CHAPTER I
I: Introduction
This thesis describes a spectroscopic and thermodynamic study of the interactions of some aqueous dyes with some surfactants and polymer-surfactant systems. The background of the work including the nature of surfactants, the nature of dye-surfactant interactions and the nature of polymer-surfactant interactions together with the motivation and the strategy of the work has been presented in this chapter.

I.A: Surfactants and micelles

I.A.1: Surfactants
The word ‘surfactant’ is the abbreviation for the surface active agents, which literally means active at surfaces and interfaces.\textsuperscript{1,2} Surfactants are amphiphilic in nature with a hydrophilic charged head group and a long hydrophobic hydrocarbon tail. The head group of a typical surfactant molecule may consist of an ionic or a highly polar nonionic group and the hydrocarbon chain consists of 7-20 carbon atoms.\textsuperscript{1}

Surfactants have been broadly classified into two groups, viz., naturally occurring surfactants and synthetic surfactants. The typical examples of naturally occurring surfactants are lipids and the bile salts. Depending upon the nature of the hydrophilic head group synthetic surfactants are primarily classified into four sub groups: (i) anionic, (ii) cationic, (iii) nonionic and (iv) zwitterionic. Some common examples of synthetic surfactants of various types are illustrated in the Table I.A(1).

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>Sodium dodecyl sulphate</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{11}\text{SO}_4\text{Na}^+$</td>
</tr>
<tr>
<td>Cationic</td>
<td>Cetyl trimethylammonium bromide</td>
<td>$\text{CH}_3(\text{CH}<em>2)</em>{15}\text{N}^+(\text{CH}<em>3)</em>{3}\text{Br}^-$</td>
</tr>
<tr>
<td>Nonionic</td>
<td>Polyoxyethylene octyl phenyl ether</td>
<td>$\text{C}<em>{14}\text{H}</em>{29}\text{O}(\text{C}_2\text{H}_4\text{O})_n$ (n = 9-10)</td>
</tr>
<tr>
<td>Zwitterionic</td>
<td>Dodecyl betaine</td>
<td>$\text{C}<em>{16}\text{H}</em>{33}\text{NO}_2$</td>
</tr>
</tbody>
</table>

Apart from the above class of surfactants a new group of surfactants known as ‘gemini surfactant’ have been identified. Gemini surfactants differ from the traditional surfactants in that they contain two hydrophilic groups and two (sometimes three) hydrophobic groups.\textsuperscript{3}
I.A.2: Micellization and CMC

Surfactants in solutions have a tendency to adsorb at the interfaces. On increasing the surfactant concentration in aqueous solution, as the concentration exceeds a certain value, the surfactant molecules aggregate to form a nearly spherical shape called micelles (Fig. I.A.1). This critical concentration, characteristic of a surfactant is called its critical micelle concentration. While, in nonpolar medium, the aggregates are oriented in such a way that the polar head groups of the surfactants shielded from the solvent by the hydrocarbon tails. These aggregates have been termed as “reverse micelles”. Amphiphiles with short alkyl influence the hydrogen-bonding structure of water and are termed as hydrotropes. The earliest works on micelle were by J. McBain and Hartley. The solubilization power and other properties exhibited by the micelles are very useful in various fields of science and technology and have been the subject of excellent reviews and reports. The IUPAC definition of CMC is, “There is a relatively small range of concentration separating the limit below which virtually no micelles are detected and the limit above which virtually all additional surfactants form micelles. Many properties of the surfactant solution, if plotted against concentration, appear to change at a different rate above and below this range”. The temperature at which the concentration of the surfactant reaches the CMC is defined as the Krafft point or Krafft temperature. 

![Schematic representation of (a) a surfactant monomer, (b) spherical micelle, (c) reverse micelle and (d) vesicle.](image)

**Fig. I.A.1:** Schematic representation of (a) a surfactant monomer, (b) spherical micelle, (c) reverse micelle and (d) vesicle.

The CMC can be determined by plotting the various physical properties against the concentrations of surfactants which is illustrated by Preston’s classic graph (Fig. I.A.2). The CMC’s of some common surfactants at 298 K in aqueous medium are shown
in Table I.A(2). The CMC of surfactants depend on a number of factors: (a) the length and structure of hydrocarbon chain, (b) the nature of the head group, (c) the presence of additives, (d) the temperature, etc.\textsuperscript{10,41-43}

![Diagram of CMC and physical properties of surfactant solution](image)

**Fig. I.A.2:** Changes of some physical properties of aqueous surfactant solution (in arbitrary scale) with concentration of the surfactant.

**Table I.A(2):** The CMC’s of some common surfactants at 298K in water.\textsuperscript{38-40}

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC/ (mol dm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Dodecyl Sulphate (SDS)</td>
<td>8.0x 10(^{-3})</td>
</tr>
<tr>
<td>Sodium Dodecyl Benzene Sulphonate (SDBS)</td>
<td>1.2x 10(^{-3})</td>
</tr>
<tr>
<td>Cetyl trimethylammonium bromide (CTAB)</td>
<td>9.2x 10(^{-4})</td>
</tr>
<tr>
<td>Tetradecyl trimethylammonium bromide (TTAB)</td>
<td>3.6x 10(^{-3})</td>
</tr>
<tr>
<td>Dodecyl trimethylammonium bromide (DTAB)</td>
<td>16.0x 10(^{-3})</td>
</tr>
<tr>
<td>Polyoxyethylene(20) sorbitan monolaurate (Tween-20)</td>
<td>5.0x 10(^{-5})</td>
</tr>
<tr>
<td>Polyoxyethylene(20) sorbitan monopalmitate (Tween-40)</td>
<td>2.3x10(^{-5})</td>
</tr>
<tr>
<td>Polyoxyethylene(20) sorbitan monostearate (Tween-60)</td>
<td>2.1x10(^{-5})</td>
</tr>
<tr>
<td>Polyoxyethylene(20) sorbitan monooleate (Tween-80)</td>
<td>1.0x10(^{-5})</td>
</tr>
<tr>
<td>Iso-octylphenoxy-polyethoxy-ethanol (Triton X-100)</td>
<td>3.0x10(^{-5})</td>
</tr>
</tbody>
</table>

**I.A.3: Micellar features**

Each micelle consists of a definite number of monomer molecules, termed as aggregation number (N), usually ranging from 10 to 150, which determines its general size.
The sizes of the micelles normally cover the range of 1-10 nm. Ionic micelle forms an electrical double layer, in which the Stern layer encompasses the interfacial region containing the head groups and extends to about one half of the counterions associated with the micelle and water. In case of nonionic micelles, the hydrated polyoxyethylene chains comprise the outer region. A schematic representation of a spherical micelle with illustration of its different regions is shown in Fig. I.A.3. The micelle can assume different shapes depending on the nature of the surfactant and its concentration. Some of the principal morphological structures are shown in Fig. I.A.4.

