

CHAPTER - 1

INTRODUCTION

1.1 Surfactants

Surfactants or surface active agents are a special class of versatile amphiphilic compounds that possess spatially distinct polar (hydrophilic head) and non-polar (hydrophobic tail) group.¹ They show interesting phenomena in solution by modifying the interfacial and bulk-solvent properties. The unusual characteristic properties of surfactants in solution especially at the interfaces owe it to the presence of distinct hydrophilic as well as hydrophobic domains in the same molecule.^{2,3} In view of its amphiphilic nature and distinctive capability of lowering the interfacial tension, surfactant finds applications in almost every aspects of our daily life directly or otherwise in household detergents and personal care products, in industrial process as in pharmaceuticals, food processing, oil recovery and in nanotechnologies, etc.³⁻⁸ Detergents, a term often used interchangeably with surfactants especially the anionic ones, refer to a combination of synthetic surfactants with other substances - organic or inorganic - formulated to enhance functional performance specially as cleaning agents.⁸ Colloids and surface science have emerged as a versatile interdisciplinary subject, which have made inroads, inter alia, into the study of mimetic chemistry that play a vital role in understanding a variety of functions in the living cells and also the intricate life processes.⁹⁻¹¹

1.2 Classification of Surfactant

Generally, based on the nature and the type of the surface active moiety group present in the molecule, surfactants are classified as anionic, cationic or non-ionic surfactants and in case both cationic and anionic centres are present in the same molecules, they are termed as zwitterionic (amphoteric) surfactants.^{1,3} Figure 1.1 represents a schematic representation of a surfactant molecule. Anionic surfactants, which are relatively less expensive, are employed in an extremely wide variety of surfactant based applications. While anionic surfactants mostly contain carboxylates, sulfonates, sulfates or phosphates moiety as hydrophilic head group, it is often an amine or ammonium groups in case of cationic surfactants. On the other hand, non-ionic surfactants generally have ethylene oxide chains or hydroxyl groups as polar centre and are less reactive compare to the ionic ones.

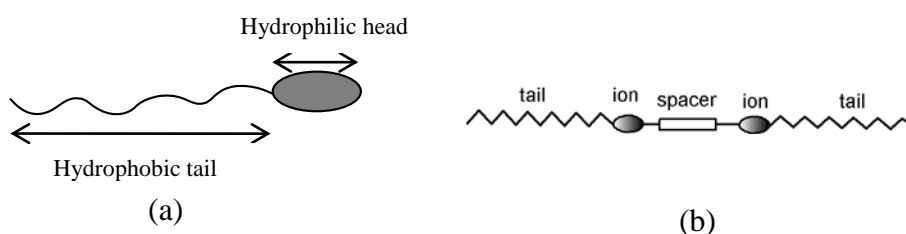


Figure 1.1: Schematic representation of (a) a typical surfactant molecule, (b) a Gemini Surfactant

Zwitterionic surfactants contain both cationic and anionic centres, the ionic behaviour of which is altered according to pH of the solvent. These surfactants are effectively used in personal care and household cleaning products because of the excellent dermatological properties of the surfactants. There is yet another newer class of surfactants known as Gemini

(or dimeric) surfactants which are considerably much superior to the conventional surfactants in many ways.¹² Gemini surfactants (Figure 1b) consist of two hydrophobic tails each attached to a hydrophilic head group connected at the level of head groups by a spacer group.¹³⁻¹⁶ The length and type of this spacer moiety dictates the conformation of the dimeric molecule having a high diffusion rate, high surface activity, and low CMC.¹⁷ In recent years, studies on Gemini surfactants are being directed towards changes associated not only with the variation in the length of the spacer group but also with the introduction of various substituent groups within the spacer.¹⁷⁻¹⁹ Some representative surfactants along with their chemical formulae are listed in Table 1.1.

