CHAPTER - 1

INTRODUCTION

1.1 General Introduction
1.2 Water-Soluble Polymers
1.3 Surfactants
    Classification
    Factors Affecting Micellization
    Performance Properties
1.4 Polymer-Surfactant Interactions
    Factors Affecting Polymer-Surfactant Interactions
1.5 Models and Various Proposed Theories
1.6 Experimental Evidences of Polymer-Surfactant Interactions
1.7 Thermodynamic Parameters
1.8 Surface Activity
    Thermodynamics of Adsorption
    Interfacial Properties
1.9 Applications
1.10 Scope of the Present Work

1.1 General Introduction

At the beginning of this century, the concept of colloidal dispersions was very new. During the same time Wolfgang Ostwald coined the picturesque phrase[1], 'the land of neglected dimensions' to describe the range of sizes for colloidal particles. Colloidal dispersions play a pivotal role in our everyday lives; and it is simply a fact that colloids constitute the most universal and commonest of all things we know. Colloid science enjoys a prominent position in modern day technology and yet the scientific efforts expended over the years have not been commensurate with their technological importance. The world of colloidal science wraps up two very important components - the world of 'polymers' and 'surfactants', without which it would be difficult to imagine modern day living. Polymer-surfactant interactions are in fact manifestations of lipid-protein systems which biological membranes constitute of[2].

Polymers are large molecules built up by repetition of small chemical units. Both synthetic and biological polymers are usually found. Biological polymers form the very foundation of life and intelligence and provide much of the food on which man exists. The world of synthetic polymers which was unknown some fifty years ago have become truly indispensable to mankind today being essential to his food, clothing, shelter and transportation as well as for the conveniences of modern living.

Surfactants are ubiquitous in man's multiferous needs. Surfactant is an abbreviation of **surface active agent** which literally means 'active at the surface'. Their unique amphipathic nature has made them useful in many ways.

Applications of polymers and surfactants together are legion and their properties together, inter alia, are of great importance. Frequently they occur together in colloidal systems to achieve colloidal stability, emulsification or flocculation, structuring property, as well as rheology control[3]. Interest in properties of polymers and surfactants in aqueous solutions is quite old. The formation and existence of lipoprotein aggregates in biological fluids was recognized in the early part of the

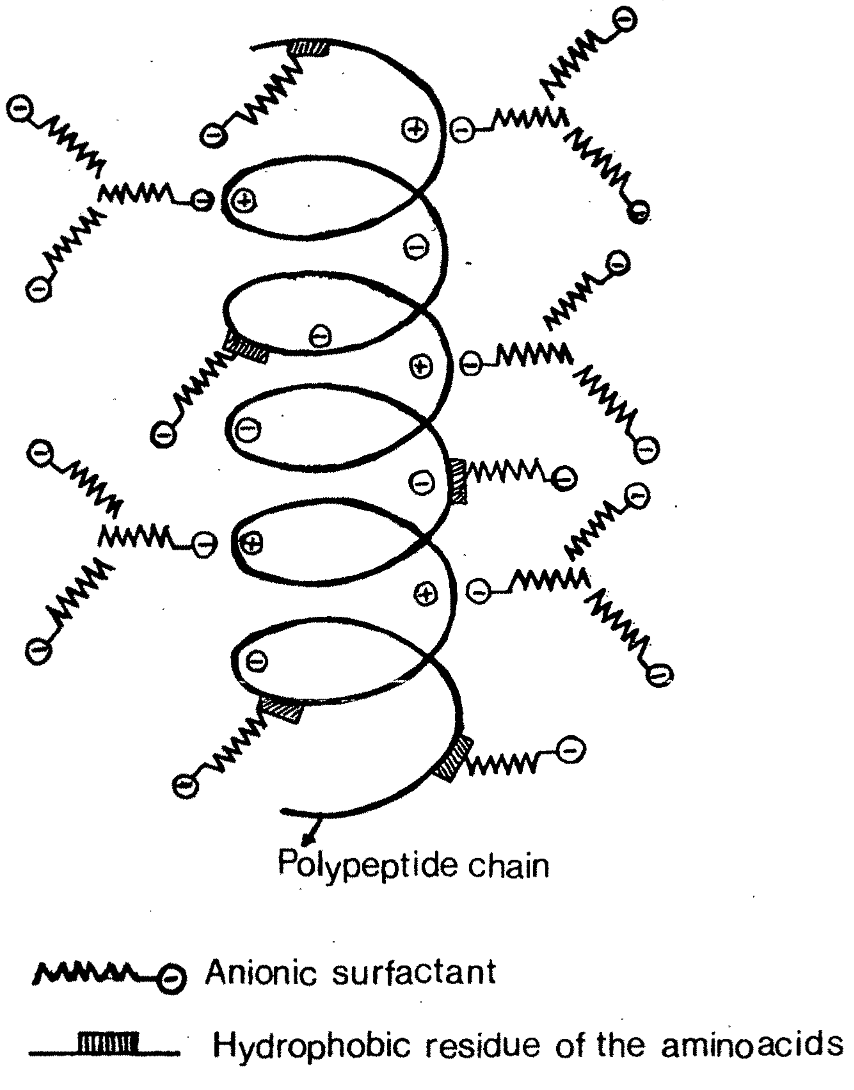


Fig. 1 : A diagrammatic representation of modes of binding of an anionic surfactant to a protein (Ref. 266).

century[4]. Interactions between surfactants and proteins lead to solubilization of insoluble membranes and lead to changes in biological activity of the enzyme systems[5]. The binding of anionic surfactant to a protein molecule is represented in Fig. 1. The foundation of present day's work was laid nearly fifty years ago with Saito's pioneering article[6] which marked the beginning of modern day research in this field. Extensive research has been carried out in this area on the complexation phenomena between polymers and surfactants. Present day fundamental studies are aimed at elucidating the detailed aspects of structure and composition of polymer-surfactant aggregates and the mechanism of association phenomena.

1.2 Water-Soluble Polymers

Polymers are large molecules in which many small units (repeat units) are linked together. Molecular weight of these polymers range from 20,000 and up depending upon their type and structure. The majority of polymers are organic chemicals - mainly based on carbon and hydrogen. The vast majority of polymers used today are plastics, rubber, adhesives and are made from chemicals derived from oil[7]. Properties of a polymer depend on chemical structure and composition. Among the various types of polymers available today is a class of polymers called 'water-soluble' polymers; also known as 'hydrophilic polymers'.

There is no precise definition of 'hydrophilic' or 'water-soluble' polymers except for the functional statement[8] that "water-soluble polymers are those polymers which dissolve in or are swollen by water". They can be divided into three main groups :

- Natural polymers, most of them based on carbohydrates or proteins, usually of complex chemical structure.
- Semisynthetic polymers, mainly based on celluloses which reacts with functional polymers of semisynthetic origin.
- Synthetic polymers, prepared by polymerization of monomers of petrochemical origin.

Applications of water-soluble industrial polymers are diverse. Over two hundred important applications have been identified. Fig. 2 gives a schematic representation of their varied uses.

Estimates of use of water-soluble polymers are difficult to establish. The natural water soluble polymers are used in food, drugs etc. Among the synthetic water-soluble polymers, the most extensively used ones are polyvinyl alcohol, polyacrylamide, polyacrylic acid and their derivatives[9].

In the present studies; water-soluble polyacrylamide, polyacrylic acid and the copolymers of acrylamide and acrylic acid are used in different monomer feed ratios. Copolymers are polymer chains which consist of two types of repeat units[10]. Homopolymers generally have a single repeat unit. The properties of copolymers depend upon the nature of constituent units and their relative amounts in the chain. There are four types of arrangement in principle[11] : block, graft, random and alternating copolymers. Random copolymers tend to be amorphous especially if both units are present in significant amount. This is because the random nature of the chains do not allow regular arrangement of polymer chains in crystalline structure.

In case of an alternating copolymer the structure will be -
A B A B A B A B A B A B A B
whereas a random copolymer will have a structure of -
A B A A B B B A A B A B A A B B A   or similar structures
where A and B are repeat units.

The properties of copolymers also are intermediate to those of the corresponding homopolymers e.g. the glass transition temperature of a random copolymer lies in between the glass transition temperatures of the homopolymers made from constituent repeat units.

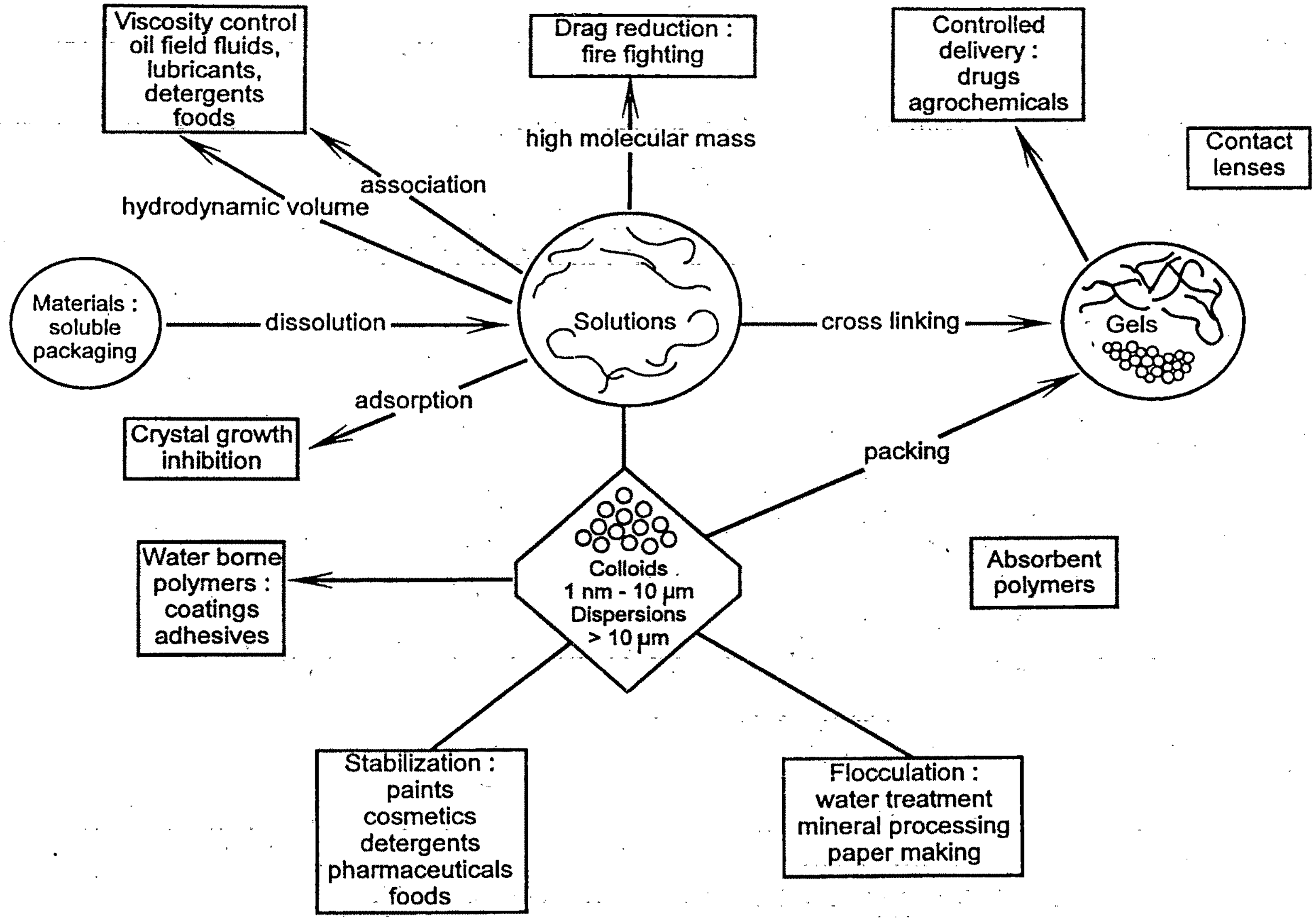


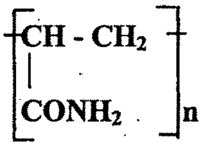
Fig 2 : SOME IMPORTANT PROPERTIES AND APPLICATIONS OF WATER SOLUBLE POLYMERS

A convenient equation to estimate copolymer glass transition temperature Tg is[12]

$$\frac{1}{Tg} = \frac{W_a}{Tg_a} + \frac{W_b}{Tg_b}$$

where W_a and W_b are weight fractions of two units of copolymer chains and Tg_a and Tg_b are the glass transition temperatures of the respective homopolymers.

Acrylamide $CH_2 = CHCONH_2$, the monomer for polyacrylamide, when pure, is a white crystalline powder of moderate toxicity which can be polymerized in aqueous solution to yield polymers of high molecular weight



$$\left[\begin{array}{l} CH-CH_2 \\ | \\ CONH_2 \end{array}\right]_n$$

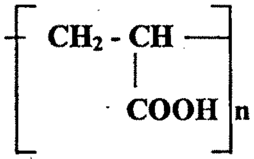
Pure polyacrylamide is relatively inert, but can be converted by hydrolysis of some of the amide groups into the acid form. The most common comonomers are[13] :

Weak acids [acrylic acid and methacrylic acid]

Strong acids [vinyl sulphonic acids]

Bases [dimethyl aminoethyl methacrylate, diallyl dimethylammonium chloride and their quartenary salts]

Acrylic acid ($CH_2 = CH\text{-}COOH$) at room temperature is a colorless liquid with sharp penetrating odors of acetic acid. At low temperatures they freeze to colorless prismatic crystals. Acrylic acid too can be polymerized in aqueous medium to yield high molecular weight polymers of the form



$$\left[\begin{array}{r} CH_2-CH \\ | \\ COOH \end{array}\right]_n$$

Polyacrylic acid as well as the copolymers of acrylamide and acrylic acid behave like polyelectrolytes. The term polyelectrolyte refers to a substance that contains polyions which are macromolecules bearing a large number of ionizable groups[14]. To preserve the electroneutrality of a polyelectrolyte, the polyion charges must be compensated by counterions typically ions of low atomic weight such as H^+ or Na^+. Unlike uncharged polymers, polyelectrolytes are soluble in polar solvents. The viscosity behaviour of polyelectrolytes show an unique dependence on concentration[15]. In ionizing solvents such as water, the reduced specific viscosity may first rise rather than decrease with dilution, pass through a maximum and then decrease at very low concentrations. Addition of a salt restores conformity with the Huggins equation[16]. Generally, when aqueous solutions of polyacids are neutralized, the molecules expand and viscosity greatly increases.

