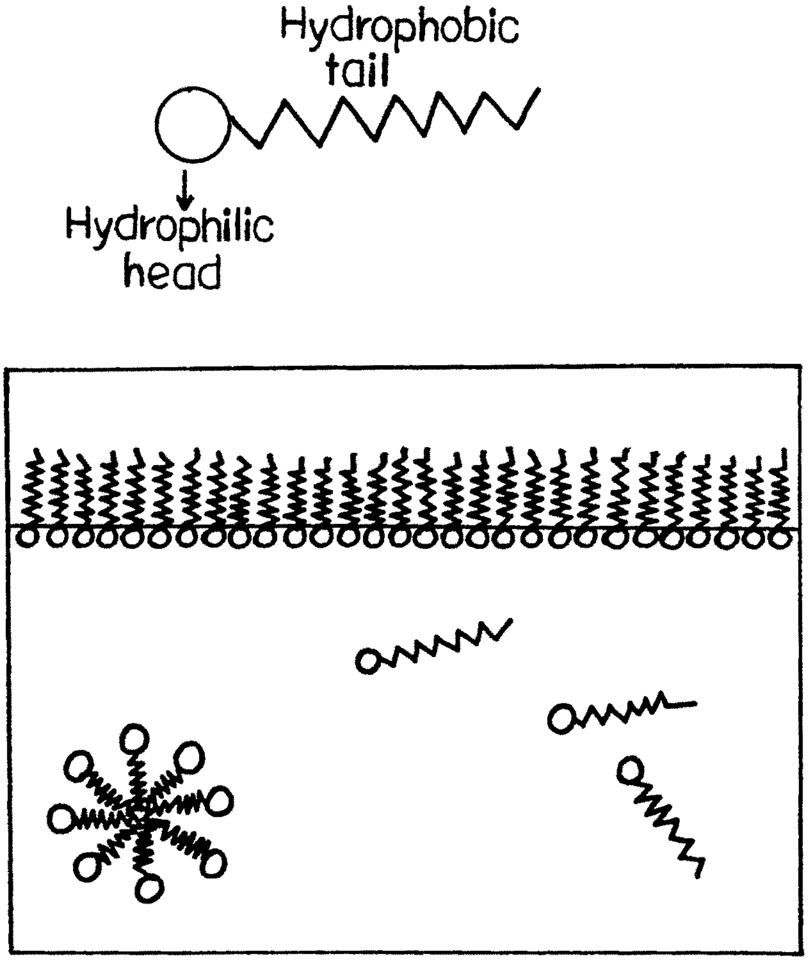


Fig. 6 : Adsorption of surfactants at air / water interface.

where C is the concentration of surfactant.

In case of ionic surfactants in absence of any added electrolyte -

$$\Gamma_2 = \frac{-1}{2\,RT}\,\frac{d\gamma}{d\,\ln C}$$

where γ is in dynes/cm (= erg cm^{-2}), concentration of surfactant in molarity, R in ergs $mol^{-1}\ K^{-1}$ then Γ_2 is expressed in mol cm^{-2}. The slope $d\gamma/d\ln C$ is obtained from the linear portion of the surface tension - log concentration plot. If γ-logC plot is not linear then that indicates that Γ_2 is a function of concentration, which is quite often observed.

From the surface excess the limiting area per molecule of the surfactant at the interface is computer as

$$A = 10^{14}/N\Gamma\ \ nm^2$$

where N is the Avogadro number and Γ is the surface excess concentration in mol cm^{-2}.

The surface excess concentration under the conditions of surface saturation Γ_m is generally used as a measure of the maximum extent of surfactant adsorption. There are many factors that affect the adsorption of surfactant at air / water or liquid / water interfaces. Γ_m depends on the surfactant structure. Increase in the hydrophobic chain length of the surfactants does not monotonically increase the adsorption rather levelling off takes place[194].

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

However, the adsorption of nonionic surfactants is not largely affected. Increase in temperature decreases Γ_m for ionic surfactants and increase in nonionic surfactants[195]. Rosen et al[33]. have reported a decrease in the surface excess concentration as the oxyethylene chain length of nonionic surfactant increases. The evaluation of behavior of fluorinated surfactants at air / water interface has been done by Guittard[196]. Penfold et al.[197] have calculated the surface excess concentrations of n-dodecyl N,N-dimethyl amino acetate at the air / water interface and compared the values obtained from neutron reflection studies. Schott[198] has determined the area per molecule for octoxynol-9 nonionic surfactant. Surface properties of ethoxylated nonionic surfactant was studied by Colin[185].