Table 1.1: Some representative examples of surfactant

Class	Examples	Molecular structure
Anionic	Sodium stearate	$\text{CH}_3(\text{CH}_2)_{16} - \text{COO}^- \text{Na}^+$
	Sodium dodecyl sulfate	$\text{CH}_3(\text{CH}_2)_{11} - \text{SO}_4^- \text{Na}^+$
	Sodium dodecyl benzene sulphonate	$\text{CH}_3(\text{CH}_2)_{10} \text{C}_6\text{H}_4 - \text{SO}_3^- \text{Na}^+$
Cationic	Laurylamine hydrochloride	$\text{CH}_3(\text{CH}_2)_{11} \text{NH}_3^+ \text{Cl}^-$
	Hexadecyltrimethylammonium bromide	$\text{CH}_3(\text{CH}_2)_{15} \text{N}^+(\text{CH}_3)_3 \text{Br}^-$
	Tetradecyltrimethylammonium bromide	$\text{CH}_3(\text{CH}_2)_{13} \text{N}^+(\text{CH}_3)_3 \text{Br}^-$
Non-ionic	Polyoxyethylene(4)dodecanol	$\text{CH}_3(\text{CH}_2)_{11} - \text{O} - (\text{CH}_2 - \text{CH}_2\text{O})_4 \text{H}$
	Polyoxyethylene(9)hexadecanol	$\text{CH}_3(\text{CH}_2)_{15} - \text{O} - (\text{CH}_2 - \text{CH}_2\text{O})_9 \text{H}$
Zwitterionic	Dodecyl betaine	$\text{C}_{12}\text{H}_{25} \text{N}^+(\text{CH}_3)_2 \text{CH}_2 \text{COO}^-$
	Dodecyl dimethylammonium acetate	$\text{CH}_3(\text{CH}_2)_{11} (\text{CH}_3)_2 \text{N}^+ \text{CH}_2 \text{COO}^-$
Gemini	Bis (quaternary ammonium bromide)	$\text{C}_{12}\text{H}_{25} \text{N}^+(\text{CH}_3)_2 - (\text{CH}_2)_8 - \text{N}^+(\text{CH}_3)_2 \text{C}_{12}\text{H}_{25} \text{Br}^-$

1.3 Micellization

One of the most interesting properties of surfactants in solution is their ability to self aggregate to form association colloids known as micelles, accompanied by an overall decrease in the free energy of the system.^{2,4} At very low concentration, the surfactant molecules are preferentially adsorbed at air water interface with its hydrophobic tail pointing away from the water surface thereby lowering the interfacial tension.³ As the concentration increases, the adsorption at the air water interface becomes stronger forming a condensed monolayer, known as Gibb's monolayer at the interface after which any further addition of surfactant molecules remain in the aqueous phase.^{2,20} When the concentration of the surfactant molecules in the bulk of the solution exceeds a limiting value, the surfactant molecules self aggregate to form micelle which is manifested by an abrupt change in many physico-chemical properties. A schematic representation of surfactants in solution is shown in Figure 1.2.

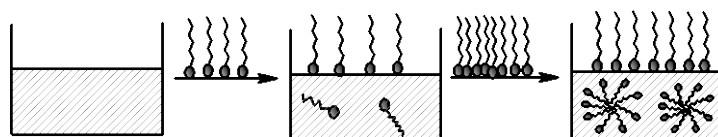


Figure 1.2: Diagram showing surfactant monomers at interface

The narrow concentration range over which these changes occur is known as critical micelle concentration (CMC) and is perhaps the most important characteristic property of a surfactant.^{1,21} The CMC may also be considered

as the concentration at which micelles first appears in solution and is determined from the marked changes in the plot of some physico-chemical properties of the solution against the surfactant concentration. Some of the most commonly employed techniques in determining the CMC include surface tension, conductivity, turbidity, osmotic co-efficient, viscosity, density, spectrophotometer, calorimeter, light scattering, etc.^{2,22-27} A Schematic representation of the changes in some physico-chemical properties of sodium dodecyl sulfate (SDS) is shown in Figure 1.3 .

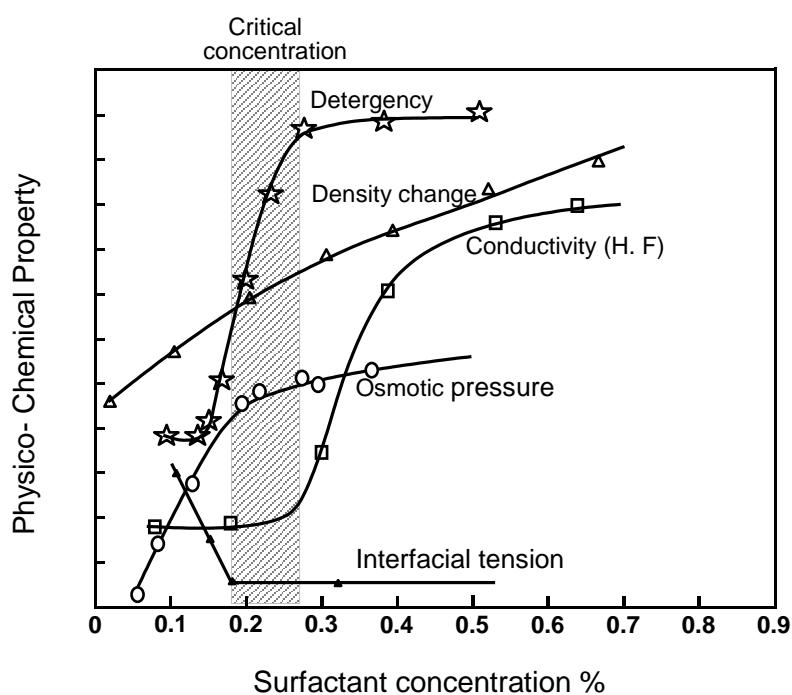


Figure 1.3: Changes in some Physico-chemical properties of SDS (Ref. 4)