1.3 Surfactants

Surfactants or surface active agents as the name indicates are the substances that adsorb at interfaces even at low concentrations[17]. The main constituents of surfactants are the hydrocarbon portion - a non polar group and a ionic or polar group. The polar or ionic portion of the molecule, usually termed the head group interacts strongly with water via dipole-dipole or ion-dipole interactions. Consequently, the head group is said to be hydrophilic. The balance between the hydrophilic and hydrophobic properties of the molecule gives special properties which we associate with surface active agents. The existence in the same molecule of two moieties, one of which has affinity for solvent and other which is antipathic to it, is termed as being amphoteric. Such characteristics are responsible for the phenomenon of surface activity, micellization and solubilization[18]. These materials are often called by other names which include association colloids, colloidal electrolytes, amphipathic compounds, tensides etc. They can be classified in the following manner :

(a) Classification :

Depending on the charge on the polar head group and its molecular structure they can be classified as follows :

Ionic Surfactants :

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

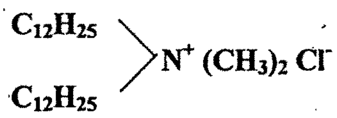
Sodium dodecyl sulfate (SDS) $C_{12}H_{25}SO_4\ Na^+$

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

- **Cationics** : The surface active portion bears a positive charge e.g.

Cetyl trimethyl ammonium bromide (CTAB) $C_{16}H_{33}\,N^+\,(CH_3)_3\,Br^-$

Didodecyldimethyl ammonium chloride



Nonionic Surfactants : The surface active portion bears no apparent charge e.g.

Dodecyl hexaethylene glycol monoether ($C_{12}E_6$)

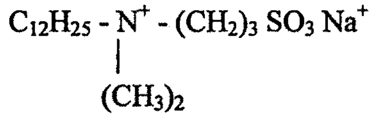
$\mathbf{C_{12}H_{25}\,(OCH_2CH_2)_6\text{-}OH}$

Brij 35 $\mathbf{CH_3\,(CH_2)_{11}\,(OCH_2CH_2)_{23}OH}$

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

3-dimethyl dodecylpropane sulphonate

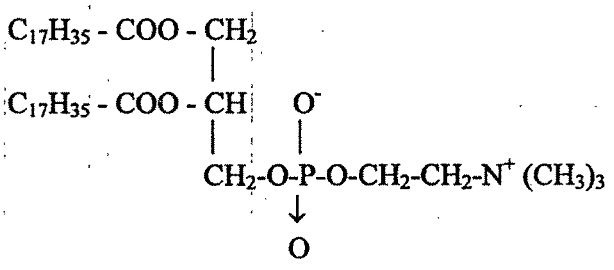
Betaines.



$$C_{12}H_{25} - \underset{\displaystyle (CH_3)_2}{\underset{|}{N^+}} - (CH_2)_3\,SO_3\,Na^+$$

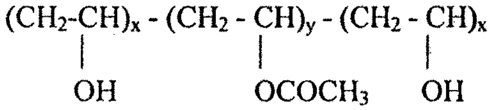
3-dimethyl dodecylpropane sulfonate

Lecithin, a triglyceride



Polymeric Surfactants :

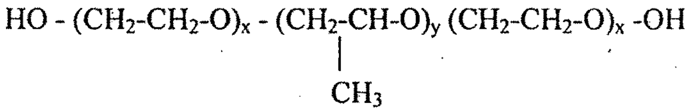
Partially hydrolyzed poly(vinyl acetate)



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

Block polymers called pluronics

PEO - PPO - PEO

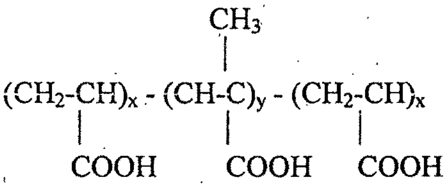


$$HO - (CH_2\text{-}CH_2\text{-}O)_x - (CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}O)_y\ (CH_2\text{-}CH_2\text{-}O)_x\ \text{-}OH$$

Polyelectrolytes :

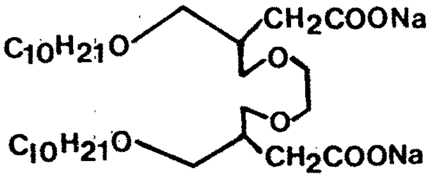
Ligno sulphonates : anionic polyelectrolytes prepared by sulfonation of wood lignin.

Polyacrylic acid and polyacrylic / polymethacrylic acid.

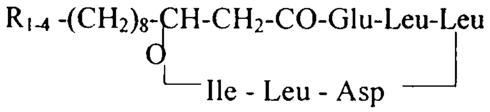


$$(CH_2\text{-}\underset{\underset{COOH}{|}}{CH})_x - (CH\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}})_y - (CH_2\text{-}\underset{\underset{COOH}{|}}{CH})_x$$

Gemini Surfactants : Two amphiphilic molecules connected together by a small hydrophobic chain.



Bio Surfactants : A biosurfactant is defined as a surface active molecule produced by living cells - in the majority of cases, by microorganisms.



$$\mathrm{R_{1\text{-}4}\text{-}(CH_2)_8\text{-}\underset{\underset{\text{Ile - Leu - Asp}}{|}}{\underset{O}{CH}}\text{-}CH_2\text{-}CO\text{-}Glu\text{-}Leu\text{-}Leu}$$

Glu-Glutamic acid, Leu-Lucine
Asp - Aspartic acid; Ile - Isoleucine

$R_1 = (CH_3)_2\text{-}CH$

$R_2 = CH_3\text{-}CH_2\text{-}CH_2$
$R3 = (CH_3)_2\text{-}CH\text{-}CH_2$
$R_4 = (CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}$

Micelles :

Surfactant molecules in solution above a certain concentration will form ordered agglomerates known as micelles. The formation of micelles was originally suggested by McBain[19]. He suggested that below a certain concentration most of the surfactant molecules are unassociated whereas, in the isotropic solutions immediately above that concentration, micelles and monomer surfactant molecules coexist. This concentration - the critical micelle concentration (cmc) is due to two opposing forces of interactions between the surfactant molecules[20]. The polar groups in water, if ionic, will repel one another due to mutual charge repulsion. The larger is this charge the greater is the repulsion and less the tendency to form micelles. The hydrophilic groups also have a strong affinity for water and there will be tendency for them to be spaced out to allow as much water as possible to solvate the hydrophilic group. Another force, the hydrophobic force, comes into play when the hydrophobic groups try to come near each other. This is due to enthalpy - entropy changes when an alkyl group is transferred from a hydrocarbon environment to an aqueous environment, when the molecules are far apart both the forces are weak. When the concentration increases i.e. the surfactant molecules are more in contact with each other, the two interactions - hydrophobic and hydrophilic will increase. If the hydrophobic force is greater than the hydrophilic one, then the molecules will aggregate together at very low concentrations. The cmc depends on the relative strengths of these hydrophobic and hydrophilic effects[21]. There is an abrupt change in the physical properties above this critical concentration[22]. These physical properties include equivalent conductivity, turbidity, surface tension, osmotic pressure, magnetic resonance, solubilization and microviscosity etc. Each surfactant has a characteristic cmc value at a given temperature.

Factors Affecting Critical Micelle Concentration :

Among the factors that affect the cmc of a surfactant in aqueous solution are : structure of surfactant[23-25]; presence of an added electrolyte[26]; presence of an additive[27]; effect of temperature[28]; effect of pressure[29].

Surfactant Structure :

In aqueous medium, the cmc decrease as the number of carbon atoms in the hydrophobic tail increases to about 16[30]. In general, for ionic surfactants the cmc is halved by the addition of one methylene group to a straight chain hydrophobic group attached to a single terminal hydrophilic group. But for nonionics and zwitterionics the magnitude of decrease of cmc values is much larger. An increase in two methylene units reduces cmc to one tenth its previous value. In case of ionic surfactants with chains of greater length than 16, the effect on cmc is limited as coiling of these long chains occur in water[31]. Introduction of polar groups such as -OH in the hydrophobic chain increases the cmc. In general ionic surfactants have slightly higher cmc values compared to zwitterionics which is again higher than nonionics for the same number of carbon atoms. In case of polyoxyethylene nonionics of the type C_nE_8 (n = 9-15) as the number of carbon atoms increases the cmc decrease[32]. Rosen[33] et al. have reported the cmc values of $C_{12}E_m$ (m = 1-8) showing that the cmc increases with increasing hydrophilicity in the molecule. The counterions associated with an ionic amphiphile have a pronounced effect on micellar properties. In conventional ionic surfactants, a change in counterion to one of greater polarizability or valence leads to a decrease in cmc. Supelveda[34] et al. have reported the cmc values of hexadecyl and tetradecyl trimethyl ammonium micelles with various counterions.

Effect of Additives :

The presence of an additional component in the surfactant solutions alters the micellization process to a great extent. Addition of an electrolyte modifies the micellization process in two ways (i) through specific interactions with the surfactant molecules; (b) by changing the solvent nature. The addition of an electrolyte is more pronounced in case of ionic surfactants. An electrolyte causes reduction in the thickness of the ionic atmosphere surrounding the polar head group which consequently decreases the ionic repulsions between them and thereby decreasing the cmc. Extensive studies on this effect has been done by Mukerjee[35] et al. The effect of an added electrolyte on micellar size of sodium dodecyl sulphate (SDS) in presence of NaCl has been extensively investigated by a variety of techniques[36-37] viz. quasi elastic light scattering, classical light scattering etc. Somasundaran[38] et al. have reported the cmc values of SDS in presence of various electrolytes like LiCl, NaCl, Na_2SO_4, Cs_2SO_4, $MgSO_4$. On addition of an electrolyte increase in aggregation number (N_{agg}) and consequent decrease in cmc occurs[39]. Such studies on the effect of alkali metal salts and quarternary ammonium salts on the cmc of SDS has also been done[40]. Lowering of cmc of polyoxyethylenated nonionic surfactants is observed on addition of an electrolyte, though the magnitude of lowering is not very significant[41,42]. Blankschtein[43] and others have studied the effect of LiCl, NaCl, KCl to aqueous solutions containing alkyl poly(ethylene oxide) ethers C_nE_m type of nonionic surfactants.

Other organic additives, also modify the cmc of surfactants to a great extent. They cause changes in the water structure, dielectric constant and also the solubility parameters[44]. A number of workers[45-49] have studied the effect of various linear alcohols on anionic, cationic, as well as nonionic surfactant solution properties. The effect of additives like PEG and sucrose on the cmc of nonionic surfactants have been studied in detail[50-53].

Effect of Temperature :

The effect of temperature on the cmc of ionic and nonionic surfactant systems is generally attributed to solubility - temperature relationship. For ionic surfactants the cmc - temperature relationship shows a minimum. The cmc decreases with increasing temperature, passes through a minimum at 20-30°C and then increases. The decrease in cmc at lower temperature region can be ascribed to the lowering of hydrophilicity, while further temperature increase causes disruption of the water structure around the hydrophobic group which opposes micellization, hence higher cmc[54,55]. In case of nonionics a temperature increase causes decrease in cmc values. However, for some systems a minimum is observed at relatively higher temperatures e.g. octylphenoxyethoxyethanol with oxyethylene chain lengths between 6-10 show a minimum at approximately 50°C[56]. The lowering of cmc with increasing temperature is predominantly due to the dehydration of the ethylene oxide segments at higher temperatures. Many factors contribute to the temperature effect on nonionic surfactants e.g. (i) the change in water structure around the ethyleneoxide segments; (ii) change in hydrogen bonding networks around the EO group; (iii) changes in conformation of the EO group[57,58]. Not much literature is however, available on the temperature effect on Zwitterionics. There appears a steady decrease in cmc of alkyl betaines with increase in temperature in the range of 6-60°C[58].

Effect of Pressure :

For ionic surfactants the cmc values increase with increase in pressure upto a certain threshold value followed by a decrease at higher pressures. Such behaviour is attributed to a pressure induced increase in dielectric constant of water, and other aspects related to the water structure[59].

For nonionics a pronounced increase in cmc is observed at lower pressure and with further increase in pressure the cmc values remain almost constant. Mesa et al.[60] have discussed the effect of cmc and applied pressure using an experimental data fit. Nishikido et al.[61] have discussed the effect of pressure on $C_{12}E_6$ micellization. Various factors determine the structure, shape, size and cmc which are the inherent properties of a micelle.

Structure and Shape of Micelles :

The shape of micelle produced in aqueous media is of great importance in determining various properties of surfactant solution. Viscosity, the capacity to solubilize water insoluble materials, cloud point and other properties depend on the structure and shape of micelles.

Adam[62] and Hartley[63] were the first ones to put forward a model of a spherical micelle. The spherical micelles have the following properties[64];

- The association unit is spherical with radius approximately equal to the length of hydrocarbon chain.
- There are 50-100 monomers in the micelle and the number increases as the hydrocarbon chain length increases.
- The counterions are bound to the micelles of ionic surfactant thus reducing its mobility compared to the nonionics.
- Due to higher association number of surfactant micelles, micellization occurs over a narrow range of concentration.
- The micelle interior has essentially the properties of liquid hydrocarbon as a result of which it solubilizes oily substances.