The surface behavior of surfactant mixtures has been investigated by many authors[199-201]. Sodium dodecyl sulfonate / T X 100 and dodecyl polyoxyethylene sulfate / decylmethyl sulfoxide mixed systems were studied in reasonable detail. Structure of mixed cationic-nonionic surfactant monolayer of hexadecyl trimethyl ammonium bromide and monodecyl hexaethylene glycol at air / water was also studied. Neutron reflectivity has also been used to study the effect of temperature on the adsorption of nonionic surfactant mixtures like polyoxyethylenated alcohols of $C_{12}E_n$ types i.e. $C_{12}EO_3$ / $C_{12}EO_8$[195]. The effect of temperature on the adsorption of dodecane onto nonionic and ionic surfactant monolayers at the air / water interface was reported by Aveyard et al.[202]. They also investigated the mixing of alkanes with surfactant monolyers at the air / water interface. The adsorption of ionic surfactants at the air / water interface of sodium n alkyl sulfate and the influence of sorbitol on the adsorption of ionic surfactants have been studied[203] quite recently. Also, Zhao and Zhu[204(a)] have reviewed single and mixed surfactants adsorption. Ottewill[204(b)] and coworkers have investigated the behavior of ammonium perfluorooctanoate at the air / water interface in presence of salts. The composition of mixed surfactants and cationic polymer / surfactant mixtures adsorbed at the air / water interface was recently reported[205]. Barry et al.[206] have reported the self assembly of nonionic sugar based surfactants at air / water interface.

b) Thermodynamics of Adsorption :

Thermodynamic investigations of adsorption of surfactants can provide atleast two types of important information about the adsorbed films i.e. Gibb's 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[207]. In the following years more detailed thermodynamic studies of adsorption from solutions at the air / water interface have been extended to more systems under different conditions. On the other hand thermodynamic studies have also dealt with the adsorption of surfactant mixtures.

Rosen[33] has shown that standard thermodynamic parameters of adsorption.

$$\Delta G^{\circ}_{ad} = RT \ln CMC - N\Pi_{CMC} A_{CMC}$$

by considering the standard state for the adsorbed surfactant here as a hypothetical monolayer at its minimum area / molecule but at zero surface pressure. The second term in the above equation is the surface work involved in going from zero surface pressure to surface pressure Π_{CMC} at constant minimum surface area / molecule A_{min} ($=A_{CMC}$). The corresponding enthalpy and entropy of adsorption are computed from the well known thermodynamic relations.

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

Recently, thermodynamics of micellization and adsorption of zwitterionic surfactants in aqueous media has been reported. Ismail et al.[208] have investigated the surface and thermodynamics parameters of sodium N-acyl sarcosinate surfactant solution.

Motomura et al.[209] have investigated the thermodynamics of adsorption at interfaces, Bian and Roberts[210] have studied thesurface and thermodynamic properties of Cholines. Manohar et al.[200] have also investigated the micellization and adsorption properties of surfactant mixtures.

Very recently the interfacial and micellization behavior of binary and ternary mixtures of amphiphiles, Triton X100, Tween 80 and CTAB have been reported by Moulik et al.[211]. Also, the properties including the standard free energy of adsorption have been studied for binary mixture of decylammonium chloride and caesium perfulorooctanoate at air / water interface [212,213].

It is well known that mixtures of surfactants often have interfacial properties that are more pronounced than those of their corresponding individual surfactants. Synergism in mixed monolayer has been related to various performance properties such as foaming, wetting, detergency, floatation, separation of minerals. Rosen et al[29]. have applied the regular solution treatment to mixed monolayer formation at air / solution interfaces in which the interaction between the surfactant molecules in the monolayer can be conveniently deduced.

1.9 PERFORMANCE PROPERTIES OF SURFACTANTS

The interfacial and solution behavior of surfactants lead to the following key surface active properties[214] :

(i) emulsification / deemulsification (ii) wetting (iii) foaming (iv)dispersing (v) defoaming (vi) detergency (vii) solubilization.