Depending on the concentration of the surfactant, the geometric and energetic factors, the size and shape of micelles fluctuate in a given system.³ Size of a micelle is expressed in terms of aggregation number i.e. the number of monomer units present in a micelle. Generally, the aggregation number is

between 20 and 100 for single chain ionic surfactants while large aggregation number of 1000 or more have been reported for non-ionic micelles especially near the cloud point.³ The shape of micelles however may vary from spherical to cylindrical, hexagonal, rod and to lamellar structure depending upon various factors. Micelles are spontaneously formed and addition of more surfactant leads to formation of more micelles increasing the micellar concentration or the micellar growth while the surfactant monomers in the system remain more or less unchanged. The result is a decrease in the average distance between the micelles and hence an increase in inter-micellar repulsion. In order to compensate it, the spherical micelles may transform into worm like micelles thereby increasing the distance between the micelles. The molecular architecture of a given surfactant determines the type of aggregate into which a surfactant associates in aqueous solution. Alternatively, the relationship between the degree of binding of surfactant monomers to an aggregate and the repulsions between the surfactant molecules was reportedly important in determining the aggregate shape.⁸

Of the various structures, the spherical micelle proposed by Hartley² is arguably the most successful one for the purpose of rationalization of observed behaviour of micelles in solution. In a typical spherical micelle, the hydrophobic tails of the surfactant monomer in aqueous solution are preferentially associated to form the core of the micelle while the hydrophilic heads are exposed to the water. Immediate environment of the hydrophobic

core that contains the hydrophilic head along with the counterions constitute the stern layer, which forms the inner portion of the electrical double layer surrounding the micelle. The Guoy-Chapman layer refers to the more diffused outer layer containing the remaining counterions. The outermost boundary of the stern layer constitutes the hydrodynamic shear surface of the micelle while the core of the stern layer is known as the kinetic micelle. In the micelles of polyethoxylated based non-ionic surfactants the core is surrounded by a layer of hydrogen bonded solvent molecules known as Palisade layer.^{2,28,29} Figure 1.4 shows a schematic diagram of a spherical micelle. Generally, un-branched single-tailed surfactants aggregate to form spherical micelles in aqueous solution above their critical micelle concentration.³

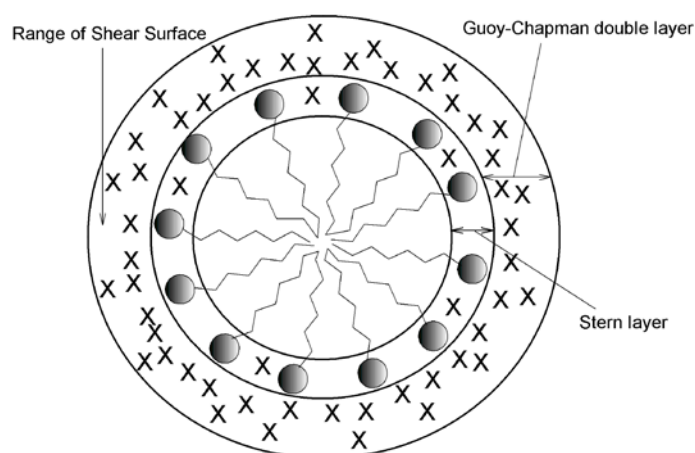


Figure1.4: Structural representation of a Spherical Micelle

The main driving force behind the formation of surfactant aggregates in aqueous solution is believed to be the Hydrophobic effect.³⁰⁻³² The hydrophobic effect promotes the aggregation of the surfactant molecules

while the electrostatic repulsion between the charged head groups opposes it.³³ Aggregation of hydrophobic groups in aqueous solution above a certain concentration is due to the overlap of hydration shells formed around the hydrophobic moieties. Water undergoes a structural enhancement in the hydrophobic hydration shells and upon aggregation, these shells overlaps and part of the water molecules surrounding the individual solutes is released thereby de-structuring the water structure. This accounts for the overall entropy gain upon micellisation.^{2,3}

The tendency of a surfactant to form micelle in solution is largely dependent on the type and nature of the surfactant.^{2,34} Surfactants with longer hydrophobic tail (i.e. more hydrophobicity) generally exhibit greater tendency towards micelles formation. With increase in the length of the hydrophobic tail, the hydrophobic effect becomes stronger and consequently the CMC decreases and larger micelles are formed. The aggregation number also increases with hydrophobic chain length.³⁵ Besides the chain length, branching in the surfactant is also known to affect the CMC and the aggregation number. The CMC of the branched surfactant has been shown to be higher and the aggregation number lower than those of their linear chain.³⁶