Apart from spherical micelles, other shapes of micelles have also been proposed[65,66] e.g. (i) relatively small spherical structures; (ii) elongated cylindrical rod-like micelles (prolate ellipsoids); (iii) large flat lamellar micelles (oblate spheroids). The surfactants, also aggregate in the form of bilayers called vesicles. Different shapes of micelle are given in Fig. 3. The shape of micelle is concentration dependent, it is sensitive to the chain length of the hydrophobic group, temperature and in case of

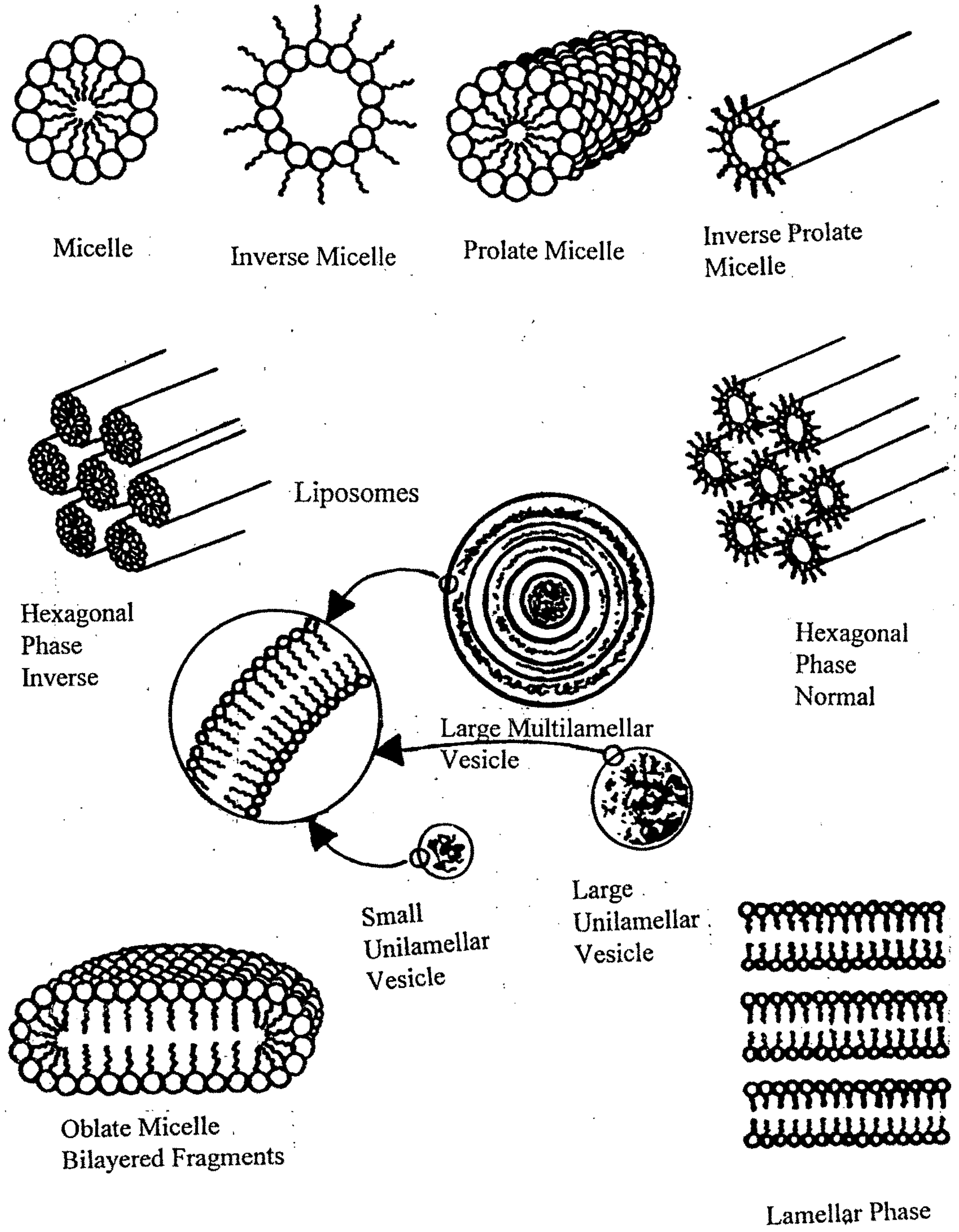


Fig. 3 : Schematic representation of various types of liposomes and lyotropic particles. Micelles, liposomes of different morphologies and liquid crystalline phases generally exists (Ref. 243).

ionic surfactants - the ionic strength of the solution. The micelles can take lamellar or planar structure when the effective areas of hydrophilic group and hydrophobic groups are nearly equal[67]. In addition, they become practically insoluble in water, though still dispersible.

Many workers have shown the changes in shapes of micelle with addition of electrolyte. Ikeda et al.[66] reported change in shape of SDS micelles from spherical to rod like in presence of increasing sodium chloride concentration. Many researchers[68-70] have worked on the theory of micellar structure, based on geometry of various micellar shapes and space occupied by hydrophilic and hydrophobic groups of surfactant molecules. The packing parameter $V_H / l_c a_o$ gives an idea of the shape of the micelle. V_H, l_c and a_o are the volume occupied by the hydrophobic group in the micelle core i.e. $V_H = 27.4 + 26.9\ n_c$ 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_o the core of cross section occupied by the hydrophilic group at micelle-solvent interface.

The nature of micelle formed depends on the solvent also[71]. In aqueous medium, the orientation of surfactant molecules is such that the polar groups are towards the solvent and the hydrocarbon chains are away from water, forming a part of micellar interior. Such micelles are termed as 'normal micelles'. In a non-polar medium, the polar groups form a part of micellar interior and hydrophobic groups in contact with the solvent. Such micelles are termed as 'reverse micelles'.

Performance Properties of Surfactants :

Surfactants have other properties, apart from micellization and adsorption at the interfaces. Due to these properties, surfactants are very versatile and are put to use in formulations in the end use domain[72] :

(i) emulsification / deemulsification; (ii) solubilization; (iii) dispersion; (iv) wetting; (v) detergency; (vi) foaming.

i) **Emulsification** :

The formation of emulsions from two immiscible liquid phases is probably one of the most useful property of surface active agents. An emulsion can be defined as a significantly stable suspension of particles of liquid of a certain size within a second immiscible liquid. At present the major types of emulsion that have been identified are[73] :

Microemulsions are transparent dispersions with particles < 100 nm in size that have been widely studied.

Miniemulsions are bluish white in color with particle sizes between 100 and 400 nm.

Macroemulsions are opaque emulsions with particle size greater than 400 nm. Paints, polishes, ice creams are some of the examples of emulsions.

ii) **Solubilization** :

Organic substances that are nearly insoluble in water may be dissolved in aqueous solutions of surfactants upto a certain level. Solubilization may be defined as the spontaneous dissolving of a substance (solid, liquid or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution. Solubilization in aqueous media is of major importance in such areas as the formulation of products containing water insoluble ingredients where it can replace the use of organic solvents or cosolvents, in detergency where solubilization is a major mechanism in removal of oil; micellar catalysis in organic reactions; emulsion polymerization. The solubilization of materials in biological systems gives information of the interaction of drugs and other pharmaceutical materials with lipid bilayers and membranes[74].

iii) **Dispersion** :

The suspension of solid particles in a liquid media, particularly water is an important technological process. Surfactants help in preparing suspensions of the right particle size and are stable on storage for a long period. In dispersion process, surfactants lower the interfacial tension and facilitate formation of new interfaces. For the stability of these particles in solution attractive forces are countered by repulsive forces, known as London forces[75]. The best known theory explaining the stabilization is the DLVO[76,77] theory which covers only lyophobic dispersions.

This theory takes into account vander Waals attractive forces and electrostatic repulsions of similarly charged particles. The particles will be stable and not coagulate if net repulsions, due to electrostatic forces are there. The influence of surfactant is that adsorption of the lyophobic tail on the solid causes a solid to acquire a charge which will repel similarly charged particles by increasing electrostatic forces. The adsorbed surfactant then produces an electrostatic barrier to prevent reaggregation of particles. The type of surfactant that will give maximum dispersing capacity will depend on the nature of solid to be dispersed. The adsorption is due to vander Waals interactions between the hydrophobic groups and the solid surface. The EO/PO type block copolymers are very good dispersing agents. A more complex approach exists in case of lyophilic solids. They acquire charge when dispersed in water. If surfactants of opposite charges are used then very high concentrations have to be used to stabilize the particles. Polymeric surfactants are increasingly being used for such purposes. They can adsorb yet give electrical barrier on opposing charged particles and give a steric barrier to coalescence.

iv) **Wetting** :

The term 'wetting' is generally used for displacement of air from a liquid or solid surface by a liquid or liquid solution. Water is a very important liquid for this purpose. This process involves surfaces or interfaces and the modification of wetting power of water is possible by the addition of surface active agents. Factors which affect the wetting properties are[78] temperature, addition of an electrolyte, cosurfactants, the nature of the hydrophilic and hydrophobic groups. Increase in temperature reduces the wetting power due to better solubility and reduced adsorption. Depending on the nature of the electrolyte (if organic) the surface tension is lowered and better wetting property is observed. Also the wetting characteristics depend upon addition of cosurfactants[79], the hydrophobic chain length[80], nature of hydrophilic group (ester, amide, EO), the EO content of ethoxylated nonionics, pH and nature of the substrate. In other words, the effect of surfactant on the solid / liquid interface depends on nature of charges on the solid, the surfactant ions and the mechanism of adsorption.

v) **Foaming** :

Foams consist of a thermodynamically unstable two phase systems of gas bubbles in a liquid. Foam has more or less stable honey comb structures of gas cells whose walls consist of thin liquid films with approximately plane parallel sides. The two sided films are called the lamellae of the foam. Foam volume formed increases with increase in surfactant concentration upto cmc and above cmc the amount of foam remains relatively constant. Anionics are good foamers and nonionics have poor foam producing capacity[81]. The effectiveness of a surfactant as a foaming agent appears to depend on both its effectiveness in reducing the surface tension of the foaming solution and the magnitude of intermolecular cohesive forces. The factors which effect the foaming ability are presence of an additive (electrolyte or nonelectrolyte), temperature, and the chemical structure and concentration of the surfactants.

The effect of temperature on foaming ability is similar to the effect of temperature on solubility. Most of the work has been carried out with ionic surfactants. They show better foaming ability with increase in temperature, while nonionics will either show a decrease or go through a maximum in foam production with increase in temperature. Electrolytes do not alter the foaming capacity of nonionics to a great extent but show significant effect on the foaming of the ionics[82]. Electrolytes generally destabilize the foam and lead to faster drainage of the film. Polar organic additives which lower the cmc of a surfactant can improve foam stability. Schick[83] et al. have concluded that the foam stability of a surfactant on addition of an additive is due to their solubilization in the micelle palisade layer. Addition of nonionic surfactants to ionics show better foaming efficiency[84,85].

vi) **Detergency** :

Detergency is one of the most important areas of surfactant applications. In practice detergency involves the surface active processes of wetting, adsorption, emulsification, solubilization and dispersion. Three elements are involved in every cleaning action : (i) the substrate; (ii) the soil; (iii) the cleaning solution or bath; the cleaning mechanism involves two processes (Fig. 4) : (a) removal of soil from the substrate; (b) suspension of the soil in the liquid and prevention of its redeposition.

The removal of soil by surfactants, generally involves their adsorption onto the soil and substrate surfaces. This adsorption changes interfacial tensions and or electrical potentials at the soil bath and substrate bath interfaces in such a manner as to enhance removal of soil[86]. Several workers have deduced better efficacy of soil removal by mixed surfactant systems. Shah[87] et al. have found from the rate of solubilization of Orange OT from cotton into SDS solution that stable micelles are more efficient in detergency. When the term detergency is applied for a surface active agent it means it has special properties of enhancing cleaning action. No surfactant in itself has complete cleaning power. Practical detergents have a number of other components[20], foam control agents, antiredeposition agents such as carboxy methyl cellulose, colouring agents, perfumes and softners all of which can effect the properties of surfactants in detergency.

1.4 Polymer - Surfactant (PS) Interactions

The recognition of the interaction between nonionic water soluble polymers and surfactants occured decades later than the notion that surfactants form aggregates. This area of research is very intriguing because of the fact that many industrial work incorporates mixtures of both polymers and surfactants[88]. The fundamental studies

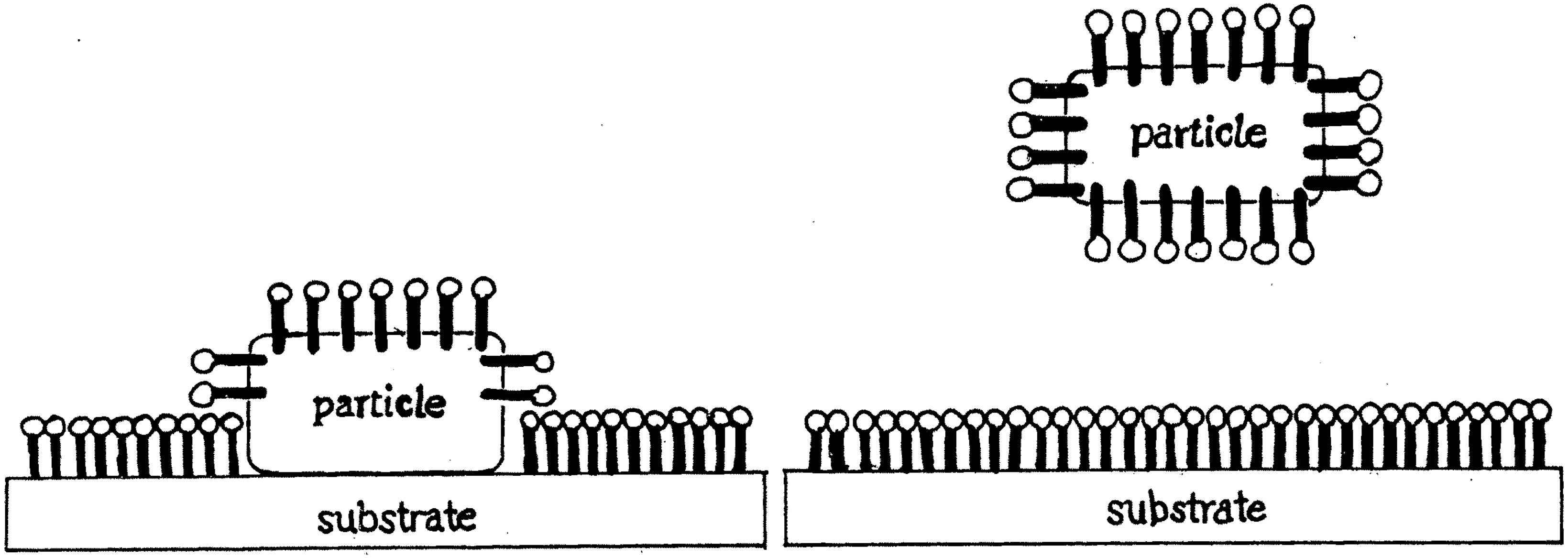


Fig. 4 : Removal of particulate soil in solution with (a) no surfactant (b) surfactant (Ref. 20).

have aimed at elucidating the structure and composition of polymer - surfactant complexes.