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

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

Many authors[215-218] have discussed the effect of inorganic salts on ionic surfactants in terms of electrostatic interactions, ionic hydratibility, changes in water structures etc. and have classified ions as water structure breakers or promoters. Some workers have studied the viscosity of concentrated solution of surfactant with inorganic salts as a function of shear rate and obtained some meaningful results[219-221].

Wang[222] has studied the effect of inorganic salts of very high concentration on the viscosity behavior of sodium dodecyl benzene sulfonate. Edward[223] has determined the viscosity of SDBS solution. Manohar et al.[224] have reported the viscoelasticity of quaternary ammonium salt solutions in presence of sodium salicylate. Effect of alcohols, amines and aromatic hydrocarbons that cause structural changes in micellar systems have been extensively reported by Kabir-ud-Din et al.[225].

Viscosity of various transition metal based surfactants in mixed benzene / methanol systems was reported[226]. Miyagishi et al.[227] have studied the effect of salts on the viscosity of fluorocarbon / hydrocarbon mixed surfactants.

The effect of electrostatic charge on the viscous flow has been investigated as the electroviscous effect[228]. Also, aggregation number, volume of the hydrocarbon core, oxyethylene layer of the micelle have been calculated using intrinsic viscosity, as the intrinsic viscosity depends upon the micelles, micelle solvent and micelle-micelle interactions[229-232]. The relationship between the structure of the micelles and its viscosity was correlated to the sharp increase in the viscosity of concentrated surfactant solution to the formation of rod like micelles that forms network in solution. The variation of the second virial coefficient described by Scatchard equation (1946) for micellar systems of SDS and DTAB as a function of added electrolyte was analyzed to various interactions such as micelle-micelle interactions[233].

Changes in the viscosity of aqueous solutions of nonionic surfactant in presence of additives has been investigated[234-235]. Rhodes et al.[236] have reported the effect of oxyethylene chain length on the viscosity. Viscosity studies on mixed surfactants have been thoroughly investigated[237,238] and the relative viscosity of mixed surfactant system with respect to the mole fraction of one of the surfactants are reported.

Foam is produced when air or some other gas is entrapped beneath the surface of liquids that expands to enclose the gas with a film of liquid. Foaming is a property inherent to all surfactant solutions. The theoretical basis of foam has been extensively studied and its physicochemical principles are well documented[239]. Anionics are good foamers and nonionics are poor foamers[240]. Most of the work is reported only in anionics. The foaming power of the detergent solution generally show significant variations with respect to (i) addition of small amounts of additives or electrolytes; (ii) its chemical structure; (iii) the surfactant concentration and temperature.

Although electrolytes do not influence significantly either the foaming power or foam stability of nonionics, they do show significant effect for ionic surfactants[241]. Electrolytes generally destabilize the foam by screening the repulsive forces between the ionic head groups that lead to reduced repulsion between surfactant layers or opposing film interfaces which in turn lead to faster film drainage.

The effect of additives on the CMC of the surfactant is correlated to foam stabilization. Schick and Fowkes[242] have studied the interaction of additives and surfactant and concluded that the effective foam stabilizing additives are those that solubilize in the micelle palisade layer.

The foaming efficiency decreases as the cloud point of the nonionic surfactant is approached. Colin et al.[243] have discussed the reduced foamability of dilute solutions of chemically modified ethoxylated nonionic surfactants. Also, foaming studies have been used to estimate the changes in the composition of surfactant at air / water interface[244]. Foaming power of lauryl alcohol ethoxylates is reported by Domingo[245].

The addition of surfactants to water is a well known method to improve the ability of aqueous solutions to wet and spread over solid surfaces. Janczuk et al.[246] have quite recently studied the wetting efficiency of SDS on cassiterite. Enhancement in the wetting properties of water insoluble surfactants by Draves cotton skin wetting test is reported by Rosen et al.[247]. This test is a commonly used technique for evaluating the textile wetting behavior of surfactants related to dynamic surface tension of the solution.