1.4 Counterion Variation

Counterions also have a large influence on the aggregation of the surfactant molecules in solution mainly through changes in the ionic strength of the

solution.^{34,36} In addition, the valency of the counterion also influences the CMC to a larger extent. The degree of the counterion binding is due to the balance between the electrostatic forces which pull the counterion towards the oppositely charged head group of micelles and the hydration forces which tends to inhibit the binding.³⁷ The CMC value normally decreases as counterion binding increases. Counterions or ions with opposite charge to that of the surface active moiety of the surfactant are known to have an additional specific effect. For example, sodium bromide was found to induce the growth of micelles of the cationic surfactant cetyl pyridinium bromide whereas sodium chloride did not.³⁸ Aromatic counterions like benzoate, tosylate, salicylate, because of their strong binding at the micellar surface lower the CMC while increasing the counterion binding.³⁹ Salicylate in particular is effective in inducing micellar growth. The counterion binding also increases with increasing counterion hydrophobicity enhancing the micelle formation.⁴⁰ Hydrophobic counterions are interesting as charge carrier or quencher in biomembranes and membrane photochemistry.⁴¹ Addition of cationic surfactant to SDS is a special case of hydrophobic counterion interaction. The CMC of a mixture of anionic and cationic surfactant in aqueous solution is considerably lower than that of the individual surfactants due to the synergistic interaction between the surfactant molecules and they exhibit properties superior to their constituent single surfactant in many surfactant applications.⁴²

1.5 Solvent Effect on the Aggregation of Surfactant

The formation of micelles and its stability is considerably solvent dependent. Solvent polarity and its ability to form H-bond in solution are of considerable interest in understanding the micellar behavior of surfactant. Besides water, micelle formation has been observed in solvents which are analogous to water. There has been report of micelle formation in solvents such as hydrazine, formamide, glycerol, which have high degree of hydrogen bonding.⁴³⁻⁵¹ The ability of the solvent to form hydrogen bonding was considered to be a prerequisite for the micellisation to occur.⁵² However, micelle formation also occurs in solvents which has little or no hydrogen bonding, for examples in solvents like acetone, acetonitrile and dimethyl sulfoxide where the hydrogen bonding ability is minimal.^{53,54} Formation of micelles of SDS and cetyl triethyl ammonium bromide in dimethyl sulfoxide and N,N- dimethyl formamide has also been reported.⁵⁵ More than the H-bond or the electrostatic forces criteria, changes in the solvent hydrophobicity are expected to play a role in determining the micellar behaviour. Besides the hydrophobicity of the surfactant molecule, hydrophobicity of the solvent media also plays a critical role in micellisation process.^{45,56-59} The more hydrophobic the solvent media, lesser is the tendency of the surfactant molecules to form micelle. In non polar solvents which offer environment similar to the hydrophobic part of the surfactant, the self-aggregating tendency of the surfactant is reduced.⁶⁰ Addition of small amount of an organic solvent has been known to produce marked changes in

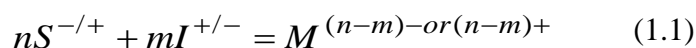
the CMC thereby highlighting the importance of co-solvent in the micellisation process.^{56,61} The micellar behaviour is greatly influenced by the presence of co-solvent due to the tendency of the added organic solvent either to break or make the water structure through solvation of the hydrophobic tail of the surfactant by the hydrocarbon part of the organic solvent.⁴⁵ It is reported that the presence of ethylene glycol delayed the micelle formation in SDS.⁴⁵ Ethylene glycol acts as the water structure breaker and in the aqueous phase it disrupts the water structure enforced by the dissolved hydrophobic group thereby decreasing the entropy increase on micellisation. The tendency to form micelles in non polar solvents (reverse micelle) like benzene, carbontetrachloride, decreases in general with increase polarity of the solvent.⁶⁰ The solvent effect on the micellar behavior in case of sodium 2,6-di-n-dodecyl-naphthalene-1-sulphonates in benzene and n-decane has been reported by Heilweil⁶² highlighting the role of co-solvent and its importance in understanding the phenomenon of formation of micelles.

1.6 Thermodynamics of Micellization

The primary reason for the formation of the molecular aggregates is the overall decrease in the free energy of the system resulting from the preferential self association of the hydrophobic hydrocarbon chains of the surfactant molecules accompanied by desolvation. The formation of micelles disrupts the iceberg structure of water surrounding the non polar segment of

the surfactant with a resultant gain in entropy and heat content. The process of micellization has mostly been treated theoretically either by applying the Law of Mass Action⁶³ to the equilibrium between monomers and aggregates or by considering the micelles as a separate but soluble phase, the so called pseudo phase separation model.⁶⁴

According to Mass Action principle, micellization of ionic surfactants ($S^{-/+}$) along with counter ion ($I^{+/-}$) can be represented as



where n is the aggregation number and m is the number of counterions that associate with the ionic micelle. Neglecting charges on the surfactant and the counterion, the equilibrium constant or micellization constant can be written as

$$K_M = \frac{[M]}{[S]^n[I]^m} \quad (1.2)$$

The free energy of micelle formation expressed per mole of monomer unit (ΔG^0) is then given by

$$\Delta G^0 = RT(-1/n \ln[M] + \ln[S] + m/n \ln[I]) \quad (1.3)$$

At CMC, $[S] = [I] = CMC$ and since n is large $1/n \ln[M]$ may be ignored (for very small fraction of surfactant ions form micelles), then we have

$$\Delta G^0 = (1 + f)RT \ln CMC \quad (1.4)$$

where $f = m/n$ is the fraction of counterion bound to the micelle.