The general image emerging from these studies is that the surfactant molecules interact with polymers at a critical aggregation concentration (cac) forming micellar clusters along the polymer chain. The cac is usually lower than the critical micelle concentration (cmc) of the surfactant in the polymer free solution. The polymer becomes saturated with surfactant molecules and free micelles appear in the system[89]. The earlier image was that polymer presents adsorption sites along its backbone[90]. The presently accepted model was proposed by Cabane[91] on the basis of comprehensive studies on polyethylene oxide (PEO) - sodium dodecyl sulfate (SDS) system. According to this model segments of polymer bind to the surface region of the surfactant micelles and the polymer is converted into a 'necklace' decorated with surfactant micelles (Fig. 5). Stabilization of the interface between the hydrophobic core of the micelles and water is considered to be a major driving force for polymer - micelle interactions[92]. The various factors that effect the polymer - surfactant interactions are nature of surfactant; nature of polymer; amount of polymer; temperature and pH of the systems.

Nature of Surfactant :

The stabilization of the interface between the hydrophobic core of the micelles and water is one of the factors responsible for polymer - surfactant interactions. The chain length of the surfactant which controls the hydrophobic character is another important factor[93]. At a constant temperature, the higher the alkyl chain length in the homologous series the lower is the cmc. The polymer - surfactant (PS) interaction is enhanced with an increase in surfactant alkyl chain length[94]. The structure of the surfactant i.e. whether anionic, cationic or nonionic has a lot to do with PS interaction. The surfactant used in most polymer / surfactant studies is SDS. Several workers[95-97] have shown that interactions of water-soluble polymers is much more facile with anionic surfactants than with cationics. The interactions between dodecyl

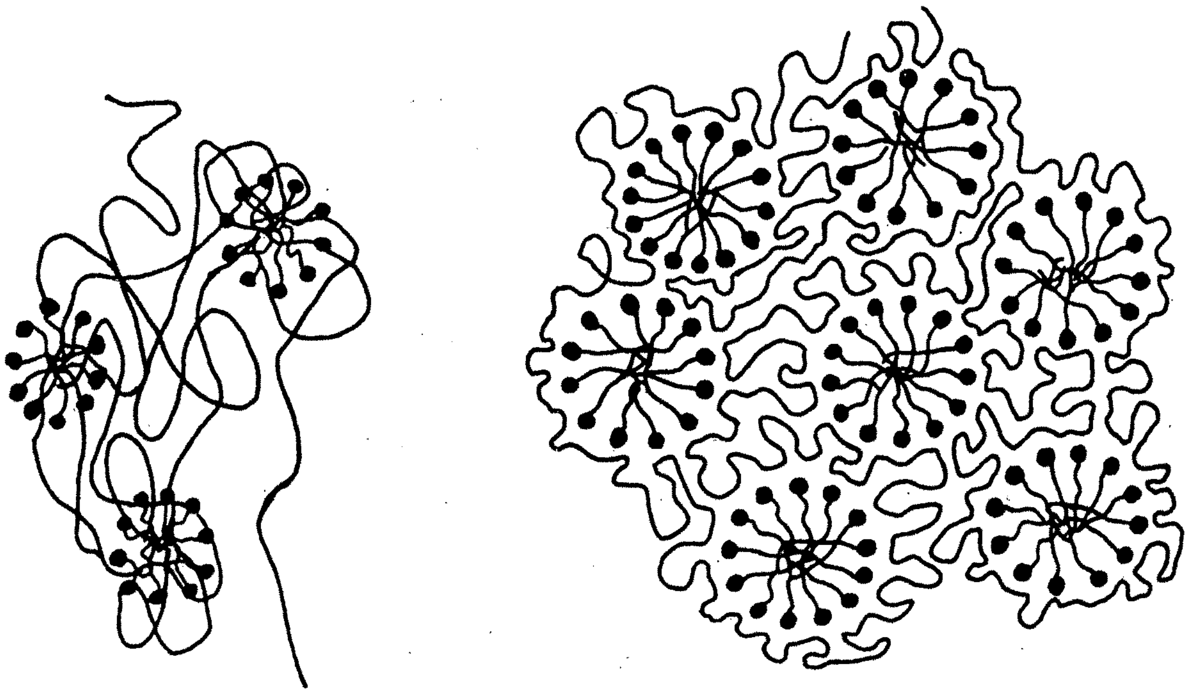


Fig. 5 : Schematic representation of a polymer-surfactant complex. Reproduced from ref. 113.

ammonium chloride ($DA^+ Cl^-$) and dodecyl ammonium bromide ($DA^+ Br^-$) with polyethylene oxide (PEO) show only feeble interactions[98]. Saito and Yukawa[99,100] have shown that interaction between a cationic surfactant and polymer is possible if strongly interacting counterions are present. Dodecyl ammonium thiocyanate $DA^+ CNS^-$ interacts quite strongly with polyvinyl acetate (PVAc). Tadros[101] have shown interaction of cetyl trimethyl ammonium bromide (CTAB) with partially hydrolyzed polyvinyl acetate. Conventional nonionic surfactants based on ethylene oxide are weakly reactive or not reactive at all. The self aggregation in case of these surfactants is not opposed by electrostatic forces which are present in case of ionic surfactant systems. Moreover, the thick hydrophilic layer of the micelle in case of conventional nonionic surfactants with a bulky PEO head group prevents the penetration of the polymer chains. However, reactivity has been reported[102] for a nonionic surfactant based on (thio) glucopyranoside head group with PVP. Conventional nonionic surfactants are found to react with poly (acrylic acid), poly(methacrylic acid) type of polymers[103-105].

Polymer Structure :

The hydrophobicity of a polymer makes them interact more with surfactants. Nonionic polymers are found to interact with anionic surfactants. For anionic surfactants[106] adsorption increases in the order polyvinylalcohol (PVA), polyethylene glycol (PEG), methyl cellulose (MC), polyvinyl acetate (PVAc), polyvinyl pyrrolidone (PVP) whereas the strength of interaction of cationic surfactants and polymers do not follow the same dependence on the nature of the polymers as shown by anionic surfactants. A possible reason is that in aqueous solution, the dipole of the polymer is preferentially protonated on the oxygen atom, leaving a slight positive charge on the nitrogen[107]. This weak positive charge would reduce interactions with cationic surfactants, but would enhance interactions with anionic surfactants. The interaction between a polyelectrolyte and ionic surfactants is dominated by charge-charge interactions. Initially the charges on the polyelectrolytes are neutralized by adsorption of the oppositely charged surfactants, further addition of surfactant to the uncharged complex converts it to a polyelectrolyte of opposite charge to that of the original polyelectrolyte. For a typical synthetic water-soluble polymer having hydrophobic and hydrophilic segments, there can be ion-dipole association between the dipole of the hydrophilic group and ionic head group of the surfactant and between the hydrophobic group of polymer and hydrocarbon areas of the micelle - in effect resulting in screening of the electrical charges. Reactivity increases with polymer hydrophobicity since the driving force for association is reduction of polymer hydrophobic segment / water interfacial area. The interaction between DTAC with two different copolymers of differing hydrophobicity - poly (maleic acid-co-methylvinyl ether) and poly (maleic acid-co-butylvinyl ether) have been studied by Zana[108] et al. The differences in binding behaviour between the two copolymers is essentially controlled by short range electrostatic forces.

The molecular weight of a polymer is another important factor. It has been suggested that polymers should have a minimum threshold value to have significant interaction and below this threshold value the effect is negligible. Schwuger[109] found that PEG of molecular weight - 600 weakly interacts with SDS but polymer of MW beyond - 1500 interacts strongly. After a certain value of the molecular weight, the nature of interaction does not vary much.

Other factors like temperature, effect of solvent environment, pH and so on serve as basis for interpretation of molecular forces involved in these interactions[110]. The nature of interactions is mainly attributed to the balance of forces involved[106]. The dominating forces are electrical, hydrophobic interactions and dispersion forces. Electrical forces exists between polyelectrolytes and surfactant head group, whereas, hydrophobic interaction arises from the solvent nature i.e. water. Water molecules, in addition to normal vander Waals forces, form strong hydrogen bonds with one another. In order to dissolve a hydrocarbon chain in water, some of the hydrogen bonds must be broken and the water close to the hydrocarbon chain, will adopt a different structure than the bulk structure. Since water prefers to be in the bulk phase, it behaves as if it 'squeezes' the hydrocarbon chains out of water. The two isolated hydrocarbons, form a joint interface by coming out of water, and reduce their contact with water, the force of the water 'squeezing' on the hydrocarbon chains will be reduced and a stable structure will be formed. The reduction in water 'squeezing' can be termed as hydrophobic interaction. The vander Waals forces are important between nearest molecules and are generally attractive. The forces between water - water or water - hydrocarbon is the same within an order of magnitude. Hence, the effect of these forces is small compared to hydrophobic or electrical forces. From the above considerations, it is clear that the strength and nature of interactions between macromolecules and surfactants do not only depend on the nature of both the polymer and the surfactant but also on the medium in which they are dissolved.

1.5 Models Proposed for Polymer - Surfactant Interaction

One of the most important characteristics of surfactant solutions is the micellization process. This process in water is a highly cooperative one. Various models depicting the types of interaction between the macromolecule and surfactant have been proposed. Several aspects of polymer - micelle interaction have been investigated and a model for the morphology of the complex has emerged, that is almost widely accepted. According to this model, the polymer segments are thought to reside at and stabilize the interface between the micellar hydrocarbon core and water. The aggregation number of polymer bound micelles is smaller and the counterion binding is lower, compared to that of free micelles. Usually, the polymer asserts a stabilizing influence on the micelles, which is reflected in a lower cmc value.

The simple model of Smith and Muller[111] which proposes that each polymer molecule comprises a number of "effective" segments of mass (MS) and total concentration [P], that act independently of each other and are able to bind n surfactant ions D^-, according to the equilibrium reaction

$$\mathbf{P + nD^- \leftrightarrows PD^{n-}_n}$$

with the equilibrium constant given by

$$K = [PD_n^{n-}] / [P] [D^-]^n$$

K is derived from the half saturation condition -

$$K = [D^-]^n_{0.5}$$

Assuming various trial values of n and using experimental values of other parameters one has all the information to calculate a series of experimental isotherm. The best fit yields the parameters MS, K and n. The above treatment was applied to PEO / F_3 SDS and the data indicated the cluster size n to be about 15, MS = 1830 which was in agreement with the experimental findings that PEO of molecular weight 1500 is relatively ineffective for surfactant binding whereas higher molecular weight PEO members are effective. The free energy of binding is obtained from the expression

$$\Delta G^\circ = -RT \ln K^{1/n}$$

and the value obtained i.e. - 5.07 k cal mol^{-1}, is closer to that of micelle formation for the surfactant employed [F_3SDS] suggesting that binding and micellization are related process.

Gilanyi, Wolfram[112] and Nagarajan[113] further developed the above model by including the complex formation in addition to the micelle formation in the mass balance equation. Gilanyi and Wolfram treated the case of an anionic surfactant binding to a neutral polymer, but allowed in addition, for degree of binding of the surfactant counterion, analogous to the treatment of micellization of surfactants. This was done by considering the degree of ionic dissociation of the bound surfactant aggregates. The expression for the free energy of transfer of surfactant [K^+ D^-] from the solution to the bound state as complex is

$$\Delta G^\circ = RT \ln [D^-] + RT (1-\alpha) \ln [K^+] - RT [Complex] / [Po] - [Complex]$$

where [Po] is the initial total concentration of "active" polymer site.

The same authors have stressed the applicability of a Langmuir adsorption of surfactant clusters on the 'adsorption sites' of the polymer and an analogy is drawn between the process of transfer of surfactant molecules to polymer bound clusters with that to surfactant micelles. They state that this process provides with the essential driving force for the formation of the complex.

Shirahama[114] has pointed out that the binding of SDS to PEO fitted a Langmuir adsorption equation if there was a provision that the binding was accompanied by cluster formation of the surfactant molecules ($n \approx 20$ monomers). Thus, the two equations then took the form

$$\theta = KC^n / (1 + C^n)$$

where θ is the degree of binding, n is an empirical exponent, C is the equilibrium concentration of bound species and K is a constant. Shirahama also used statistical mechanical approach to account for the binding[115].

Similar to Gilanyi and Wolfram, Nagarajan[113] also proposed a theoretical description of the surfactant aggregation in presence of water - soluble polymer. The main feature of this model can be summarized as follows :

The aqueous solution of surfactant and polymer is assumed to contain both free micelles and micelles bound to the polymer molecule. The total surfactant concentration X_t is thus partitioned into singly dispersed surfactant, X_1, surfactant in free micelles, X_f, and surfactant bound as aggregates X_b, in the mass balance equation

$$X_t = X_1 + g_f\,(K_f X_1)^{g_f} + g_b n\, X_p \left[\frac{(K_b X_1)^{g_b}}{1 + (K_b X_1)^{g_b}} \right]$$

the second and third terms represent X_f and X_b respectively; g_f is the average aggregation of the free micelles and K_f is the intrinsic equilibrium constant for the binding of the surfactant on the polymer or the formation of the polymer bound micelles, X_p is the total concentration of the polymer. Polymer influences the above equation through the term nX_p, its effective mass concentration which is independent of polymer molecular weight. The parameters K_b, g_b or n are assumed not to be affected by the conformational changes attending the polymer - micelle complexation. The relative magnitudes of K_b, K_f, g_b and g_f determine whether or not complexation occurs with the polymer. If $K_f > K_b$ and $g_b \approx g_f$ the formation of free micelles occur. If $K_f < K_b$ and $g_b \approx g_f$, complexation / aggregation on the polymer takes place first, upon saturation of the polymer, free micelles are formed. If $K_f < K_b$, and g_b is much smaller than g_f then micelle formation can occur even prior to the saturation of the polymer. A first critical surfactant concentration will be observed close to $X_1 = X_b^{-1}$ and a second critical concentration will occur near $X_1 = K_f^{-1}$. Nagarajan verified this model from the experimental specific ion activity data of Gilanyi and Wolfram, for the PEO / SDS system in presence of 0.1 M $NaNO_3$.