Addition of polyoxyethylenated nonionics to anionics generally increases the wetting power and decreases when added to a cationic surfactant[248]. Surfactants with a centrally located hydrophilic group are especially good textile wetting agents. Among the isomers of polyoxyethylenated straight chain amines the compounds with two OE groups of approximately equal oxyethylenes attached to nitrogen showed the best wetting property[249].

It was suggested that the solubilization behavior in hard water is an important factor in understanding the behavior of anionic detergents in soil removal. Technical literature indicates that LABS (Linear Alkylbenzene Sulfonates) detergency increases when water hardness decreases with the maximum value of 10^{-6} M Ca^{2+} concentration[250]. Cohen et al.[250] have studied the detergency behavior of LABS in presence of Mg^{2+} ions.

Alcohol sulfates are known to be excellent detergents but very sensitive to water hardness and show less performance at cooler temperature[251]. Peterova et al.[252] have studied the wetting, foaming and detergent efficiency of inclusion complexes of some nonionic surfactants with cyclodextrin. Suri et al.[253] have reported the effectiveness in soil removal for LABS / α olefin sulfonate mixtures. They found that the soil, ash and stain removal efficiency of LABS / AOS (80:20) are superior to pure LABS for all the fabrics studied. A comparative study of conventional and compact detergents is reported by Sanchez et al.[254]. As mentioned earlier, in detergency, the solubilization of soil from fabric into detergent solution is one of the important event. Shah et al.[255] have found from the rate of solubilization of orange OT from cotton into SDS solution that stable micelles are more efficient in detergency.

1.10 APPLICATIONS

In the last two decades surfactants have shown a major impact on all aspects of our daily life, either directly in household detergents and personal care products or indirectly in production and processing of materials surrounding us. Hence, surfactants are among the most versatile product of the industry appearing in such diverse types like mineral extraction and processing, textiles and fibres, agriculture, leather, petrochemicals, food, paints, lacquers and inks, paper and pulp, pharmaceuticals and drug delivery systems. Apart from all these, applications have extended to high technology areas such as electronic printing, magnetic recording, microelectronics, solar energy conversion, biotechnology and viral research.

Surfactants due to their unique amphipathic nature can cause the dissolution of both polar and nonpolar compounds. Therefore, these micellar solutions are also called as "compartmentalized liquids". Due to this they possess the solubilization and dispersion characteristics[235].

One of the reasons for the increasing technological application of surfactants are due to their fundamental properties of adsorption at interfaces and formation of micelles in solution.

The major usage of surfactants is in the detergent industry[256]. In detergency the micelles supply amphiphiles to act on the dirt fabric interface for dislodging the dirt which is finally dispersed in the aqueous medium by the incorporation in the micelle for removal by washing. Surfactants adsorb both on fibres and on soil particulates (Fig. 7). Extensive studies have been done related to soil removal and laundering. Also, the adsorption of mixtures of nonionic and ionic surfactants which is of vital importance in detergency has also been investigated.

The adsorption of various surfactants on minerals has been investigated within the scope of tertiary oil recovery processes[257]. About 50% of the underground oil is recovered by pumping and water as well as stream flooding, the rest 50% remains trapped in the pores and cracks of underground rocks which is difficult to recover. By the flooding of micellar and microemulsion solution in underground rocks, the interfacial tension between oil and aqueous solution can be greatly reduced to decrease the Laplace pressure under the curved oil meniscus in the pores to help mobilize the oil for easy recovery. The technology developed for surfactant enhanced oil recovery was applied to the clean up of JP4 jet fuel spills on air bases[258]. The removal of petroleum films fouling hard surfaces is a common industrial problem.