![Schematic representation of a spherical micelle](image)

**Fig. I.A.3:** A two dimensional representation of the regions of a spherical micelle: ~-hydrocarbon chain, O-head group, X-counterion.

![Schematic picture of some surfactant micelles](image)

**Fig. I.A.4:** The schematic picture of some surfactant micelles: (a) spherical, (b) oblate, (c) cylindrical and (d) lamellar.

Israelachvili, et al. established a relationship between the shape of the surfactant monomer and the aggregate morphology on the basis of packing parameter approach. Some researchers criticised this packing parameter approach for predicting the aggregate
pattern.\textsuperscript{56,57} Dobes \textit{et al.} identified a new parameter, micellar proportion, for expressing the time spent by the analyte in the micellar phase.\textsuperscript{58}

The micellization is governed by the hydrophobic interaction between the alkyl chains and the polar repulsion between the head groups.\textsuperscript{59-61} The formation of micelles in aqueous surfactant solutions occurs primarily as a result of an increase in entropy of the resultant solution,\textsuperscript{6} negative values are rarely observed.\textsuperscript{62,63} The thermodynamic analysis of micelle formation process has been treated using a mass action model and phase separation model,\textsuperscript{64} where the standard free energy of micellization $\Delta G^\circ_{\text{mic}}$ is described by Eq. I.A(1),

$$\Delta G^\circ_{\text{mic}} = -RT\ln\chi_{\text{cmc}}$$ \hspace{1cm} \text{I.A(1)}$$

where, $\chi_{\text{cmc}}$ is the surfactant mole fraction at CMC.

\textbf{I.A.5: Surfactant assemblies other than micelles}
Surfactant may self assemble to form a variety of aggregates including the microemulsions and biological membranes apart from the micelles and reverse micelles. Microemulsions are thermodynamically stable, macroscopically homogeneous dispersions of water-in-oil (W/O) or oil in water (O/W).\textsuperscript{65,66} O/W microemulsions can be formed by dispersing oil in an aqueous surfactant solution and adding a short chain alcohol or amine as a cosurfactant. On the other hand, when water droplets are dispersed in oil the W/O microemulsion is formed.\textsuperscript{67,68} Sometimes a cosurfactant, generally an alcohol of intermediate chain length, is required for microemulsion formation.\textsuperscript{18,69} Biological membranes are made up of phospholipid bilayers. There are two layers of phosphate "heads" with fatty acid "tails" in the biological membranes.\textsuperscript{10,18}

\textbf{I.A.6: Applications of surfactants}
Surfactants play an important role in many aspects of our day to day life ranging from the formulation of industrial products to biological applications.\textsuperscript{2,18,70-100} Apart from the household detergency,\textsuperscript{18,70,71} surfactants are used in the production and processing of foods,\textsuperscript{72-74} agrochemicals,\textsuperscript{75-77} pharmaceuticals,\textsuperscript{78-80} petroleum,\textsuperscript{2,81-83} mineral ores,\textsuperscript{81,83} fuel additives and lubricants,\textsuperscript{84-86} paints,\textsuperscript{85,86} coatings and adhesives,\textsuperscript{85,87,88} in removing hazardous materials from industrial waste water.\textsuperscript{89,90}
I.A.7: Solubilization by micelles

Solubilization into aqueous media is of practical importance in many industrial processes such as detergency, \(^{18,70,71}\) emulsion polymerization, \(^{101}\) micellar catalysis, \(^{10}\) oil recovery, \(^{81-83}\) drug delivery, \(^{102,103}\) etc. The extent of solubilization of the solubilizate depends on the structure of the surfactant molecule, concentration of the surfactant, molecular properties of the solubilised species, temperature and added electrolytes. \(^{104-109}\) The sites on solubilization in the micelles have been determined by various methods including X-ray diffraction, \(^{110,111}\) UV-visible spectroscopy, \(^{112}\) and NMR spectroscopy. \(^{113,114}\)

There is a linear relationship between the free energy of solubilization with the number of carbon atoms of the solubilizate as well as with the number of carbon atoms in the hydrocarbon chain of the surfactants. \(^{115,116}\) A number of experimental techniques have been used to study the solubilization equilibrium, ion-ion, ion-dipole, dipole-dipole as well as hydrophobic interactions of solubilizate with surfactant micelles, such as vapour pressure measurements, \(^{117}\) maximum solubility, \(^{118}\) calorimetry, \(^{42}\) semi-equilibrium dialysis, \(^{119-121}\) etc. Additives considerably affect the solubilization process. \(^{122-127}\) In presence of a polymer the surfactant aggregates are formed which solubilise the solubilizate at concentrations below the normal CMC of the surfactant. \(^{128-133}\)

I.A.8: Micellar catalysis

The presence of micelles markedly alter the reaction rates and equilibria of many organic reactions. \(^{10,134,135}\) The micellar catalysis can be explained in terms of the differences in the reactivity of the substrate in the micellar phase and in bulk medium and the degree and nature of the micelle-substrate binding, which is analogous to the enzyme-substrate binding in Michaelis-Menten kinetics. \(^{119-121,136-140}\) Kinetic considerations are most frequently based on the so-called pseudophase model. \(^{137,141,142}\) The acceleration of the rate of reactions by micelles is often interpreted as solvent effects. \(^{143}\) A number of reactions are carried out in micellar medium; some examples are: electrophilic and nucleophilic reactions, \(^{144,145}\) electrochemical reactions, \(^{146}\) redox reactions, \(^{140,147}\) hydrolysis, \(^{139,158,150}\) electron transfer reactions, \(^{150,151}\) proton transfer reactions, \(^{152}\) electron donor-acceptor equilibria, \(^{153}\) etc. Many micelle catalysed reactions are \(pH\) dependent. \(^{154,155}\) Micellar catalysis has also been successfully explained in terms of an electrostatic model. \(^{156}\) Micellar catalyzed acid dissociation reactions are known to shift acid-base
equilibrium of indicator dyes in micellar medium. The dye-surfactant interactions also involve micellar catalysis.

I.B: Dye-surfactant interactions

Dye-surfactant interactions are important in textile industry as well as chemical research, such as biochemistry, analytical chemistry, environmental chemistry and photosensitization. Therefore, the investigation of dye-surfactant interaction mechanism and its effect on fabrics dyeing has been the subject of many previous works. In order to understand the chemical equilibria, mechanisms and kinetics of micelle-sensitized color and fluorescence reactions the knowledge on the property of micelle-solubilized dye is very important.