A detailed thermodynamic treatment using a Donnan equilibrium approach of the binding of ionic surfactants with the polymers was presented by Hall[116]. He predicts for systems containing salt, monomeric surfactant, micellar surfactant and adsorbed surfactant. There can be many possibilities such as (a) amount of bound surfactant may decrease if micelles are present; (b) the surfactant monomer concentration may exhibit two maxima. His theory suggests that the bound surfactants exists in two forms - the polymer molecules saturated with clustered surfactant coexists with polymer containing nonclustered surfactant and also predicts about the various conditions which can exists in solution. Finally this theory predicts that bound surfactant is divided equally among the macromolecules as evidenced from SANS[117], sedimentation[118], gel filtration[119] experiments.

Further refinements to the models continue to appear. One being the inclusion of a surface in the free energy equation term for aggregation as in the equation of Ruckenstein[120] et al. in Nagarajan's[121] new model and the dressed micelle theory of Evans[122] et al, Brackman, Lindman and Thalberg[123] have summarized the developments of these models and discussed the computer simulation approach to polymer / surfactant interaction developed by Balazs and Hu[124].

Similar to the co-operative binding model developed by Shirahama, one of the binding model was adapted by Satake and Yang[125] based on the Zimm-Bragg theory for coil - helix transitions of the polymers. Hayakawa and Kwak[126] have done extensive studies of cationic surfactants to estimate their free energy of binding to different polyions using this approach. Lindman and co-workers[3] have described the phase separation behaviour using the Flory-Huggins approach.

Granfeldt[127] et al. have performed Monte Carlo simulations to investigate the interaction between two charged micelles carrying adsorbed polyelectrolytes. No noticeable interaction between the micelles at distances larger than twice the micelle radius was obtained which means that for low concentrations of micelle and polyelectrolyte, we can regard the micelles as independent of each other. However, for higher micelle and polyelectrolyte concentration these aggregates form large clusters macroscopically observed as gels or phase separations occur.

Nikas and Blankschtein[128] have proposed a molecular thermodynamic theory of complexation of nonionic polymers and surfactants in dilute aqueous solutions. This theory explains factors describing the solvent quality, the polymer hydrophobicity, flexibility and specific interactions between polymer segment and surfactant head groups.

Wallin and Linse[129,130] have recently studied the complexation of a charged micelle and an oppositely charged polyelectrolyte using a simple model system (Fig. 6). The structural data of the micelle-polyelectrolyte complex as a function of micellar aggregation number were obtained by the Monte Carlo simulation technique and thermodynamic integration. This model takes into consideration that the addition of a polyelectrolyte to a solution of oppositely charged surfactants facilitates the micelle

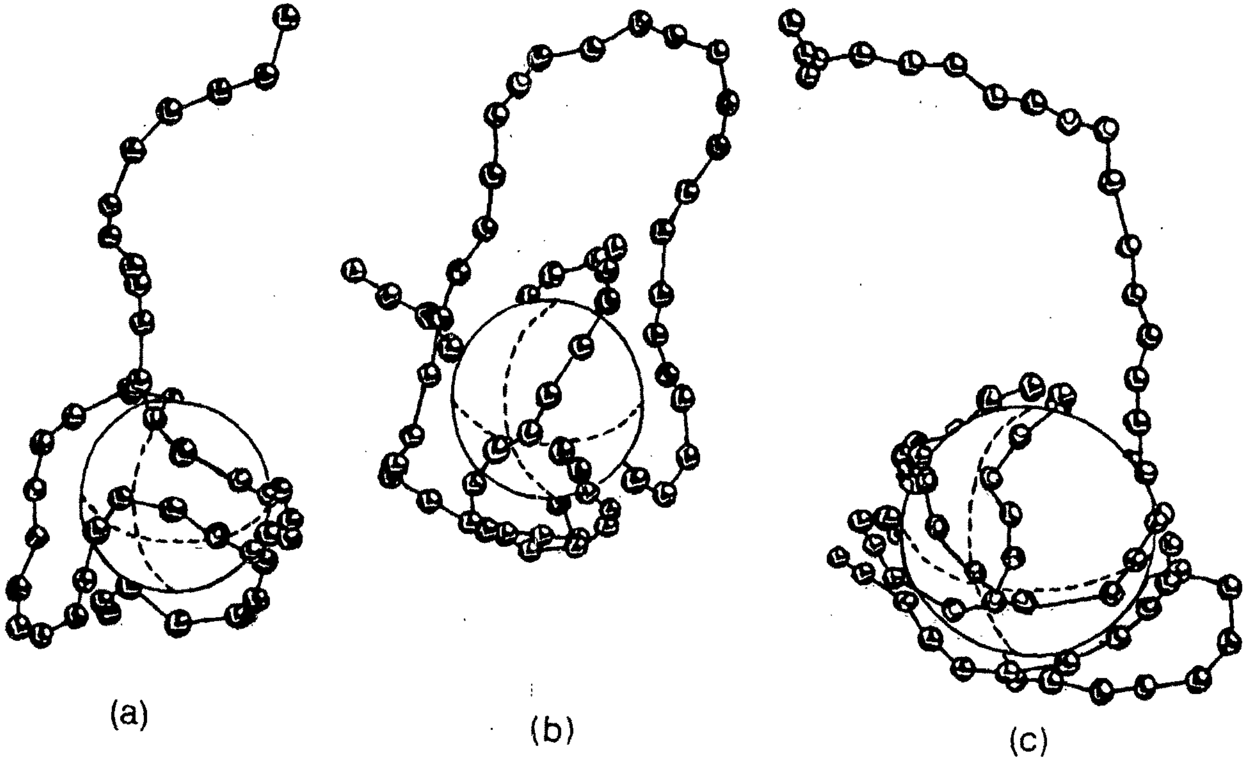


Fig. 6 : Images of the micelle and the polyelectrolyte system at different aggregation numbers (a) $N_{agg} = 30$; (b) $N_{agg} = 41$; (c) $N_{agg} = 53$ (Ref. 129).

formation of the surfactants. The factor by which the cmc is reduced upon addition of a polyelectrolyte is given by

$$\frac{\text{cac}}{\text{cmc}} = \exp\left[\frac{\Delta A_{pe}}{N_{agg}\,RT}\right]$$

where ΔA_{pe} is the change in the free energy of the complexation between one micelle, with its concomittant counterions and one polyelectrolyte with counterions. N_{agg} is the micellar aggregation number, R is the gas constant, T is the absolute temperature. This model also assumes that N_{agg} is not affected by the presence of the polyelectrolyte and the volume - pressure work caused by addition of polyelectrolyte is neglected.

To calculate ΔA_{pe} they have used a simple model, which takes into account a number of approximations : (1) The so-called primitive model is used i.e. (i) the water is treated as a dielectric medium and it enters the model only through its dielectric permittivity; (ii) all other constituents are described in terms of hard spheres, with point charges in the centre of the spheres. (2) The cell model is applied; one micelle and/or one short polyelectrolyte plus counterions are enclosed in a spherical cell. (3) The concentration of free surfactants is neglected. (4) The polyelectrolyte is modeled as a chain of charged hard spheres joined by harmonic bonds with the flexibility controlled by harmonic angular energy terms. (5) The micelle is assumed as a hard sphere with fixed charge and radius.

1.6 Experimental Evidences of Polymer-Surfactant Interactions :

Experimental methods for investigating polymer - surfactant interactions vary widely, but they generally fall in two categories[131], those that measure macroscopic properties of a system (viscosity, conductivity, dye solubilization, etc.) and those that detect changes in the molecular environment of the interacting species (nuclear magnetic resonance, small angle neutron scattering, fluorescence spectroscopy etc.). The experimental results of various studies depend upon the sensitivity of experimental techniques and the physical manifestations of interactions occuring. A brief account of the commonly used methods is being given below.

The most important characteristic of a surfactant solution is the magnitude of surface tension. The change in surface tension in presence of polymers has been used as a criterion for PS interaction[131]. Changes in surface tension, determine the cmc of a surfactant and changes in the magnitude of cmc of a surfactant is a measure of polymer-surfactant interactions. The plot of surface tension against surfactant concentration in presence of a soluble polymer has two transition points - whereas for surfactant solution alone there is only one break point. Representative plots of surface tension - concentration is shown in Fig. 7 and 8. At lower concentration individual surfactant molecules get attached to the polymer segments. As the concentration of surfactant is increased more and more an initial break is observed. This point (T_1) is known as the critical aggregation concentration (cac). Further addition of surfactants leads to a second break point (T_2) which is termed as the polymer saturation point (psp) or the cmc of the surfactant in presence of the polymer. At this point all the available sites on the polymer for binding are saturated and further addition of surfactant will only form pure micelles. Generally cac i.e. T_1 and psp i.e. T_2 are located above and below the cmc respectively of a pure surfactant. The first experimental investigations were done by Cockbain[133] on the bovine serum albumin / SDS systems by measuring the interfacial tension. The surface tension studies by Jones[134] on properties of mixed polyethylene oxide / SDS systems formalized the concept of two critical concentrations in the surface tension - log C plots. Several workers[135-137] have shown that the first break cac is independent of polymer concentration and temperature, while T_2 or psp which represents the saturation of polymer and increases with the amount of polymer. Surface tension measurements have extensively been done on polyvinyl pyrrolidone / SDS systems by a number of workers[138-139]. The two critical concentrations have also been observed for polyacrylic acid and the nonionic surfactant $C_{12}E_8$[140]. The T_2 values for these systems increase with increase in polymer concentration. The surface pressure - area isotherm of

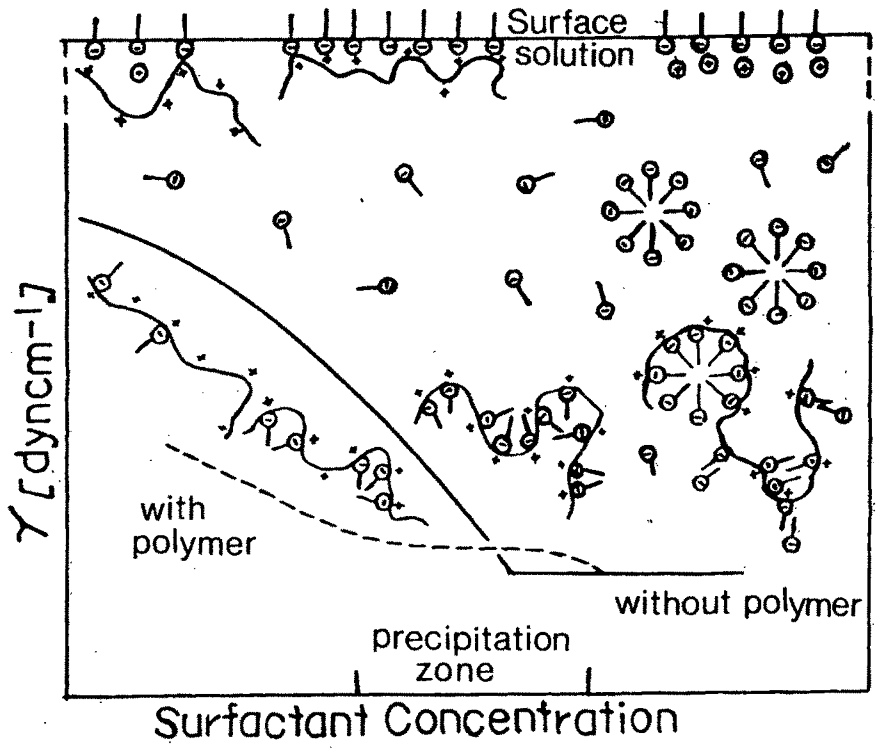


Fig. 7 : Diagrammatic representation of conditions in bulk and surface of solutions of a polycation and anionic surfactant. Full line is the hypothetical surface tension concentration curve of the surfactant alone : dotted line is that of mixture with polycation (Ref. 131).

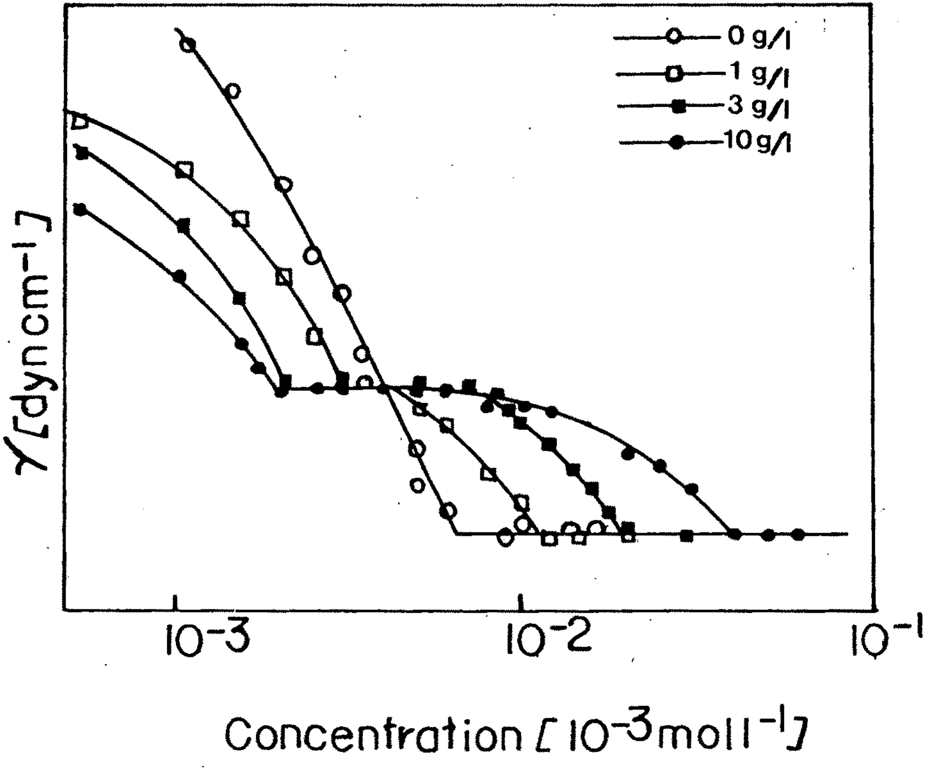


Fig. 8 : Surface tension (γ) / concentration plots of SDS in presence of PVP at various concentrations (Ref. 131).

insoluble monolayer can also be used to study PS interaction. Homopolymers and copolymers of methylacrylate and acrylonitrile were used to study pressure area isotherm on an aqueous subphase and on aqueous SDS solution[141]. An insoluble monolayer of polymers form a more condensed film in presence of SDS due to PS interaction. Surface pressure measurements were used to study the interactions between polyoxyethylene oxide and a nonionic surfactant $C_{12}E_5$[142]. They have shown that the area per molecule is important criterion for polymer surfactant interaction. Stebe et al.[143] have used a theoretical approach to study the insoluble monolayers formed by polymer / surfactant systems.