The Mass Action treatment predicts increase in the monomer concentration, although at much reduced rate above CMC. However, it fails to account for the variations in aggregation numbers and is generally not applicable to multicomponent micelles and systems in solubilizates.

In Pseudo-Phase Separation Model, the micelles are considered to form a separate phase (pseudo phase) within the system at and above the critical micelle concentration. The increase of the surfactant concentration above the CMC results into formation of micelles while the monomer concentration remains constant. Above the CMC, both the micelles and the monomers are present and the two phases are in equilibrium:



Since the two phases are in equilibrium, their chemical potential must be equal,

$$\mu_m = \mu_M \quad (1.5)$$

where, μ_m is the chemical potential of the monomer in solution and μ_M is the chemical potential of the micelles in pseudo phase. Then,

$$\mu_m^0 + RT \ln a_m = \mu_M^0 + RT \ln a_M \quad (1.6)$$

where, μ_m^0 and μ_M^0 are the standard chemical potentials of the monomer and micelles with activities a_m and a_M respectively.

The monomer concentration in the micellar solution which is assumed to be constant is equal to the CMC and for the pseudo phase, $a_M=1$. The standard free energy of micellization can be written as

$$\Delta G_M^o = (1 + f)RT \ln X_{cmc} \quad (1.7)$$

The Pseudo Phase Model, besides its simplicity, has the added advantage of treating micelles containing number of components including mixed micelles.

The two models have been shown to merge asymptotically with increasing micellar aggregation number giving similar expression for G_M^o . The enthalpy and the entropy of micellization are given by the relations

$$\Delta H_M^o = (1 + f)RT^2 \left[\frac{\delta(\ln X_{CMC})}{\delta T} \right] \quad (1.8)$$

and

$$\Delta S_M^o = \left[\frac{\Delta H_M^o - \Delta G_M^o}{T} \right] \quad (1.9)$$

Neither the mass action model nor the phase separation model is rigorously correct and the computed thermodynamic functions of micellization will depend to a larger extent on the model and the approximations used. However, the models described above are significant enough to be applied to the systems under investigation and for the evaluation of the associated thermodynamic parameters.

1.7 Dye and its Self Aggregation

Dyes are an important class of organic compounds which contain chromophores, delocalized electron system with conjugated double bonds and auxochromes, electron withdrawing substituent that cause or intensify the colour of the chromophores.⁶⁵ One of the important features of dye is their ability to self aggregate in solution. Despite having similar charges the dye molecules undergo spontaneous aggregation in solution leading to formation of dimers and other higher aggregates.⁶⁶⁻⁶⁸ The aggregation of dye in solution is of extreme importance from fundamental as well as applied viewpoints especially in biological, colloid, surface, textile, photographic and analytical chemistry since the photophysics and photochemical properties are largely dependent on the aggregation of dye.⁶⁹⁻⁷³ The aggregation of dye is accompanied by the changes in the absorption spectra of the dye compared to the individual monomeric molecules.^{72,74} Hence the spectrophotometric method is most commonly employed in the study of the aggregation phenomena of dyes as a function of concentration.⁷⁵⁻⁷⁶ The dye molecules possess strong intermolecular van der Waals like attractive forces between them which favors the dye molecules to aggregate.⁷⁴ The presence of dye molecules causes disruption in the H-bonded water structure and the high dielectric constant of water causes a reduction in the electrostatic repulsion between the charged dye molecules, thus facilitating the aggregation of dye. Besides, the water structure and the hydrophobic interactions are the predominant factors which enhance the aggregation of

dye.^{68,77} Aggregation of dyes is strongly affected by dye concentration and its structure, ionic strength, temperature and presence of organic solvent or surfactants.^{70,78} It may increase with an increase of dye concentration or ionic strength and decrease with raising the temperature or adding organic solvents.

Aggregation of dyes also occurs in mixed solvents and in heterogeneous media including micelles.⁷⁹⁻⁸² Aggregation of dyes can be induced by surfactants at low concentrations below the CMC.⁷² Changes in the local microenvironment of the dye in solution can produce measurable spectral shifts. The spectral behavior of the dye vis-a-vis its aggregation is greatly influenced by the nature of the solvent media and exhibits either a bathochromic or hypsochromic shifts in solvents of different polarity.^{83,84} From the aggregation behavior of a large number of synthesized squaraine dyes in aqueous and mixed aqueous-organic solution, Chen et al⁸⁵ reported the importance of hydrophobic effects in the aggregation process by observing that the tendency for aggregation increases as the length of the hydrophobic chain of the dye increases while squaraines with quaternary ammonium head groups exhibited less tendency for aggregation. Wurthner et al⁸⁷ reported the occurrence of dimeric aggregates from the concentration dependence of the dipole moment of some polar merocyanine dyes. From the studies on the dimerization of polar merocyanine dyes they also concluded that hydrophobic effect is one of the major driving forces behind the dye aggregation, which is again controlled by changes within the microstructure