Spectral variations of dyes induced by surfactants are also been used to measure the CMC of amphiphiles and surface property of micelles. The studies on the dye-surfactant interactions have been reviewed by Diaz Garcia and Sanz-Medel and Barni et al. There are some other reviews on dye-surfactant interactions by Love et al. Hinze, Kert and Simoncic, Oakes and Dixon, which deals with its industrial and analytical applications. Surfactants, both in micellized and premicellized form, affect the spectral characteristics of dyes leading to a shift in wavelength of maximum absorption or emission and sometimes the appearance of new bands and consequent disappearance of the original ones. Such solvatochromism is observed in all types of dyes, both synthetic, e.g., azo, azine, cyanine, acridine, triphenylmethane, arylmethane, anthraquinone etc. and natural, e.g. curcumin.

I.B.1: Dye-surfactant interactions in submicellar surfactants

If a surfactant is added to a solution of a dye at submicellar concentrations, specific molecular interactions occur between the dye and the surfactant, which primarily occurs with surfactants that are oppositely charged to the dye. In the presence of a dye, the formation of premicellar aggregates at concentrations below the CMC of some surfactants is a well known phenomenon. Molecular complexes having specific and characteristic physicochemical features may be formed at concentrations below the CMC of the surfactant. The characteristic changes occur in the absorption spectra of the dye can be attributed to self-assembly of dye-surfactant complex, formation of dye-
surfactant salt,\textsuperscript{158} ion-pair,\textsuperscript{261,262} dye-rich induced micelles,\textsuperscript{263} induced self-assembly of dyes,\textsuperscript{161} change in microenvironment of the dye\textsuperscript{264} and formation of charge transfer complex.\textsuperscript{213}

Some of the systems studied on the interactions of dyes with surfactants in submicellar concentration ranges of the surfactants are listed in the Table IA(3).

Table IA(3): Some dye-surfactant systems studied in submicellar surfactant region.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Nature of interaction (observations and conclusions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azo dyes-cationic surfactant</td>
<td>Complex formation,\textsuperscript{187,206,263-268} Induced dye aggregation\textsuperscript{195,203,204} Metachromism,\textsuperscript{190} Ion pair formation\textsuperscript{190,202,212,269-271}</td>
</tr>
<tr>
<td>Azo dyes-anionic and cationic surfactants</td>
<td>Complex formation\textsuperscript{272}</td>
</tr>
<tr>
<td>Azo dyes-cationic and cationic gemini surfactants</td>
<td>Ion pair formation\textsuperscript{273}</td>
</tr>
<tr>
<td>Acridine orange-anionic surfactant</td>
<td>Electrostatic-hydrophobic interaction,\textsuperscript{133,274} Induced dye aggregation\textsuperscript{275}</td>
</tr>
<tr>
<td>Alizarin red S-cationic surfactant</td>
<td>Soluble dye-surfactant complex\textsuperscript{276,277}</td>
</tr>
<tr>
<td>Arylazonaphthol dyes-anionic, cationic nonionic and zwitterionic surfactants</td>
<td>No interaction in nonionic or anionic, Complex with cationic or zwitterionic\textsuperscript{172-177}</td>
</tr>
<tr>
<td>Basic yellow 2-anionic surfactants</td>
<td>Ion pair formation\textsuperscript{278}</td>
</tr>
<tr>
<td>Congo red-cationic surfactant</td>
<td>Poorly soluble complex formation\textsuperscript{115}</td>
</tr>
<tr>
<td>Cyanine dyes-cationic surfactant</td>
<td>Induced dye aggregation\textsuperscript{230}</td>
</tr>
<tr>
<td>Cyanine dyes-anionic surfactant</td>
<td>Induced dye aggregation,\textsuperscript{279,280} Metachromism\textsuperscript{233}</td>
</tr>
<tr>
<td>Esters of azonaphtholsulphonate-cationic surfactant</td>
<td>Induced dye aggregation\textsuperscript{193,194}</td>
</tr>
<tr>
<td>8-Hydroxyquinoline-5-sulphonic acid-cationic surfactant</td>
<td>Metachromism\textsuperscript{281}</td>
</tr>
<tr>
<td>Iodaniline dyes-cationic and anionic surfactants</td>
<td>Complex formation\textsuperscript{282}</td>
</tr>
<tr>
<td>Indigo carmine and amaranth-cationic</td>
<td>Complex formation\textsuperscript{283}</td>
</tr>
<tr>
<td>Surfactant Type</td>
<td>Interaction Type</td>
</tr>
<tr>
<td>----------------------------------------------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>Multicharged anionic planar dyes-cationic surfactant</td>
<td>Complex formation</td>
</tr>
<tr>
<td>Metal-chrome azurol S-cationic surfactant</td>
<td>Complex formation</td>
</tr>
<tr>
<td>Phenoxazine dyes-anionic surfactant</td>
<td>Ion pair formation</td>
</tr>
<tr>
<td>Phenazine dyes-anionic surfactant</td>
<td>Induced dye aggregation, Ion pair formation</td>
</tr>
<tr>
<td>Phenazine dyes-anionic and cationic surfactants</td>
<td>Complex formation</td>
</tr>
<tr>
<td>Phenazine dyes-anionic, cationic, nonionic and zwitterionic surfactants</td>
<td>Complex formation</td>
</tr>
<tr>
<td>1-Phenylazo-4-naphthol dye-cationic surfactant</td>
<td>Induced dye aggregation</td>
</tr>
<tr>
<td>Picric acid-cationic surfactant</td>
<td>Ion pair formation</td>
</tr>
<tr>
<td>Pinacyanol chloride-cationic surfactant</td>
<td>Induced dimerization of dye</td>
</tr>
<tr>
<td>Pinacyanol-anionic surfactant</td>
<td>Insoluble dye-surfactant salt</td>
</tr>
<tr>
<td>Rhodamine 6G-cationic surfactant</td>
<td>Salt formation and Induced dye aggregation</td>
</tr>
<tr>
<td>Sulfonephthalein dyes-cationic surfactant</td>
<td>Salt and ion pair formation, Turbidity, Metachromism</td>
</tr>
<tr>
<td>Thiazole orange-anionic surfactant</td>
<td>Induced dye aggregation</td>
</tr>
<tr>
<td>Triphenyl methane dye-anionic surfactant</td>
<td>Complex formation, Induced dye aggregation, Ion pair formation</td>
</tr>
<tr>
<td>Triphenyl methane dyes-cationic surfactant</td>
<td>Ion pair formation</td>
</tr>
<tr>
<td>Xanthene dyes-anionic and cationic surfactants</td>
<td>Induced dye aggregation</td>
</tr>
<tr>
<td>Xanthene dyes-anionic surfactant</td>
<td>Ion pair formation</td>
</tr>
</tbody>
</table>

**I.B.2: Interaction of dyes with micellized surfactants**

All type of surfactant micellar systems are known to dissolve insoluble dyes, disintegrate dye aggregates into monomers or partition soluble dyes via incorporation into surfactant micelles. Generally, hypsochromic and bathochromic shift of...
the original dye bands are observed upon interaction of a dye with oppositely charged
micelles. Micelles affect not only the electronic structure of the dye but also the
$pK_a$ of indicators. The nature of interactions of various types of dyes with micellized
surfactants are listed in Table I.A (4).