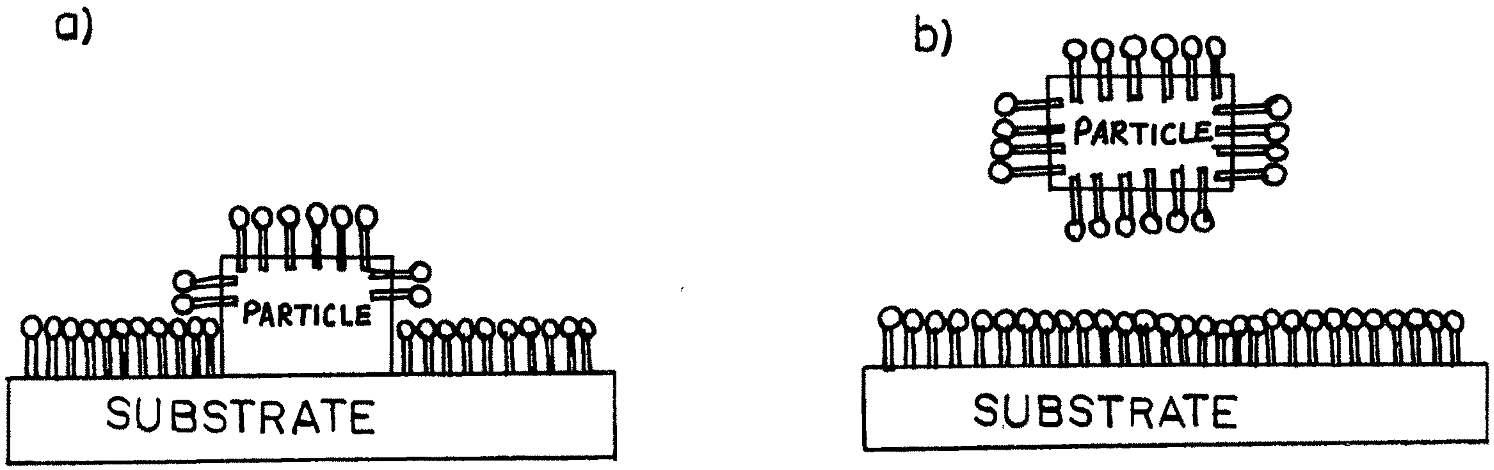


Fig. 7 : Removal of particulate soil in solution (a) no surfactant (b) with surfactant.

This legend is not correct - surfactant is present in a) and b) here!

The Arabian light crude from stainless steel surfaces have been efficiently removed by surfactant[259].

The effects of micellar systems on many photochemical and thermal electron transfer reactions have gained much attention in recent years[260]. Moreover, kinetic treatments have been developed most extensively for reactions in presence of aqueous micelles. Some of the reactions are oxidation of L-ascorbic acid and other related diols, intramolecular base catalyzed hydrolysis of phenyl and methyl salicylates, oxidation of aldehydes, etc. Micellar medium has also been utilized for stereospecific reactions : one enantiomer may be favored over another by virtue of strong orientational effects of polar amphiphilic reactants[261-263].

During the process of manufacturing synthetic fibres, a spin finish is applied to the yarn to control static electricity to ensure proper winding of the yarn on the bobbin and as an aid in further processing. These spin finishes are normally composed of a lubricant, an emulsifier and an antistatic agent, as well as some other components that may be included to impart special characteristics to the finish[264]. Surfactants have found wide application also in fire extinguishers, corrosion inhibitors, water leak preventors for roofs and walls.

The remediation of metal / organic contaminated soils by combined acid extraction and surfactant washing is one of the recent applications. Enhanced recovery of the explosive hexahydro 1,3,5-trinitro-1,3,5-triazine (RDX) and residual tetrachloroethylene and other nuclear wastes from soil was effectively done by the use of surfactant[265]. Pollutants can be solubilized by the micelles for which both organic and inorganic pollutants are highly amenable to such conditions. The scavenging of superoxide ion released by cultured macrophages was effective in micellar medium[266].

Both emulsion liquid membrane (ELM) as well as surfactant liquid membranes (SLM) have shown significant advantages over solvent extraction in the removal of rare earths from soil and nuclear wastes including Pu (IV), Cs, U, lithium and recovery of phenols, p-cresols, p-chlorophenols etc. By this in nuclear industry, during contamination of protective wears and contaminated materials, detergents are employed to bring down the level of raidoactive contamination within safe limits[267-269]. Multivalent cations have also been removed by micellar enhanced ultrafiltration method[270].

A variety of surfactants are utilized in the industry in order to achieve the desired dispersion - flocculation of particulate suspensions, concentrated emulsions and dispersions. Silicone surfactants for water borne coatings have shown to be stable under conditions commonly encountered with such formulations. The screen printing precision like printing pattern and printing line width is influenced by the rheology of inks controlled with surfactants. Also emulsion explosives is one such application wherein a large volume of an oxidiser solution is dispersed in a small volume of a hydrocarbon fuel[271,272].