of water around the solute. The solvent dependence of the aggregation behavior of the merocyanine is again confirmed by Ashwell⁸⁷ who reported that the formation of dimeric aggregates is favored in less polar solvents. Goni et al⁸⁸ quantified the monomer and dimer components of the merocyanine 540 using curve fitting techniques and showed that the maximum absorption wavelength of the monomer band was sensitive to polarity changes in the chromophore region and a blue shift indicating a more polar environment. Tatikolov et al⁸⁹ studied the spectral and fluorescence properties of the heterogeneous aggregates formed by some cation-anionic polymethine dyes in weakly polar and non polar solvent media. From a large number of fluorescence and absorption studies on the carbocyanine, thiazine and azo dyes, it has been found that the aggregation behavior of the dye have been very sensitive to solvent polarity.^{68,90} Patil et al⁶⁹ studied the aggregation of thiazine dyes in aqueous and mixed media highlighting the importance of hydrophobic effects in the aggregation behavior of the dye. Recently the effect of the poly electrolytes on the dimerisation of methylene blue had been studied by Ghasemi et al⁹¹ who reported that the addition of the inorganic salts increases the ionic strength of the solvent media promoting the dye molecules to aggregate.

1.8 Dye Surfactant Interactions

Dye surfactant interactions are of great interest in dyeing and photographic industries, in biological and medicinal photosensitization, designing of

supramolecular nanostructures, etc.⁹²⁻⁹⁵ In various dyeing industries, the dye surfactant interaction is important because surfactants are used as solubilizers for various water insoluble dyes.⁹⁶ The sensitivity of dyes to the polarity of the medium in which they are dissolved makes them suitable for studying the spectral changes of dyes in presence of hydrophobic microdomains in aqueous solution.⁹⁷ Dyes are often used for determining the critical micelles concentration (CMC) of surfactants since presence of surfactants affect the electronic spectra of many dyes.^{98,99} For example, Pinacyanol chloride is used to determine the critical micelle concentration of ionic surfactants.¹⁰⁰ Successive addition of small concentration of surfactant changes dramatically the absorption spectrum of a dye and upon increasing the surfactant concentration, dye spectrum shifts from that in aqueous solution to a spectrum of the dye similar to that in apolar solvents when micelles are present since solubilisation of the aggregates occurs into the surfactant micelles.^{101,102} The interactions of dyes with the surfactant either decreases or increases its CMC depending on the nature of the dyes, the surfactant and their aggregation behavior.¹⁰³ Mukherjee and Mysel¹⁰⁴ observed lowering in the CMC value in dye surfactant systems. Rio et al¹⁰⁵ also reported lower CMC value of SDS in SDS - crystal violet system than the one obtained by conductivity method. Presence of surfactant above or below the CMC dramatically changes the solution properties of the dye resulting into changes in the absorption spectra of the dye due to the formation of dye surfactant premicellar aggregates.¹⁰⁶⁻¹⁰⁸ The micelle/water interface favors complex

formation due to absorption of dye from solution and increases the concentration of complexes.¹⁰⁹ Although neutral dyes can induce the formation of submicellar aggregates, they are commonly formed when the charges of the ionic groups of the surfactant and dye are opposite.^{110,111} The dye can participate in the formation of these aggregates through its charged groups which compensate the repulsion forces between ionic surfactant molecules bearing the same charge. Hydrophobic and specific interactions between the hydrophobic alkyl chains of surfactants with the hydrophobic portion of the dye have also been reported to govern dye induced pre-micellar aggregate formation.^{112,113} However, the electrostatic repulsion forces facilitate the interaction between the similarly charged dye and surfactant, and hence, the complexation between such system was found to be lower by two to three orders as compared to systems with oppositely charged dyes and surfactant molecules.¹¹⁴ When two surfactants are present in aqueous dye solution, preferential interaction between the surfactants impact a decrease in the degree of binding of either surfactants to dye molecules.¹¹³

Many investigations on dye surfactant interactions in aqueous system have been studied in the last few decades of which the peculiar behavior in absorption spectra were attributed to the formation of a continuum of dye surfactant aggregates.¹¹²⁻¹²⁰ The formation of these dye surfactant aggregates have been understood in terms of hydrophobic effect.^{118,119} Models of interactions have been proposed in which the observed changes were

attributed to the change in the microenvironment of the dye resulting from its incorporation inside the micelle.¹²⁰ Estelrich and co-workers^{121,122} studied the behavior of pinacyanol dye in the presence of surfactant at different solvent media and found that the transfer of pinacyanol from a polar aqueous medium to a relatively non polar site in the micellar environment or to organic phases affects its spectral properties leading to bathochromic shift. The Menger micelle model¹²³ also predicts the distribution of cationic dye in a large region surrounding the relatively small hydrophobic core. The spectral resolution of overlapping bands for quantitative analysis was studied by Karukatis et al^{124,125} to characterize multiple sites for aromatic chromophore within aqueous and reverse micelles.