Table I.A(4): Some dye-surfactant systems studied in micellized surfactants.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Nature of interaction (observations and conclusions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acridines-anionic surfactant</td>
<td>Localization at the hydrophobic interior and hydrophilic interface of the micelle, Association with micelles</td>
</tr>
<tr>
<td>Acridines-anionic, cationic and nonionic</td>
<td>Association with micelles, CT complex formation</td>
</tr>
<tr>
<td>surfactants</td>
<td></td>
</tr>
<tr>
<td>Alizarin red S-anionic, actionic and nonionic</td>
<td>Association with micelles</td>
</tr>
<tr>
<td>surfactants</td>
<td></td>
</tr>
<tr>
<td>8-Anilino-1-napthalenesulfonic acid</td>
<td>Binding constants decreases with increasing number of ethylene oxide</td>
</tr>
<tr>
<td>ammonium salt-nonionic surfactants</td>
<td></td>
</tr>
<tr>
<td>8-Anilino-1-napthalensulfonic acid</td>
<td>Association with micelles</td>
</tr>
<tr>
<td>ammonium salt-nonionic surfactant</td>
<td></td>
</tr>
<tr>
<td>Arylazonaphthol dyes-nonionic surfactants</td>
<td>Solubilisation</td>
</tr>
<tr>
<td>Azo dyes-anionic surfactant</td>
<td>Molecular interaction with hydrophobic dyes, CT interactions, $pK_a$ shift</td>
</tr>
<tr>
<td>Azo dyes-cationic surfactant</td>
<td>Solvatochromism, Electrostatic interactions, Association with micelles</td>
</tr>
<tr>
<td>Azo dyes-cationic surfactant</td>
<td></td>
</tr>
<tr>
<td>Azo dyes-cationic surfactant</td>
<td>Induced tautomerism</td>
</tr>
<tr>
<td>Azo dyes-anionic and cationic surfactants</td>
<td>Induced tautomerism, Micelles alter enthalpy and entropy of ionization of dyes</td>
</tr>
<tr>
<td>Azo dyes-cationic and cationic gemini</td>
<td>Association with micelles, Solubilization</td>
</tr>
<tr>
<td>surfactants</td>
<td></td>
</tr>
<tr>
<td>Basic yellow 2-anionic surfactant</td>
<td>Association with micelles</td>
</tr>
<tr>
<td>Basic yellow 25 and acid orange 7-cationic</td>
<td>Complex formation</td>
</tr>
<tr>
<td>surfactant</td>
<td></td>
</tr>
<tr>
<td>Cyanine dyes-anionic and cationic surfactants</td>
<td>Hydrophobicity of the dyes increases, Solvatoforhism</td>
</tr>
<tr>
<td>Cyanine dyes-anionic surfactant</td>
<td>Dye hydrophobicity plays the key role, Solubilisation, Aromatic part plays the key role</td>
</tr>
<tr>
<td>Cyanine dyes-anionic, cationic and nonionic surfactants</td>
<td>Localisation at micelle-water interface, Deggregation of the dye</td>
</tr>
<tr>
<td>Cyanine dyes-nonionic surfactant</td>
<td>CT complex formation</td>
</tr>
<tr>
<td>Disperse dyes of N-Alkyl and N-Carboxylic acid naphthalimides-cationic gemini surfactant</td>
<td>Solubilisation</td>
</tr>
<tr>
<td>4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide-cationic surfactants</td>
<td>Complex formation</td>
</tr>
<tr>
<td>2-(4-(Dimethylamino) styryl)-1-methylpyridinium iodide-anionic and cationic surfactants</td>
<td>Dye enters in different positions of the micelles</td>
</tr>
<tr>
<td>2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)-cationic and cationic gemini surfactants</td>
<td>Polarity dependent localisation of dye</td>
</tr>
<tr>
<td>Light yellow-cationic surfactant</td>
<td>Solubilization</td>
</tr>
<tr>
<td>Orange II, direct red 80, indigocarmine-cationic surfactant</td>
<td>Free micelles occur before the dyes become fully saturated with bound surfactant</td>
</tr>
<tr>
<td>(2-P-toluinylnaphthalene-6-sulphonate) and (1-aminonaphthalene-8-sulphonate)-anionic surfactant</td>
<td>Molecular interaction</td>
</tr>
<tr>
<td>Phenazine dyes-anionic surfactant</td>
<td>Association with micelles</td>
</tr>
<tr>
<td>Phenazine dyes-nonionic surfactant</td>
<td>CT complex formation</td>
</tr>
<tr>
<td>Phenazine dyes-anionic, cationic and nonionic surfactants</td>
<td>Association with micelles, CT complex formation</td>
</tr>
<tr>
<td>Pyranine-nonionic surfactant</td>
<td>Modification of dye</td>
</tr>
<tr>
<td>Pyrene-anionic surfactant</td>
<td>Partitioning into micelles</td>
</tr>
<tr>
<td>Pyrene-cationic surfactant</td>
<td>Mixed micelle formation</td>
</tr>
<tr>
<td>Pyridinium N-phenolate betaine dyes-</td>
<td>sphere → rod transition of micelles</td>
</tr>
<tr>
<td>cationic surfactant</td>
<td>Hydrophobic dyes penetrate deeper into the micelle&lt;sup&gt;348&lt;/sup&gt;</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Quinolinium betaine dyes-cationic surfactants</td>
<td>CT complex formation&lt;sup&gt;224&lt;/sup&gt;</td>
</tr>
<tr>
<td>Riboflavin-nonionic surfactant</td>
<td>Association with micelles&lt;sup&gt;349&lt;/sup&gt;</td>
</tr>
<tr>
<td>Rivanol-anionic, cationic and nonionic surfactants</td>
<td>Combined electrostatic-hydrophobic interaction&lt;sup&gt;350&lt;/sup&gt;</td>
</tr>
<tr>
<td>Styryl pyridinium dyes-anionic surfactant</td>
<td>Association with micelles&lt;sup&gt;351&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sulfonephthalein dyes-anionic surfactant</td>
<td>Micellar catalysis&lt;sup&gt;352&lt;/sup&gt;</td>
</tr>
<tr>
<td>Sulfonephthalein dyes-anionic, cationic and nonionic surfactants</td>
<td>Association with micelles, Mixed micelle formation, Metachromism, Micellar catalysis&lt;sup&gt;355,356&lt;/sup&gt;</td>
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<td>Thiazine dyes-anionic surfactant</td>
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The interactions of surfactants of the dyes with other types of systems such as reverse micelles, microemulsions, polymers, polymer membranes, microcrystalline cellulose, proteins, lipid assemblies, nucleic acids, clay minerals, etc. are similar to dye surfactant interactions. The similarities observed for these systems have been attributed to the presence of amphiphilic characters in the aggregates similar to that in the micelles.