Surfactants play a major role in agrochemicals both in formulation and optimization of biological efficacy[273]. Since, surfactants lower the surface tension of water one would expect that their presence in the spray solution would result in the formation of smaller droplets. The presence of micelles and microemulsions have significant effects on biological efficacy of insoluble pesticide. Also, the adsorption of surfactant can aid wetting of particles or agglomerates.

In the manufacture of NH_4NO_3-TNT fuel oil explosives, NH_4NO_3 was treated with different surfactants to prevent particle seggregation[274].

Some workers have found the application of surfactant[275,276] in solar energy conversion and in field of semiconductors. Thionine, EDTA and Triton X100 were used as photosensitizer, reductant and surfactant in a photogalvanic cell for solar energy conversion. Similarly also Azure B glucose and SDS, TTAB and Brij 35 have been used in photo galvanic cell. Nonaqueous light metal batteries containing polyethylene glycol type nonionic surfactant in their electrolytes or cathodes have shown improved charge / discharge efficiency.

The preparation of ultrafine monodisperse particles of colloidal dimensions is of great need in heterogeneous catalysis, magnetic tapes, biomedical applications. These were conveniently prepared in compartmentalized (reverse micellar) media, thus microfine particles or nanoparticles of desired sizes could be obtained[277].

Apart from above applications, surfactants are widely found in cosmetic and pharmacological formulations. One such application is in intravenous injections. Micellar vesicles are used in targeting tumours in humans. The patients who are given i.v. injections of radiolabelled micellar particle showed tumour image without developing symptoms related to micellar particles[278]. Also, a new synthesized sugar based surfactant possessing biological activity against HIV and *Aspergillus fumigatus*, a yeast responsible for opportunistic infections in AIDS patients[279].

1.11 SCOPE OF THE PRESENT WORK

Surfactants are often used in colloidal chemistry because of its amphiphilic nature. As mentioned earlier, they find importance in numerous applications / technologies. Understanding the behavior of surfactant systems is very important factor from both theoretical and practical interest.

In the last few decades, inspite of the growing interest in the additive - surfactant - water ternary systems, mostly the studies are on only pure ionic or nonionic surfactants and to a lesser extent on mixed surfactant system. Most of the technological applications of surfactants involve mixtures, either because they deliberately mix in order to optimize their performance or because commercial surfactants contain mixtures of different alkyl chain lengths and isomeric forms. Until relatively recently the quantitative aspects of the science of surfactant mixing was not a topic of research.

It has also been recognized that the partition coefficient of neutral solutes in micellar solutions can be computed with reasonable confidence from CMC determinations. Also, the CMC based methods could be of great value in the evaluation of the effect of structure on the micellar solubilization of neutral additives[280]. Because of the increasingly, widespread uses of such systems in modern applications, we studied the effect of various neutral additives like PEG 400, sucrose and urea on ionic, nonionic and mixed surfactant system.

The additives were chosen keeping in mind their wide range of properties. Polyethylene glycol (PEG 400), a short chain water soluble oligomer used extensively in preparation of cosmetics and pharmaceuticals. Sucrose, is nonionic by itself and highly hydrophilic, acetamide having the -CONH linkage and polar in nature and urea a strong protein denaturant and effective modifier of various aqueous solution properties.

In the first chapter of the thesis, a thorough review of literature on single and mixed surfactants are presented, including the scope of the present work. The methods and materials with experimental techniques are presented in chapter two.

In the third chapter of the thesis, we have reported the effect of these additives on the interfacial and micellar properties of Myrj 45, SDBS, $C_{12}E_{10}$ and SDBS/$C_{12}E_{10}$ mixed system. The thermodynamic characterization of water-additive-surfactant ternary system was done using temperature dependence ~~on~~ of the critical micelle concentration (CMC).

With the knowledge of the interfacial and solution properties of surfactants a number of key performance properties could be well understood. Hence, in the fourth chapter of the thesis various performance properties such as foaming, wetting, viscosity and detergency were studied for different systems and the role of these additives on its properties.

In the last chapter of the thesis, a summary of the conclusions derived from our studies are reported.