1.9 The Molecular Exciton Model of Dye Aggregation

Absorption spectra of dye aggregates usually show large differences when compared with individual monomeric species. From the spectral shift, various aggregation patterns of the dye in different solvent media have been proposed. These differences in the spectral behavior have been explained in terms of molecular exciton coupling theory based on the coupling between the transition dipole moments of the individual dye molecules.^{65,126} According to this theory, the dye molecule is regarded as a point dipole and the excitonic state of the dye aggregate splits into two levels through the interaction of the dipoles.¹²⁷ The spectral shift from the monomer peak position is a function of the magnitude of the transition dipole moment, the

distance between the dipoles, and the slip angle between the chromophore axes and the chromophore center-to-center line.^{12,7} The chromophores should preserve their individual characteristics in the aggregates, i.e. it is assumed that there is negligible overlap of respective molecular orbitals. Moreover, the transition moment of the electronic transition is assumed to be localized in the center of the chromophore and its polarization axis parallel to the long axis of the chromophore. The angle between the line of centres of a column of dye molecules and the long axis of any one of the parallel molecules is called the angle of slippage (θ). Large molecular slippage results in a bathochromic shift and when θ is less than 32° , hypsochromic shift results.

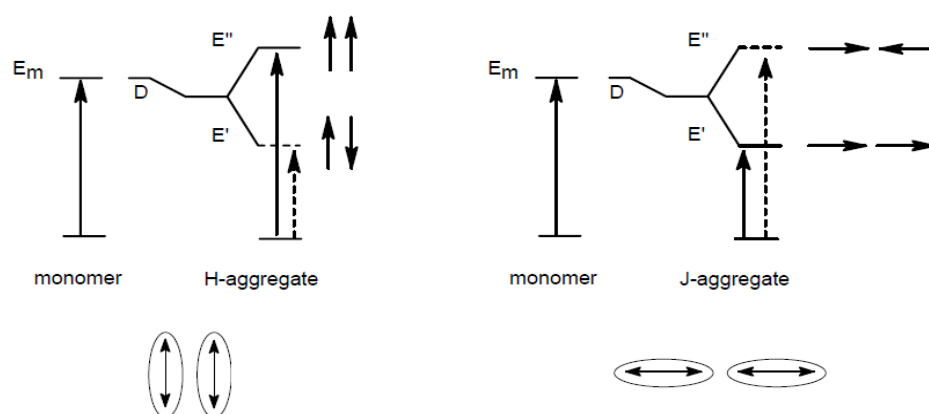


Figure 1.5: Schematic representation of the exciton splitting of the excited state of dye aggregates in a parallel (left) and head-to-tail (right) fashion.

Dye molecules can aggregate either in a parallel (H-aggregation) or in a head-to-tail (J-aggregation) fashion leading to hypsochromic (blue) and bathochromic (red) shifts respectively.^{12,7} A schematic representation of the exciton splitting of dye aggregates is shown in Figure 1.5. In the case of parallel dye aggregation, transition dipoles can either be aligned in a parallel

or in an antiparallel fashion. The former situation leads to an excited state that is higher in energy than the excited state in the monomer due to electrostatic repulsion between the transition dipole moments whereas when the transition dipoles are in a head-to-tail orientation, it leads to a decrease in the excited state energy. The absorption band caused by the dimer consisting of parallel dye dimers will be blue-shifted with respect to that of the monomeric dye. A red shift is observed for the dye dimer consisting of J-aggregates compared to that of the monomer. If the arrangement of the two chromophores is neither in-line nor in parallel, both states are allowed and can be seen in the spectrum as two separate bands or as a broadened band depending on the interaction energy.

1.10 Scope and Objective of the Present Study

One of the most important features of surfactants, as briefly highlighted above, is their tendency to form micelles in solution, which is generally understood in terms of CMC and other associated thermodynamic parameters. Since surfactant forms micelles in solution, understanding the behavior of the surfactant solutions in different mixed media is of considerable relevance not only from fundamental but from applied view points also. A perusal of literature reveals that though the behavior of surfactant solutions has been widely studied both in aqueous and mixed aqueous media, the role of solvent hydrophobicity in the micellization process of surfactant in mixed media including the mixed aqueous organic

solvent has not been adequately appreciated. A proper understanding of the role of the solvent hydrophobicity on the micellar behavior is, therefore, of fundamental importance in designing and characterizing a surfactant and in surfactant based applications.