Among the various methods used for the study of dye-surfactant interactions in micellar medium, conductometric method, Job’s method, principal component analytical method, Stark effect spectroscopy, Method of continuous variations, potentiometric method, electrical impedance spectroscopy (EIS), along with conventional spectroscopic and thermodynamic methods are worth mentioned. The various interactions of ionic dyes with surfactants of various charge types as a function of the surfactant concentration may be summarized schematically as shown in the Fig. I.A.5.

I.B.3: Acid-base equilibrium of dyes in aqueous micellar medium

The acid-base reactions are studied extensively as proton transfer reactions are all-pervading in chemistry. The acid dissociation reaction in aqueous medium can be represented as,

\[ A^z \rightleftharpoons K_{a,w} B^{z-1} + H^+ \]  

I.A (2)

where, \( A^z \) and \( B^{z-1} \) are the acid and the conjugate base respectively and \( K_{a,w} \) is the acid dissociation constant and represented as \( pK_{a,w} \). The acid-base indicators absorb light and the absorption by the protonated, \( A^z \) and that of the deprotonated, \( B^{z-1} \) species are different. Depending on the medium \( pH \), the equilibrium in Eq. I.A(2) shifts to the left or right with accompanying changes of color. A characteristic property of indicator dye is the \( pK_a \), which is the \( pH \) of the aqueous indicator solution at which the activity of the acid form of the indicator dye is equal to that of the conjugate base form.
Micellar system leads to the shift of acid-base equilibrium of dyes which was first observed by Hartley\textsuperscript{48} and since then the acid-base properties of dyes were studied in micellar media for a number of dyes.\textsuperscript{42,118,158,249,420} The protonation constants of several azo compounds in aqueous solutions of SDS surfactant were studied by Romero et al.\textsuperscript{200} Reeves et al. studied the effect of DTAB and CTAB surfactants on the hydrazo-azo-tautomeric equilibrium of 4-phenylazo-1-naphthol-2,4'-di-sulphonate and the results obtained explained in terms of the formation of kinetically controlled small dye-surfactant aggregates.\textsuperscript{192} The influence of nonionic surfactant TX-100 on the dissociation equilibrium of a number of phenols and naphthols are investigated by Tong and Glesmann.\textsuperscript{421} In each case, an increase in $pK_a$ was observed.

A number of researchers studied the effect of cationic and anionic surfactants on the dissociation equilibria of similar type of aromatic indicators.\textsuperscript{47,118,242,247,248,255,259,349,422} The shift in $pK_a$ of the indicator has been attributed to the association of the dye with ionic micelles.\textsuperscript{10,160,307,357} The color change of an anionic dye induced by a cationic surfactant is similar to the color change observed on increasing pH in absence of the surfactant.\textsuperscript{158,191}
Minch et al. studied the effects of cationic micelles on the acid-base equilibrium of a number of carbon acids and phenols and from the results obtained they concluded that the shift in $pK_a$ of the indicators depends on the hydrophobicity of the carbon acids and phenols.$^{423}$

Hartley and Roe observed that the apparent shift of the $pK_a$ in the micellar medium, is due to the change of the local interfacial proton activity at the surface of the charged micelle as compared to that in the bulk water.$^{182}$ Mukherjee and Banerjee opined that the total apparent shift of the $pK_a$ value in the micellar solutions is due to a shift of the intrinsic $pK_a$ as well as due to the change in local pH or interfacial potential at the micellar surface.$^{40}$ On the other hand, Pal and Jana interpreted that the acid-base equilibrium of an indicator dye, bound to micelle, may be affected not only by an electrostatic potential but also by a local environment.$^{424}$ Fernandez and Fromherz provided a quantitative description of the micelle-induced $pK_a$ shifts of two coumarin dyes, bound to both anionic and cationic micelles by taking into account two factors, viz., the shift due to polarity of the interface and the surface $pH$. $^{425}$ Funasaki suggested that the difference in the bulk and micellar $pK_a$ values is due to lower dielectric constant at micellar surface.$^{426}$ According to Niazi et al. the acidity constant of the indicators viz., methyl orange, methyl red and methyl violet are influenced as the percentages of the surfactants added to the solution of these indicators.$^{427}$

Drummond et al. systematically investigated the acid-base equilibria of various weak acids and bases, viz., sulphonephthalein indicators, azine derivatives and azo indicators in aqueous micellar medium of ionic and nonionic surfactants, ionic micelles having opposite charge to the ionic form of the indicators.$^{242,247,248}$ The variation in the apparent $pK_a$ values in pure water and in the interfacial microenvironment of a micelle is attributed to the difference in intrinsic solvent characters, i.e., dielectric constants of the two solvating media in case of nonionic surfactants. Whereas, in case of phenols, amines and carboxylic acids and the azo indicators were attributed to the contribution of electrostatic micellar surface potential in addition to that due to lower effective dielectric constant of the interface. However, the calculated and observed apparent $pK_a$ of sulphonephthalein indicators in the interfacial microenvironment of micelles of DTAB and that of the azine indicators in micelles of SDS did not agree well. Therefore, in order to account for the differences between the observed and calculated values of the apparent $pK_a$, an additional parameter, ‘interfacial salt-effect’ was proposed. In the case of azine
derivatives, *viz.*, acridine and neutral red in SDS micelles, a specific molecular interaction (either ion-pair or hydrogen bond formation) was believed to contribute to the dielectric and electrostatic effects.