The changes in the specific conductance / concentration plots are consistent with the surface tension measurements[144]. The appearance of a premicellar breakpoint where the plot departs away from that of the surfactant alone - and second post micellar breakpoint - the psp or T_2 can be noted. A direct complex formation in case of PEO / SDS[88] is attributed to a direct interaction between ionic head group and a EO chain. Candau et al.[144] carried out conductance measurements for SDS and copolymers of acrylamide and N-(4-ethylphenyl)-acrylamide of varying molecular weights. Conductance measurements have been done for various systems like PPO - CTAB, PEO - CTAB, PEO - SDS, PVP - SDS by a number of workers[145-147]. Important parameters of aqueous micelles such as degree of ionization (α) can be evaluated from the conductance data[148]. The degree of ionization is an important property of ionic surfactant assemblies and knowledge of it is important to explain the effect of overall reaction rates[149]. Several methods are used to evaluate α-values the simplest one being the method of slopes. Zana et al.[96] have calculated α values of PVP-SDS and PEO-SDS systems.

Viscosity is one of the important properties of polymer solutions. It is necessary to know about viscosity of polymer solutions to get an idea about their molecular weight[11]. The viscosity property of mixed polymer / surfactant solutions shows several interesting properties. The viscosity of hydrophobically modified[150] polyacrylic acid with cationic and nonionic surfactants were studied. The reduced viscosities of modified polymer solution with their non-modified ones were compared. At higher surfactant concentrations, increase in viscosity was observed due to occurrence of intermolecular hydrophobic associations. The effect of anionic SDS, cationic DTAB, and nonionic $C_{12}E_{23}$ on viscosities of polyethylene oxide didodecyl ether has been reported[151]. Binding of ionic surfactants to the uncharged polymer chain builds up electrical charges and as surfactant ions tend to cluster on the chain, the chain builds up and expands in solution by repulsion of charge density acquired and this gives rise to a pronounced viscosity[152]. The chain length of the surfactant also effects the rheological property of PS interaction. Addition of DTAB solution gave an increase in reduced viscosity to a hydrophobically modified polyacrylamide solutions whereas on addition of SDS showed a pronounced minimum[153]. The effect of two nonionic surfactants - $C_{12}E_5$ and $C_{12}E_8$ on the viscosity of hydrophobically modified poly (sodium acrylate) was seen. The differences in viscosity between the two surfactants was observed due to change in alkyl group to surfactant ratio[154]. In case of ionic surfactant such as SDS, the cluster growth or association results in pronounced increase in viscosity whereas nonionic surfactants do not disturb the polymeric network. Shear viscosity measurements were done for hydroxyethyl-cellulose[155]. Different nonionizable water-soluble polypeptides were studied with SDS and tetramethyl ammonium dodecyl sulfate (TDS) viscosimetrically[156]. The reduced viscosity (η_{sp}/C) shows a maximum for certain peptides giving an indication of binding. The interaction of the hydrophobically modified ethyl hydroxy ethyl cellulose (HMEHEC) have been studied by viscosity measurements[157] with surfactants like sodium 10-undecanoate (SUD), sodium-11 (n-ethyl acrylamido undecanoate) (SEAAU) which are polymerizable ones and exert varying degrees of hydrophobic interaction with HMEHEC via the formation of mixed micelles as clusters. Interactions have been observed for associative polymer and SDS. These associative polymers (AP) are hydrophobically modified and at low concentrations they self associate and form primary aggregates and at higher concentrations they form network like clusters. Addition of a surfactant to an AP solution with hydrophilic chains with hydrophobic end groups increases the amount of hydrophobic aggregates which act as junction in polymer clusters[158]. Addition of surfactants to polymers generally increase the viscosity due to increase in polymer chain length because of electrostatic interactions.

The different spectroscopic techniques involved to detect changes at the molecular level are

Fluorescence probe : Fluorescence probe technique is comparatively new addition to the field of investigations of PS interactions. They are used to determine (a) cac of polymer - surfactant systems; (b) N_{agg} (aggregation number) of polymer - surfactant systems and (c) the microenvironment within the complexes. A good deal of review articles on photophysics and photochemistry of micellar solutions have been published during the last few years[159]. Pyrene has most often been used as a fluorescent probe but other compounds like 2-methyl anthracene, perylene, 2-naphthalenesulfonate etc. having low water solubility, have also been used[160]. The steady state fluorescence quenching methods for N_{agg} determination was originally developed by Turro and Yekta[161] for micellar solutions and have been extended to PS aggregates[162]. In microviscosity studies the ratio of I_1/I_3 peaks are used to determine cac values. The ratio of I_1/I_3 of pyrene solubilized Cu $(DS)_2$ micelles and SDS micelles were determined. When PVP and PEO were added to Cu $(DS)_2$ micelles the ratio of I_1/I_3 increased with polymer concentration[163]. The effect of PVP was larger than PEO suggesting stronger interaction.

Zana et al.[108] have studied the interaction of PEO as well as PVP with TTAB by conductance and fluorescence methods. They observed that PEO and TTAB interact above 35°C because at that temperature PEO becomes reasonably nonpolar. PEO also interacts with SDS. Maltesh and Somasundaran[164,165] have worked extensively on

PEO-SDS systems by using fluorescence spectroscopy. They have probed the effects of different cations on the size and number of SDS-PEO aggregates, under conditions of dilute polymer and surfactant concentrations where there was no unbound SDS micelles[164]. A recent study[166] has been done by means of static and dynamic fluorescence measurements of the interactions between SDS and fully hydrolyzed polyvinyl alcohol or PEO. The study indicates that interaction begins at cac below the cmc at both 20°C and 40°C. Aggregation numbers are also effected by the addition of polymer. A comprehensive review of the fluorescence spectroscopic method used to study PS aggregates have been done by Winnik et al.[92]

Nuclear Magnetic Resonance Studies :

Muller and Johnson[167] as well as Cabane[91] did some early studies on PS interaction by NMR. The latter carried out extensive studies on PEO / SDS systems where he investigated the shifts in ^{13}C NMR spectra of various dodecyl chains with increasing amounts of PEO added to micellar SDS solution. No changes were observed in carbon C_4 to C_{12} environments, whereas the shifts experienced by C_1, C_2, C_3 in polymer / surfactant aggregate indicate carbon atoms encounter a different environment and EO groups replace water in the outer region of the micelles and does not penetrate the hydrocarbon core. Kwak et al.[168] studied ^1H NMR shifts of PEO in presence of ω-phenyldecanoate. The formation of PS aggregates is clearly reflected in the chemical shifts of protons attached to the carbon atoms. These studies conclude that PEO / ω-phenyldecanoate is similar to surfactant micelle itself with the PEO monomer units distributed along the aggregate. Persson et al.[169] studied the self diffusion coefficient of an associated polymer C_{12} EO_{200} C_{12} (polyethylene oxide containing 200 monomer with chain that is end capped with C_{12} alkyl groups) with the SDS system. They found the ethylene oxide peak at 3.75 ppm and as the concentration of the polymer increases in solution, the diffusion coefficient (D) decreases. The difference in the D values distribution was found in presence and absence of polymers. Larger aggregates in presence of surfactant led to smaller D values. Cationic DTAB and nonionic $C_{12}E_{23}$ were found to not interact greatly. Chari et al.[170-172] have confirmed that SDS gets associated with PEO or PVP in the form of a micelle getting attached to polymer backbone. They have studied the SDS / PEO system by ^{13}C NMR spectroscopy. The spin lattice relaxation time and the nuclear overhauser effect (NOE) are present because of ^{13}C-H inter nuclear dipole-dipole interaction. Zhang et al.[173] have used FT-PGSE-NMR technique to study the interaction of $C_{12}E_4$ - and a random copolymer of ethylene oxide and propylene oxide. The interaction of CTAB and SDS with cellulose ether was studied by the same method. Sesta et al.[174] have done the ^1H-NMR for the PVP-SDS and PVP with fluorinated surfactant LiPFN (Lithium perfluorononanoate) by varying LiPFN and SDS concentrations.

Small Angle Neutron Scattering (SANS) :

SANS is a powerful tool to study the changes occuring at the molecular level. SANS of micellar solution has been widely done and micellar structure has been described[175,176]. Also, SANS studies on polymer solutions have been done[177]. Cabane and Duplessix[178] carried out SANS measurements on PEO / SDS system by varying SDS concentration. Lin et al.[179] have done the SANS on PEO / SDS systems. They plotted the scattered neutron intensity as a function of momentum transfer Q. It could be deduced that at low concentration of SDS the polymer shrinks and as concentration of deuterated SDS increases the polymer expands. These observations were supported by the viscosity results. Goddard et al.[180] carried out SANS measurement on a polymer JR 400, a quarternized cellulose ether and on Reten 20, a copolymer of acrylamide and β-methacryloxyethyl trimethyl ammonium chloride with deuterated SDS. The plot of scattering intensity I for polymer JR in D_2O is flat i.e. the scattering intensity is independent of Q and of low intensity. The addition of small amount of surfactant changes the ionic strength and brings significant small angle scattering. The radius of gyration R_g is calculated by curve fitting of the interparticle structure factor used for the three shell model SANS measurements on gelatin with SDS[181]. A number of small angle X - ray scattering studies have also been done on PS systems[182,183].

Other methods like dialysis, dye solubilization, adsorption on solid surfaces, foaming, use of surfactant sensitive electrodes have been done by a number of workers. A popular method for measuring the extent of interaction was to determine the degree of binding by means of dialysis techniques[184]. The polymers are contained in a dialysis bag with a pore size small enough to restrict polymer molecules but large enough to allow smaller surfactant molecules to pass. The measurements were carried out in presence of salt to minimize the Donnan membrane effects[185]. Similar to surface tension studies two critical concentrations were obtained by this method. A number of studies have been carried out on protein-lipid[185,186] and polymer-surfactant systems[114].

The ability of surfactant micelles to solubilize various oil-soluble materials is well recognized. Saito[102] used water-soluble polymers to enhance the capacity of various surfactants to solubilize the oil soluble dye Yellow OB. The initiation of solubilization activity starts before the formal cmc of the surfactant and completion of PS complex formation is represented by the second breakpoint. Arai et al.[137] have shown that the T_1 and T_2 values obtained by the dye method and also from other methods are in agreement with each other. Saito[187,188] reported solubilization of Yellow OB by Poly(acrylic acid) - nonionic surfactant mixtures. His studies conclude that the synergistic solubilization of Yellow OB by nonionic surfactant-PAA complex may be called polymer binding solubilization and is different from ionic surfactant - nonionic polymers like PVP / SDS complex. In a series of papers Hayakawa and Kwak[189,190] have studied solubilization of some dyes by polyelectrolyte / surfactant complexes.

A number of studies on the stability of foams in presence of polymers have been done[191,192]. Recent studies[193] have been done on the drainage of foams produced by SDS and TX-100 in presence of sodium carboxymethyl cellulose (SCMC). The increase in bulk on addition of SCMC leads to increase in drainage half life by more than 10-fold. Goddard et al.[194] have found an increase in foam stability for cationic polymer JR-400 with surfactant SDS and sodium docosyl sulfate (SDCS). Polymers have little effect on initial foaming, but exert a pronounced effect on the foam stability. The polymers impart to the foam a definite resistance to deformation, a direct consequence of increased surface or bulk viscosity of the film, thereby increasing the film elasticity or decreasing the film drainage rate. Fig 9 represent the effect of additives, electrolytes and polymers on the foam stability.

A number of studies have been done on adsorption of P-S complexes on solid surfaces. Zhao and Brown[195] studied the adsorption of nonionic surfactant TX-100 and hepta ethyleneglycol monodecyl ether ($C_{12}E_7$) on predominantly hydrophobic polystyrene latex particles. Hydrophobic attractions seem to be the main reason for the interactions. Ma et al.[196] have studied the adsorption of SDS and PVP from their mixed solutions on a TiO_2 surface. The results show a synergistic effect at low SDS concentration and an antagonistic effect at high SDS concentration. Shubin[197] studied the adsorption of various cationic hydrophobically modified hydroxyethyl cellulose on a negatively charged mica in presence of SDS. Formation of PS complex has great effect on conformation and adsorption of polymers on the surface[96].

Light scattering studies have been used to determine the radius of gyration R_g values of polymers in presence of surfactants. The size of gelatin molecule has been determined by dynamic light scattering measurements in presence of ionic and nonionic polymers[198]. The hydrophobic binding between gelatin and nonionic surfactants did not alter the gelatin size significantly. Light scattering measurements have been done for SDS / PVP systems and R_g determinations were carried out[199]. The third virial coefficient and R_g values have been calculated for PVP-SDS systems[200]. It was found that the virial coefficients A_2 and A_3 were dependent of surfactant concentration. Dubin et al.[201] have carried out Quasi elastic light scattering (QELS) studies on PEO-SDS complexes.