As discussed earlier, the distinct behavior of the surfactant in solution was clearly understood in terms of hydrophobic effect. With increase in the hydrophobicity of the solvent media, the formation of the micelle is likely to be delayed, which would decrease the CMC of the surfactant due to interaction between the hydrophobic part of the solvent and the hydrophobic tail (hydrocarbon chain) of the surfactant. In mixed aqueous organic solvent media, the presence of co-solvent can significantly affect the micellization of surfactant due to their tendency either to make or break the water structure. It is known that $-CH_2$ group attached immediately adjacent to the polar group of a solvent contribute less to the hydrophobic character. However, with more and more such groups, the hydrophobicity gradually increases that can effectively perturb the water structure and hence delay the micelle formation leading to an increase in CMC. It was observed that the hydrophobic group of ethyl acetate or ethylene glycol solvated the hydrophobic part of an ionic surfactant through hydrophobic interactions thereby causing an increase in CMC. Similarly, Emerson et al¹²⁸ observed increased in CMC from studying the stability of the SDS micelle in aqueous acetamide solution. The inhibitory effect of acrylamide on micelle formation is less in comparison

with that of the ethyl acetate at similar mole fraction and temperature, which clearly showed the importance of the solvent hydrophobicity. With increase in the alkyl chain in alcohol, the CMC was found to increase further indicating the role of solvent hydrophobicity on the micellization process.^{47,129}

Currently, in absence of predictive theoretical approaches towards understanding the solvent hydrophobicity and its effect on the micellar behavior of surfactant, selection of solvent of different hydrophobicity are rather purely on the trial and error research. In view thereof, the study of micellization in solvent media of different hydrophobicity would help in integrating the role of the solvent media and its hydrophobicity towards development of a more comprehensive and predictive fundamental approach in the micellization process besides enriching the contemporary understanding of the micellar behavior. With a view to critically analyzing the role of the solvent hydrophobicity on the self-aggregating systems like surfactants or dyes, it has been considered worthwhile to undertake a systematic investigation on the self-aggregating behavior of some representative ionic surfactants or dyes in aqueous and mixed aqueous organic solvent media of different hydrophobicity.

The addition of electrolyte, for example NaCl, imparts an increase in the dielectric constant of the solvent media and hence enhances the dye

aggregation whereas presence of organic solvent of low polarity inhibits the aggregation process of the dye and a reduction in the formation of dye and surfactant aggregates. Though the dye molecules of similar charges are believed to be associated through H- bonding, van-der-Waals forces and other short range forces, the exact nature of the origin of the dye aggregate is still not clearly understood. From a number of studies on the dimerisation of the certain dyes such as cyanine, thiazine, azo dye, etc. and its interactions with the surfactant, it has been reported that water structural effects and the hydrophobic interactions are the major factors behind the self aggregation of the dye and their binding onto a surfactant. In view of the importance of the water structural features and the solvent hydrophobicity on the aggregation of the dye and its interactions with surfactant, the study on the role of the solvent polarity including the solvent hydrophobicity on the aggregation of not only the self-aggregation of the surfactant or the dye alone but their interactions also in the mixed media would assume greater relevance. Apparently, there has not been enough approaches towards understanding the effective role of solvent hydrophobicity vis-a-vis the hydrophobic effect in the stabilization of the aggregates in solution. With a view to critically analyzing the role of the solvent hydrophobicity, it was considered worthwhile to undertake a systematic investigation on the formation of dye surfactant complex in mixed aqueous media containing some organic solvents with different hydrophobic groups.

An attempt has also made to investigate the iodine iodide equilibrium and the formation of tri-iodide in aqueous and mixed aqueous organic media including polymers like HPC, PEO. The formation of tri-iodide may also be assumed to be formation of aggregates in solution. To the best of our knowledge, no systematic investigation has been carried out to understand how the tri-iodide formation is influenced by change in the hydrophobicity of the solvent media or in presence of a surfactant. Keeping in view the importance of the solvent hydrophobicity in the micellisation process and surfactant based systems including iodine complexes, it was considered worthwhile to investigate the effect of either anionic or non ionic surfactants on the self-aggregation of iodine into tri-iodide in the mixed aqueous organic solvent media.

The thesis, in short, is an embodiment of the results of such investigations towards re-emphasizing the importance of hydrophobic interactions in some self aggregation systems like surfactant, dye including their interactions and also formation of tri-iodide aggregates. We have undertaken a systematic investigation on the self aggregation behavior of some chosen ionic surfactants and also the pinacyanol chloride in mixed solvent media having different hydrophobicity. The interactions of PC dye with an anionic surfactant in different mixed aqueous organic solvent media have also been investigated. A modest attempt has also been made to study the effect of the solvent hydrophobicity on the iodine-iodide equilibrium in presence of an

anionic as well as a nonionic surfactant in presence of some water soluble polymer such as HPC or PEO at very low concentration. We sincerely hope that the results will enrich the contemporary understanding of the self-aggregating systems in different solvent media while highlighting the importance of the solvent hydrophobicity in such systems.

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