The acid-base equilibrium of indicator dyes depend on the concentration of the surfactants.\textsuperscript{48,242,247,248} Rosendorfova and Sermoncova had reported that the $pK_a$ of sulphonephthalein indicators decreased gradually with an increase in the concentration of cationic surfactant up to the CMC but remained constant above it.\textsuperscript{249} It has been reported by some researchers that the $pK_a$ values varied even when the concentration of the ionic surfactant were varied above CMC.\textsuperscript{48,220,242,247,248,349,427,428} The acid-base equilibrium of a dye and thus the apparent $pK_a$ is largely affected by the ionic strength of the medium.\textsuperscript{242,249} The cationic surfactant induced deprotonation of sulphonephthalein indicators are found to be suppressed by sodium chloride.\textsuperscript{249} Diaz Gercia *et al.* observed an increase in $pK_a$ of the dye-surfactant association complex with addition of electrolytes.\textsuperscript{158} On the other hand, Miyashita and Hayane pointed out that addition of strong electrolytes might assist the process of inclusion of the dye into micelle.\textsuperscript{259}

Some studies on the competitive counter ion binding results that the acid dissociation of an indicator at micellar surface is related to the concentration of the catalytically active ions such as $H^+$ and $OH^-$ at the micellar surface.\textsuperscript{316,426,429,430} A pseudophase ion exchange (PIE) model, has been developed and applied successfully to a number of protonation-deprotonation equilibria studies.\textsuperscript{142,199,431,432-436} The PIE model sometimes fails near the CMC.\textsuperscript{433} Bunton *et al.* carried out a quantitative treatment of the effects of cationic micelles on the $K_b$ of benzimidazole, phenols and oximes by using the PIE model and the calculated parameters indicated the absence of a significant micellar effect on the $K_b$ of these acids.\textsuperscript{431} Funasaki investigated the acid dissociation constant of thymol blue and first order rate constants of the basic hydrolysis of $p$-nitrophenyl butyrate in presence of CTAB, sodium bromide and 2-amino-2-methyl-1,3-propanol/HBR buffer and treated the results applying the electrostatic and ion-exchange models and both the models were found to be similar under experimental conditions.\textsuperscript{426} He *et al.* observed that the intrinsic acidity constant of the indicator, *viz.*, pyridine-2-azo-p-dimethylaniline (PADA) at micellar surface is close to that in water.\textsuperscript{199} The Poission-Boltzmann Equation (PBE) model has been developed for the ionic distributions at micellar interfaces where
the ion distributions are computed using Poission-Boltzmann equation and was applied to many organic reactions at micellar surface involving H\(^+\) and OH\(^-\) ions.\(^{437-441}\)

Pesavento has introduced another model for treating protonation equilibria of indicator dyes.\(^{156}\) The model considers micelles as a true microphase behaving like a strong ion exchange resin by setting Gibbs-Donnan equilibria at the interface between the micelle and the bulk aqueous medium. Fuguet \textit{et al.} employed a solvatochromic method to determine the CMC, partition coefficient of indicators and the solvation properties of the micellar system.\(^{442}\) Saha \textit{et al.} observed that the difference between the \(pK_a\) values of benzimidazoles, BI’s in water and TW80 is due to smaller dielectric constant (\(D_{\text{eff}}\)) in the interfacial region, whereas, the difference in the \(pK_a\) values in water and SDS is due to low \(D_{\text{eff}},\) surface potential and specific molecular interaction between the proton of the monocations of BI’s and the sulfate head group of SDS micelles.\(^{443}\) Ahmadi \textit{et al.} carried out a study on the effect of anionic and cationic surfactants on dissociation constants of some azo dyes and observed that the anionic surfactant SDS can change the color of some indicators that do not bear SO\(^3^-\) moiety in their structure by either repulsive negative forces or hydrogen bonding.\(^{444}\)

Yuanqin \textit{et al.} studied the effect of anionic, cationic and nonionic micelles on the acid-base equilibrium of thymol blue and bromothymol blue.\(^{445}\) Saikia and Dutta studied the effect of nonionic surfactant micelles on the \(pK_a\) of sulphonentalein dyes.\(^{446}\) The \(pK_a\) values are found higher in micellar medium and the values increase with increasing surfactant concentrations.\(^{446}\) Safavi \textit{et al.} reported that the presence of imidazolium-based ionic liquids (ILs) leads to decreased \(pK_a\) values of sulfonated indicators because of the stronger electrostatic interaction of cationic ILs with the basic forms of the indicators with more negative charge.\(^{447}\) Niazi, \textit{et al.} spectrophotometrically investigated the dissociation equilibrium of fluorescein in aqueous micellar solution at 298 K and at ionic strength of 0.1 mol dm\(^{-1}\). They observed that the \(pK_a\) values of fluorescein are influenced as the percentages of an anionic and a cationic surfactant and the nonionic surfactant TX-100 only affects \(pK_{a1}\.\(^{428}\) Werawatganone and Muangsiri reported that in the presence of anionic and nonionic micelles the \(pK_a\) of bromothymol blue increases confirming the facilitation of neutral species (HB).\(^{181}\) For NR, anionic micelles induce NRH\(^+\) formation and an increase in \(pK_a\) is observed. On the other hand, the \(pK_a\) of NR decreases since NR formation is promoted in the presence of CTAB and TW80 micelles.\(^{181}\)
Zarei et al. applied rank annihilation factor analysis (RAFA) for spectrophotometric analysis of acid-base equilibria of some sulfonephthalein dyes at 25°C and an ionic strength of 0.1 mol L\(^{-1}\). They reported that interaction with surfactants induces significant \(pK_a\) shifts, which can be rationalized in terms of hydrophobicity and electrostatic interactions.\(^{448}\) Wang et al. reported outstanding stabilization of the hydrophobic dye curcumin in aqueous cationic surfactant micelles due to strong interactions between the phenoxide ion of the dye and the cationic surfactant.\(^{100}\) The strong interaction of Cur\(^{-1}\) with head groups of the cationic surfactant results in a lowering of the apparent \(pK_a\) values when micelles with bromide counterions are used. Protonation equilibria of indicators are also affected by micelle like other systems such as polyelectrolytes,\(^{449}\) microemulsion,\(^{386}\) proteins,\(^{392}\) reversed micelles,\(^{186}\) polymers,\(^{388}\) etc.