The use of surfactant sensitive electrodes was done to determine the degree of binding. Keifer[202] and coworkers studied the interaction of TTAB with PAAc and

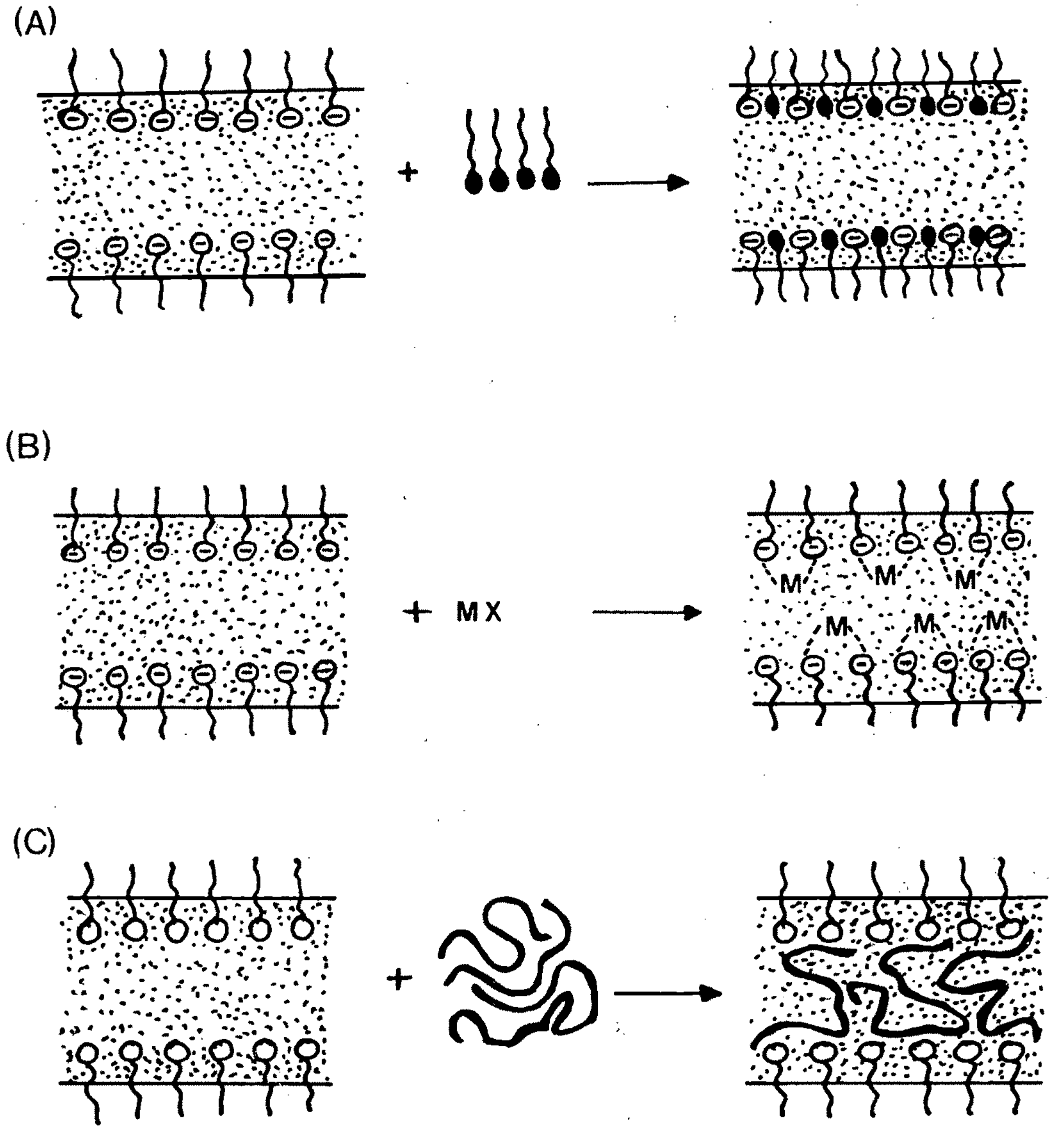


Fig. 9 : Foam stabilization in presence of an (A) organic additive; (B) electrolyte; (C) polymer.

PMAAc. Surfactant sensitive electrodes were prepared by the method suggested by Malikowa et al.[203] Various solutions of different pH were used and hence the charge density of polymer was different. They determined the binding isotherm and found that binding is significantly influenced by changes in polymer conformation, and hydrophobicity. Shimizu[204] and others have observed a two step binding. The first step is due to interaction of surfactant ion with a charged carboxyl group and adjacent hydrophobic side group. The hydrophobic interaction between the bound surfactant ion and the side group increases the binding process. The different polymers used were poly (maleic acid), poly (fumaric acid) and poly (acrylic acid) along with dodecyl pyridinium chloride (DPyCl).

1.7 Thermodynamic Parameters

The most important property of surfactant is the formation of micelles, and like most physicochemical processes it is essential to know the energetics of this process. This requires the detailed analysis of dynamics of the process wherein the laws of thermodynamics are applicable to obtain the standard free energy, enthalpy and entropy of micellization.

Two main theories for the thermodynamic analysis of the micellization process have gained wide acceptance; (i) the pseudophase separation model; (ii) the mass action model. In both these approaches the micellization phenomenon is described in terms of classical thermodynamics. Theories of micelle formation based on statistical methods have also been proposed[205,206].

The phase separation model considers the formation of micelles as a separate phase at cmc. In case of ionic micelles it also includes the counterions as a separate phase. To calculate the thermodynamic parameters of micellization it is necessary to define the standard states. The hypothetical standard state for the surfactant in the aqueous phase is taken as the solvated monomer at unit mole fraction with the properties of infinitely dilute solutions. For the surfactant in the micellar state, the micellar state is considered to be the standard state.

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 the mole fraction scale as defined by n (of surfactant at cmc) / n (of surfactant at cmc) + n (of water), n is the number of moles. The ΔG°_{m} measures the standard free energy change for the transfer of one mole of amphiphile from solution to micellar phase. The corresponding standard enthalpy and entropy of micellization can be computed from the well known thermodynamic relation

$$\Delta G^{\circ}_{m} = \Delta H^{\circ}_{m} - T\Delta S^{\circ}_{m}$$

In calculation 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 the micelle is considered. Therefore, the relation becomes[207]

$$\Delta G^{\circ}_{m} = (2 - \alpha) RT \ln cmc$$

where α is the degree of ionization of micelles computed from the ratios of the slopes of the post micellar region to that of the premicellar region in the conductance - concentration plot. The degree of ionization is an important property of ionic surfactant assemblies and the knowledge of it is necessary to explain the effect of ionic surfactants on the micellization process. Moreover, in the phase separation model, the micelles are treated as a separate phase owing to their large aggregation numbers.

Micelles and unassociated surfactant ions are assumed to be in association - dissociation equilibrium and the law of mass action is applicable. The mass action model was originally applied to ionic surfactant systems, and later on was developed for nonionics too[208-209].

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

$$\Delta G^{\circ}_{m} = RT \ln X_{cmc} \text{ (for nonionics)}$$

$$\Delta G^{\circ}_{m} = (2 - p/n)\, RT \ln X_{cmc} \text{ (for ionics)}$$

Both the models indicate $\alpha = p/n$ (where p is the effective charge per micelle of aggregation number n). Both the models differ only in the way in which mole fractions are evaluated. In phase separation model the total number of moles present is equal to the sum of number of moles of water and surfactant whereas the total number of moles in mass action model is equal to the moles of water, surfactant ions, micelles and free counterions.

These two models have been used not only to evaluate the energetics of micelle formation but also for polymer - surfactant aggregates. A number of workers have extensively investigated the thermodynamics of micellization of pure surfactants[210,211] and mixed surfactants[212,213] and also in presence of additives[213-215].

Shirahama and Ide[216] estimated the enthalpy of transfer of SDS from the micellar form to PEO / SDS aggregates by calorimetry results. Kresheck and Hargraves[94] carried out enthalpy titrations of micellar SDS into solutions of PVP. They deduced that the binding of SDS to the polymer is essentially athermal, but initial binding of the surfactant to the polymer, involved only SDS monomers. The interaction between ionic surfactant and nonionic polymer involves surfactant aggregation process akin to micellization. Heats of micellization of SDS at room temperature are small and hence in presence of polymers also it is expected to be small. Indirect estimates of the heat of aggregation ΔH of SDS, in presence of PVP were made by Murata and Arai[136]. Murai et al.[217] showed that the monomer contribution to the free energy of the micelles formed could be divided into hydrocarbon part and electrostatic part

$$\Delta G^{\infty} = RT \ln (cmc) = \Delta G^{\infty}_{HC} + \Delta G^{\infty}_{el}$$

In case of the nonionic polypeptides - SDS systems, the hydrophobic interaction between SDS and polymers predominates over electrostatic repulsive forces.

Wyn-Jones et al.[218] have used isothermal titration calorimetry to measure the enthalpy changes for the PVP / SDS systems. There is a pronounced maximum in the enthalpy profile at T_1 (i.e. cac) which corresponds to the start of SDS binding with PVP and the profile also showed a second break at T_2 (i.e. psp). Similar associations between octyl thioglucopyranoside (OTG) and PPO were observed by Engberts et al.[219] Enthalpy changes have been calculated for the PEO / SDS systems recently[220]. The standard Gibbs free energy was calculated. The workers concluded that the $\Delta G°_m$ for the two processes is rather small but favours the formation of aggregates on the polymer strand compared to normal micelles. For cationic surfactant Cetyl pyridinium chloride (CPyCl) and various water-soluble oligomers / polymers like PEG, PVP etc. it was found that the nature of interaction varies due to the hydrophobicity of the polymer[221]. A number of systems[222] make use of the method of slopes (from conductance measurements) to calculate the values of degree of dissociation 'α'. For cationic micelles the values of α was found to be 0.53 ± 0.05 with Cl as the counterions[34]. Similar values were found for PVP-cationic surfactants[221].

Shirahama and coworkers[223] have used a statistical method for the treatment of the binding process. Kwak[224] used the same for their studies of cationic surfactants to obtain free energy of binding to various polyions. The surfactants used were families of alkyl pyridinium and alkyl trimethyl ammonium salts, for a variety of binding polyelectrolytes. The free energy values ranged from 1.2 - 1.3 kJ per CH_2 group higher than simple micellization.

The standard free energy associated with the interaction between surfactants and polymers $\Delta G°_t$ is given by the difference in free energy of transfer of the surfactant monomer from aqueous solution to the micelle in presence and absence of polymers. The $\Delta G°_t$ values for[225] interaction of PVP with SDS and $Cu(DS)_2$ are - 4.6 and -2.7 kJ mol^{-1} while the values for PEO with these surfactants are -2.7 and -1.2 kJ mol^{-1} respectively. Similar studies[226] have been done with cationic surfactant n-dodecyl dimethyl amine oxide with poly (vinyl methyl ether), poly (propylene oxide) and poly (ethylene oxide). In all these cases the free energy of transfer of the surfactant monomer towards the polymer - surfactant micelles is smaller than the values corresponding to the pure micelles, indicating that the addition of polymers stabilizes the micelles. Several important calorimetric studies have given details of polymer - surfactant interaction[218,219,225].

1.8 Surface Activity

a) Interfacial Adsorption Parameters :

Surfactants owe their versatality due to their characteristic feature of adsorption. Detergents have a tendency to accumulate at the interface, be it oil / water or air / water. Several methods deduced earlier were unsuccessful to measure the amount of surface active agent adsorbed. The thermodynamic relationship between the quantity adsorbed per unit area and change in surface tension was first derived by J.W.Gibbs[227] in 1878. This relationship is one of the classical theories in surface science.

The Gibbs equation expresses the equilibrium between the surfactant molecules at the surface or the interface and those in the bulk of the solution. It is a particularly useful equation since it provides a means by which the amount of surfactant adsorbed per unit area of the surface, the 'surface excess' may be calculated. In the most general form the Gibb's equation may be written as[228]

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

where $d\gamma$ is the 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 surface of the ith component present in the system over that present in a hypothetical system of same value in which the bulk concentrations in two phases remain constant upto the imaginary dividing surface; $d\mu_i$ is the change in chemical potential of the ith component of the system.

For a two component system at constant temperature

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

where 1 and 2 are the subscripts referring to solvent and solute respectively. Assuming $\Gamma_1 = 0$, the excess concentration of the surfactant Γ_2 for a dilute solution will be

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

where C is the concentration of surfactant in solution.

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

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

For ternary systems, the surfactant-polymer-water, the Gibbs equation becomes[229]

$$-d\gamma = \Gamma_1 \, d\mu_1 + \Gamma_2 \, d\mu_2 + \Gamma_3 \, d\mu_3$$

As the polymer concentration is constant, we can assume

$$\Gamma_1 \, d\mu_1 + \Gamma_3 \, d\mu_3 = 0$$

where Γ_1 and Γ_3 refer to water and polymer surface excess, hence even for ternary systems, the surface tension data can be analyzed by equations for dilute solutions. Here γ is expressed in dynes cm^{-1}, concentration of surfactant in terms of molarity, R in ergs mol^{-1} K^{-1} and Γ_2 is expressed in terms of mol cm^{-2}. The slope $d\gamma/d \ln C$ is obtained from the linear portion of surface tension - log concentration plots. If γ-log concentration plot is not linear then 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 surface or interface is calculated

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

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

Yadav and Anand[230] have evaluated Γ and A_{min} values for a system of PVP-SDBS and PVP-SDS. A temperature effect has been seen. Increase in temperature lowers the Γ values which may be attributed to the desorption of surfactant molecules at liquid / air interface due to enhanced thermal agitation at higher temperatures, corresponding A_{min} values increase suggesting poorer packing at the air / water interface. Sesta et al.[229] have worked on SDS and LiPFN with PVP of different molecular weights, with increasing molecular weight, the hydrophobicity increases and greater is the tendency to locate at the air / water interface.