**I.C: Polymer-surfactant interactions**

In an aqueous polymer-surfactant mixture the surfactant provides control over interfacial tension,\(^{450}\) emulsification capacity\(^{451,452}\) and colloidal stability,\(^{453,454,455}\) while the polymer provides control of the rheological properties\(^{456,457,458}\) as well as colloidal stability.\(^{459}\) The high solubilization power of the mixed polymer-surfactant system makes such systems highly attractive for industrial applications.\(^{460,461}\) Many types of surfactant-polymer interactions can occur depending upon the nature of both the surfactant (cationic, anionic, or nonionic) and the polymer (neutral or polyelectrolyte).\(^{462}\) A number of excellent reviews and texts are available on this subject.\(^{462-477}\) These literatures indicate that most of the research carried out in this field focused on the interaction of anionic surfactants (typically SDS) with a variety of polymers\(^{108,458,478-483}\) and has involved a broad range of experimental methods including measurements of electrical conductivity,\(^{484}\) viscosity,\(^{485}\) surface tension,\(^{484,486-488}\) cloud point\(^{489-491}\) and solubility; binding studies using both dialysis and ion-specific electrodes; spectroscopic techniques, viz., absorption spectroscopy,\(^{455}\) fluorescence spectroscopy,\(^{488,492}\) NMR spectroscopy,\(^{493-495}\) light scattering\(^{455,496-498}\) and small angle neutron scattering (SANS);\(^{496,499,500}\) thermodynamic studies including calorimetry\(^{498,502-505}\) and volumetric methods.\(^{506-508}\)

Polymer-surfactant interaction involves a surfactant aggregation process analogous to the normal micellization process.\(^{509}\) The onset of surfactant molecules binding on the polymers is signified as the critical aggregation concentration, CAC. If the value of CAC is greater than that of CMC, the situation would suggest that the surfactant molecules
would prefer to micellize with themselves instead of forming mixed micelles, which would otherwise indicate that no polymer-surfactant interactions exist at all.

The interaction of surfactants with water soluble polymers was first reported by Saito in 1950. However, in 1967, Jones provided the conceptual framework to describe the interaction between surfactants and polymers that is still used today. Based upon observations from NMR experiments using the SDS/PEO system, the model presented by Jones was further modified by Cabane which is known as the "necklace model" of Cabane. From equilibrium dialysis and ion electrode measurements Nagarajan postulated that surfactant-polymer complex formation process is a cooperative one, though not as strongly cooperative as micelle formation itself. Nagarajan’s model has been used to predict the behaviour of various polymer-surfactant systems.

The main driving force for association of surfactant molecules in presence of polymers is thought to be the hydrophobic interaction. It has been observed that cationic surfactants interact with nonionic polymers less strongly than anionic surfactants. However, Dhara and Shah had showed that the interaction between water soluble synthetic polymers and SDS is not governed by the hydrophobicity of the polymers alone. Nagarajan and Kalpakci viscometrically examined the polymer-micelle association monitoring the conformational changes induced in the polymer.

Picullee et al. reported that the nature of the polymer-micelle association is strongly influenced by the nature of the polymer. Medeiros and Costa have showed that for non-amphiphilic polymers the association process can be described as one in which the cooperative micelle formation process of the surfactant is facilitated by the polymer-micelle association. However, a non-cooperative binding is observed in case of some amphiphilic or hydrophobically modified polymers. The interactions between the binding of dodecyltrimethylammonium chloride (DTAC) to amphiphilic polyelectrolytes of different hydrophobicity has been investigated and it has been observed that, in aqueous surfactant free medium these polymers can form hydrophobic microdomains and are referred to as polysoaps. Almgren et al. and Piculell et al. proposed that the interaction of surfactants with hydrophobically modified polymers is analogous to mixed micelle formation. The mixed micellar behaviour of the binary mixtures of zwitterionic/cationic surfactants and triblock polymers have been reported by various researchers. Using cryo-transmission electron spectroscopy (cryo-TEM) studies Shimoni and Danino reported the formation of polymer-surfactant mixed micelles.
between nonionic block copolymer and surfactant mixtures with characteristic diameters.\textsuperscript{525}

From isothermal titration calorimetry (ITC) studies Dai \textit{et al.} showed that SDS does not bind with low molecular weight polyethylene glycols, PEG (MW 400 Daltons). While with increasing molecular weight of the polymers form 900 to 1450 Daltons, an endothermic peak which is attributed to the formation of an SDS-PEG aggregation complex has been observed. Again, when the molecular weight exceeds 3350 Daltons, an endothermic peak followed by an exothermic peak has been observed.\textsuperscript{504,526} The results from the ITC curves suggested that the interaction between the polymer and the surfactant is controlled by a subtle balance of two mechanisms: the polymer induced micellization at low SDS concentrations (endothermic process) and re-hydration of the PEG chains to form the ion-dipole aggregation at high SDS concentrations (exothermic process).\textsuperscript{527} From SANS studies Cabane suggested the formation of necklace-like structure in which the PEO can either be solubilised in the hydrophobic core of SDS micelles or absorbed on the surface of SDS micelles.\textsuperscript{528,529} However, Wesley \textit{et al.} also proposed the formation necklace structure between SDS and star PEO from SANS study.\textsuperscript{530} Cui \textit{et al.} reported that the anionic polyelectrolyte hydroxypropyl guar (HPG)-borate does not promote DTAB micellization or phase separation normally seen on mixing oppositely charged polyelectrolytes and surfactants.\textsuperscript{531}

Freyssingeas \textit{et al.} examined the effect of PEG on the SDS/pentanol bilayers in the lamellar phase. They observed that increase in PEG concentration decreases the repulsive forces between the lamellae.\textsuperscript{532} Using ITC, ion-selective electrode (ISE), surface tension and dynamic light scattering measurements, Wang and Tam investigated the interaction of SDS with poly(acrylic acid) (PAA). They observed that the hydrocarbon chains of SDS cooperatively bind to apolar segments of PAA, driven by hydrophobic interaction. The interaction is entropically and enthalpically favoured.\textsuperscript{533,534} They also examined the effect of polymer charge density of PAA at different degrees of neutralization (α) on the binding of DTAB to PAA by using calorimetric titration and light scattering techniques.\textsuperscript{535}

Sachko \textit{et al.} showed that pronounced associative processes occurred in aqueous systems containing an anionic polyelectrolyte (polymethacrylic acid) (PMAA) and an anionic sodium dodecylbenzenesulfonate (SDBS) surfactant. They reported that the hydrophobic interactions between the nonpolar SDBS moiety and PMAA macrochain hydrophobic fragments might play the key role.\textsuperscript{536} Hansson theoretically analysed the
interaction of ionic surfactants with polyion networks of oppositely charged in an aqueous environment by applying the theory of surfactant ion-polyion complex salts.\textsuperscript{537,538} Ali \textit{et al.} had showed that gemini surfactants interact strongly with polyvinylpyrrolidone (PVP) as compared to conventional surfactants.\textsuperscript{539}