Factors affecting Γ_m are nature of surfactant; temperature, effect of an added electrolyte, nature of polymer. Generally for ionic surfactants, temperature increase over the range 20-85°C appears to cause a decrease in Γ_m values, and an increase in case of nonionic surfactants[231]. The extent of adsorption of an ionic surfactant is greatly affected by addition of an electrolyte. The electrolyte probably exerts its effect by decreasing the repulsion between the oriented head groups allowing closer packing in the surface layer as ionic strength is increased.

Neutron reflectivity measurements were carried out by Penfold et al.[232] for the PVP/SDS systems, to measure the amount adsorbed at the air-water interface. Neutron reflectivity profiles were obtained for SDS with varying PVP concentrations. Assuming a single layer of scattering length density ρ and thickness T, the area per molecule could be calculated using the relation

$$\mathbf{A} = \sum_{\mathbf{i}} \mathbf{n_i}\, \mathbf{b_i} / \rho\Gamma$$

where n_i is the number of atoms of i and b_i is the scattering length of atom i. The surface excess can then be evaluated from

$$\mathbf{A} = \frac{\mathbf{10^{14}}}{\mathbf{N.\Gamma}}\ \mathbf{nm^2}$$

where N is Avogadro number, Γ is the surface excess expressed in mol cm^{-2}, and A is the area per molecule. The surface excess values increase with PVP concentration. Significant changes are observed at very low SDS concentration.

Huber et al.[140] have used refractive index values, measured from a film of polymer / surfactant to estimate the amount of substance adsorbed at the air / liquid interface. For a system of poly (acrylic acid) - $C_{12}E_8$, there is a change in Γ values with change in pH. A number of studies have been carried out by several workers by different methods to measure the amount of surfactant adsorbed at the air / water interface in presence of the polymers. The use of radio tracer studies reported by Chari and Hossain[233] provided evidence for a polymer induced change in surfactant concentration at the air / water interface. The film drainage studies, coupled with X-ray reflectivity on the SDS / PEO system has been interpreted as indicating the presence of a thin layer of PEO underlying the adsorbed monolayer. Another relevant result is that of Kilau and Voltz[234] who demonstrated synergistic wetting of a hydrophobic coal surface when PEO was used in conjunction with a sulfonate surfactant. A mixed polymer / surfactant film formation occurs at the interface. Similar studies have been done by Goddard et al.[235] by a talc test method. Though this method lacks the rigour of state-of-the-art techniques of interface characterization such as neutron reflection, but certainly detects the polymer / surfactant interactions on the surface.

Thermodynamics of Adsorption :

Thermodynamic investigations of adsorption of surfactants can provide atleast two types of important information about the adsorbed films i.e. Gibbs energy of adsorption as a measure of surface activity of the surfactant and the enthalpy of adsorption of the surface active homologues from aqueous solution at the air / water interface[236].

Rosen has shown that standard thermodynamic parameters of adsorption at cmc as[33]

$$\Delta G^\circ_{ad} = RT \ln cmc - N\,\Pi_{cmc}\,A_{cmc}$$

by considering the standard state for the adsorbed surfactant here as a hypothetical monolayer at its minimum area per molecule but at zero surface pressure. The second term in this equation is the surface work involved in going from zero surface pressure to surface pressure Π_{cmc} at constant minimum area per molecule. The corresponding entropy and enthalpy are then calculated.

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

Studies of the energetics of adsorption process is very limited in case of polymer - surfactant systems. A number of workers have investigated the surface and thermodynamic properties of Zwitterionics[237], mixed surfactant systems[238], ternary surfactant[239] systems. However, scanty literature is available for the adsorption behaviour of polymer / surfactant aggregates. Anand and Yadav[230] have reported the adsorption parameters for the PVP / SDS and PVP / SDBS systems. On adding SDS or SDBS to PVP solutions, the authors found a lowering in ΔG°_{ad} values. This is probably due to cumulative adsorption of surfactant molecules both at air / liquid interface and PVP surface. ΔH°_{ad} and ΔS°_{ad} values are positive for the systems studied. These values indicate that during the process of adsorption of surfactant at the liquid / air interface, more ordered water molecules in the hydrophobic hydration zone transform to less ordered 3D water structures.

1.9 Applications

Mother nature has devised several important products of which microheterogeneous systems play an important role. The importance of microheterogeneous supramolecular systems is exemplified in many of today's modern amenities. Surfactants are vital components of biological systems and are key ingredients in consumer products and play an important role in industrial applications. The cell membranes have aggregates called lipids which are major components of the membranes. The protein - lipid interactions in the biological systems are the manifestations of polymer - surfactant interactions[2]. Increasingly, polymers are being used along with surfactants in those areas where earlier only surfactants were being used. The presence of polymer generally introduces rheological characteristics into the system and the surfactant provides the solubilization capacity. It has been well appreciated that presence of both polymers and surfactants in many formulations show enhanced performance properties. They are used in fields as diverse as detergents, drug formulations, paints, cosmetics, tertiary oil recovery, textile finishing. Their applications have also extended to advanced technologies such as electronic printing, magnetic recording, biotechnology, controlled drug delivery etc. The main technological usage of surfactants comes from their fundamental properties which are adsorption at the interfaces and formation of micelles in solutions. Probably, the most important application of surfactants is in the detergent industry. The kinetics and mechanisms by which micelles solubilize a soil has been described as adsorption of micelles on the soil surface, incorporation of soil into the micelle, desorption of the soil containing the micelle. Diffusion of micelles to and away from the soil surface preceeds and ends the solubilization process[240,241]. This mechanism of cleaning is not only limited to the surface of soiled cloth, but also dirt removal from hair or dentrifices. Majority of detergents make use of polymers along with surfactants in their formulations[242]. Homopolymers of acrylic acid and copolymers of acrylic acid - maleic acid and their sodium salt are widely used as dispersants in powdered detergent formulations. Recent advances in detergent compositions have shown enhanced rheology due to addition of poly (acrylic acid) copolymers for use on hard surfaces such as bath room fittings and toilets. Cationic polymers and anionic surfactants along with alkali metal salts are excellent conditioning shampoos. Lightly cross-linked polymers are known to add viscosity to liquid detergents, stabilize formulations that will fall apart otherwise due to incompatible components[243]. Polymers like carboxy methyl cellulose, polyvinyl alcohol, polycarboxylates are most common antiredeposition agents in detergent formulations.

Stable foams can be produced if surface active polymers such as albumins, carboxy methyl cellulose, and many vegetable gums are included in formulations. When polymers (particularly proteins) are adsorbed at the liquid-air interface they assume configurations significantly different from those in bulk solution; in case of proteins they become partially denatured. The relatively dense structured, adsorbed polymer layer will impart a significant degree of rigidity or mechanical strength to the lamellar walls, producing an increase in stability of the final foam formation. The increase in liquid viscosity will slow the process of film drainage.

Polymeric foam additives offer several advantages like being effective at low concentrations, imparts desirable properties like skin feel and mildness. Polyacrylates have also been reported to improve foam stability as well as quality. Nagarajan[244] has shown that stability of toilet soap lather can be improved by adding small amounts of carbopol - 720 (a trade name of acrylic polyelectrolyte, marketed by B.F.Goodrich) in the formulation. Metocel[245], a water soluble polymer based on cellulose derivatives represents another class of foam stabilizers. The efficacy of polymers to provide stable foams has been utilized as fire fighting aqueous foams[246]. Surfactants like betaines, quartenary ammonium chlorides along with perfluoroacrylate, methacrylate are used in such formulations, their use as soil removers, processing aids, anti redeposition agents are also important[247].

The use of polymers along with surfactants in enhanced oil recovery is well known[248]. The presence of polymer and surfactant in injection water will improve the oil recovery during a water flood. Co-injection of surfactants and polymers gives good oil recovery and low surfactant retention. This method is termed as low tension polymer flood. Austad et al.[249] have used xanthan gum, dodecyl-o-xylene sulfonate along with brine. The improved chemical flooding is possible depending upon the amount of polymer injected behind the surfactant slug.

The use of polymer-surfactant interactions has also been extended to the area of pharmaceuticals and health care. An emulsion containing PEG-400 as the hydrophilic phase, polyoxyethylene cetylether as surfactant and soybean oil as the hydrophobic phase was used in the ratio of polymer : oil : surfactant as 87 : 10 : 3. This was used as a vehicle for soft gelatin capsule[250]. The properties of this vehicle like particle size, temperature dependent sol-gel property met the requirements for encapsulation on new vehicle in soft gelatin capsule (SGC) and suggests that it can form the o/w emulsion state in aqueous environment in the stomach. The rheological properties of such polymer / surfactant emulsions make it advantageous for use in other dosage forms, such as suppository cataplasm of liniment.

Moudgil et al.[251] have shown that competitive adsorption of polymer and surfactant on solid substrates are useful in drug-delivery systems, solid state separations, dispersions and stability of particulate systems. They have discussed the competitive drug delivery in pharmaceutical applications. The role of preservative - the surfactant and the efficacy of polymer adsorption on the carrier substrate and modification of solvent properties to adsorb selectively the drug molecule on the carrier are discussed. The use of biocompatible[252] polymers for usage as artificial organs and biosurfactants to provide normal functioning capacity of these newly implanted organs have been reported. The use of artificial organs in case of acute renal failure, acute respiratory distress syndrome has led to significant reduction in mortality.

Micellar enhanced ultrafiltration (MEUF)[253] is a novel separation process for removal of organic solutes from aqueous streams. One important modification of MEUF is the use of polymer / surfactant complexes instead of using micelles alone[254]. The automated vapour pressure method is used for solubilization of trichloroethylene (TCE). The polymer used is poly (styrene sulfonate) and surfactants used are cetyl pyridinium chloride and N-hexadecyl-pyridinium chloride. The presence of this polyelectrolyte causes a small decrease in the ability of cationic surfactant to solubilize TCE but reduces the amount of surfactant required for the solubilization to occur.

During the manufacturing of synthetic fibres, a spin finish is applied to the yarn to control static electricity and ensure proper winding of yarn to the bobbin. Spin finishes are generally composed of lubricant, emulsifier having surfactant / polymer mixtures, an antistatic agent to impart special characteristics to the finish. Moreover, polymers like poly (acrylic acid) along with antistatic agents, surfactants, thickeners are used in textile processing. During textile processing, the textile fibres are subjected to much mechanical handling. To prevent damage during knitting and weaving, fibres are treated with speciality chemicals. These formulations containing polymers like PAAc and surfactants with other components have proved to be successful for the treatment of nylon fibre[255].

Polymer-surfactant interactions play a major role in agrochemicals both for formulations and optimization of biological efficacy[256]. Interactions between water-soluble polymers and surfactants used as spray drift control additives in spray tank mixtures for pesticides. Nonionic polymers like PVP, PEO and PVA are used along with sodium dodecyl benzene sulfonate in such compositions[257].

Surfactants and polymers are also used in areas of electronic printing, magnetic recording etc. With the advent of microcomputer technology there has been an increased demand for obtaining hard copy outputs of electronically stored documents. The placement of electronic document creation and management systems in office environment is occuring with increasing frequency. These devices allow documents to be created, manipulated and stored in electronic form. This technological change has resulted in demand for improved methods of obtaining hard copy images of these electronic signals and consequently numerous printing technologies have emerged to meet this demand. In an electronic fluid the following components are required as dispersion media - components having low viscosity and allow particles faster migration. Surfactants are used and due to low surface tensions the size of droplets becomes smaller in spray solutions. Polymers are used as a stabilizer for the surfactant[258]. The purpose of the stabilizer is to help 1) disperse the dry particles in dispersion medium; 2) to stabilize particle against flocculation and to fix the toner particle to the paper after the development of the latent image. Other things include charge control agent and particles which function as colourants.

In magnetic media also surfactants are used to disperse particles uniformly in organic solvents. The polymer plays the role of a binder. The surfactant optimises the magnetic properties and reduction in milling time. The important role of binders is to avoid coatings with poor surface quality and maximize the amount of magnetic material in a coating[259].

Gelatin is a biopolymer derived from the denaturation of collagen and is widely used in food and photographic industries. The formation of gelatin - surfactant complexes is particularly relevant in the later application since surfactants are commonly incorporated into gelatin containing solutions to promote emulsification and to control surface tension during coating operations. The rheology, surface tension, equilibrium dialysis studies of gelatin - surfactant systems are very important[260].

1.10 Scope of the Present Work

The synergism in properties of surfactants and polymers in aqueous solution has been the focus of intense fundamental and applied research. The large polymeric structures are usually rigid and static in nature, compared to surfactant micelles which have a very dynamic nature. Aqueous solutions of both polymers and surfactants together exhibit properties which are exploited in many industrial fluids.

In the past, most of the studies have focussed attention on anionic surfactants with nonionic polymers. It is only recently that studies of cationic and nonionic surfactants and studies on polyelectrolytes have become subjects of great interest. Due to large sized head group of cationic and nonionic surfactants, the physical looping of the surrounding polymer is hampered. Again, the nature of polymer also influences the extent of interactions with surfactants.

In the present studies the surfactants chosen were Cetyl trimethyl ammonium bromide (CTAB) and nonionic Triton X100. They are widely used and widely studied surfactants, but very few studies on polymer - surfactant interactions with these surfactants have been done. The polymers chosen for these studies were homopolymers of acrylamide, acrylic acid and their copolymers. Both polyacrylamide and polyacrylic acid were chosen keeping in mind their widespread use in enhanced oil recovery, textile sizing and other important applications.

A review of available literature points out that most of the work done in this field has been done using commercially available polymers. In the present work, the aim was to use self synthesized and characterized polymers for studying the interaction with surfactants. The details of synthesis and characterization like various methods adapted for evaluation of reactivity ratios, empirical equations to calculate activation energy values from the thermograms along with the usual spectroscopic techniques are mentioned. The viscosity of polymer solutions have also been studied.

The thesis also has a comprehensive review of literature on various experimental investigative methods used for studying polymer - surfactant interactions and the major fields of applications are summarized. The physicochemical characterization of polymer - surfactant systems has been done and thermodynamic and interfacial parameters are also evaluated. Different methods like surface tension, conductance, fluorescence spectroscopy, small angle neutron scattering (SANS) have been used for the studies. The thermodynamic and interfacial parameters give details of the energetics and solution properties of the process which are key to a number of performance properties. Finally, the summary and the conclusions drawn from the current work are presented.