Conductometric and surface tensiometric studies on the interaction of surfactants with bovine serum albumin (BSA) were carried out by a number of researchers.\textsuperscript{540-545} The protein-surfactant association is a cooperative phenomenon, promoting micelle formation and stabilization.\textsuperscript{540-545} The association of the gemini surfactants derived from cystine and a monomeric surfactant derived from cysteine with BSA were studied by Faustino \textit{et al.}\textsuperscript{546} The association of enantiomerically pure surfactants with BSA is favored when compared to the racemic mixture and pure L-stereochemistry is favored over D-stereochemistry.\textsuperscript{546} Le \textit{et al.} reported that bound surfactants largely minimise heat-induced protein intermolecular interactions and thus prevent heat-induced protein aggregation from a study of the effect of lysophospholipids, the main components of lysolecithins, as well as alternative surfactants, on heat induced whey protein aggregation.\textsuperscript{547}

Chitosan is a positively charged linear polysaccharide,\textsuperscript{548} it has many applications in the food and pharmaceutical industries,\textsuperscript{549,550} etc. Using ITC, surfactant ion-selective electrodes (SISEs) and turbidity measurements, Thongngam \textit{et al.} examined the influence of the solution, environmental conditions and ionic ratio on the interaction of the SDS/chitosan system.\textsuperscript{551} Onesippe \textit{et al.} used SISEs, surface tension measurements, ITC, turbidity and zeta potential measurements to study the binding of SDS to chitosan in aqueous solution.\textsuperscript{552} They observed that at optimal ionic ratio, the SDS/chitosan system is capable of encapsulating hydrophobic molecules. Pepic \textit{et al.} studied the bulk properties of the nonionic surfactants-chitosan mixtures by fluorescence spectroscopy, dynamic light scattering and zeta potential measurements. They observed that the addition of chitosan to triblock copolymers, Lutrol F127 systems in water had little effect on CMC values.\textsuperscript{553,554}

Lam and Walker reported the pH induced alteration of the surfactant aggregates with polyelectrolyte those of oppositely charged from cylinder to a string-of-pearls structure (spherical micelles connected by the partially solubilized polyelectrolyte chain).\textsuperscript{555} Pispas reported that well defined nanoassemblies can be formed in mixed solutions of a double hydrophilic anionic-neutral block copolymer, poly[(2-sulfamate-3-carboxylate)isoprene-b-ethylene oxide] (SCIEO) and the vesicle-forming surfactant, didodecyldimethylammonium bromide (DDAB) at certain mixing ratios through a
vesicles-to-micelles transition, driven by electrostatic interactions and packing constraints.\textsuperscript{556}

Bellettini, \textit{et al.} recently studied the aggregation of four modified hyperbranched polyethylene imines (PEI) in presence of SDS. The small-angle X-ray scattering (SAXS) data showed that the radius of gyration of the polymer molecules decreases with an increase in the alkyl chain length of the polymer, while the viscosity data indicated a decrease in the intrinsic viscosity under the same conditions.\textsuperscript{488} Petkova \textit{et al.} investigated the effects of polymer-surfactant interactions on the foamability and foam stability in mixed polymer-surfactant systems.\textsuperscript{557} They clearly showed that the presence of opposite charges is not a necessary condition for boosting the foaminess and foam stability in the surfactant-polymer mixtures studied. Liu, \textit{et al.} studied the interaction between a cationic surfactant (1-dodecyl-3-methylimidazolium bromide, C12mimBr) and a water-soluble polyanion (sodium carboxymethylcellulose, NaCMC) in aqueous solution by ITC, conductivity, surface tension and rheological measurements. They suggested that the electrostatic attraction between the cationic surfactant and anionic polyelectrolyte is an endothermic process and the C12mimBr monomer binding to the NaCMC chains through hydrophobic interaction is an exothermic process.\textsuperscript{484}

**I.D: Interaction of dyes with surfactants in presence of polymers**

The formation of polymer-surfactant complex can be realized from the marked change observed in the spectroscopic properties of dyes.\textsuperscript{558,559} A very few spectrophotometric analysis of polymer-surfactant system has been carried out by using indicator dye as a probe.\textsuperscript{560} Analysis of wavelength shift of a solution of a polymer, labeled with a dye, following addition of surfactant has been found to be successful in a number of studies.\textsuperscript{133,561-565} Changes in the local microenvironment around the probe can produce measurable spectral changes which can be monitored easily. The spectral changes allow illumination of the influence of the immediate environment on the probe and give evidence of specific interactions.\textsuperscript{256,566-570} Photochemical techniques such as luminescence techniques have been employed to determine micellar parameters such as aggregation number, CMC and partition of solute between the micellar and aqueous pseudo phase.\textsuperscript{366,565,571,572}

Hayakawa \textit{et al.} studied the spectroscopic properties of the cationic dyes, \textit{viz.}, rhodamine 6G, proflavin and acridine orange in the presence of anionic polyelectrolytes,
i.e., sodium salts of dextran sulphate (DxS) and poly(vinyl sulfate) (PVS), with and without the cationic surfactant DTAB.\textsuperscript{133} They reported that proflavine and rhodamine 6G dissolved into DTA\textsuperscript{+}-polyanion complexes in the monomeric form. They also examined the effective energy transfer from excited proflavine to rhodamine 6G when both are solubilised in DxS/DTAB and that of pyrene (donor) to proflavine (acceptor) when the dyes are solubilised in DxS/DTAB, DxS/DTAC, poly(vinyl sulfate)/DTAB and poly(styrenesulfonate)/DTAB aggregates, where no energy-transfer effect is observed in solutions of either the surfactant or the polymer alone.\textsuperscript{573,574} The same group reported that the free energy of transfer of the water-insoluble dye, oil yellow OB from the solid phase to poly(vinyl sulfate)/alkyltrimethylammonium complex is found to be 3.1 kJ mol\textsuperscript{−1} from the solubilizing capacity.\textsuperscript{575}

Kwak \textit{et al.} used the \textsuperscript{1}H NMR shifts to determine the location of aromatic solubilizates including probes in aggregates of Poly(maleic acid-co-butyl vinyl ether) (PMA-BVE) and cationic surfactants.\textsuperscript{576,577} Das \textit{et al.} studied the interactions of BSA and SDS using ethyl \textit{p}-(dimethylamino)cinnamate as a fluorescence probe for monitoring the interactions.\textsuperscript{566} Upon analysis of the fluorescence spectra of the probe resulted in cooperative protein-surfactant binding and the polarity of the BSA-SDS aggregates formed has been found in between that of hydrophobic regions of BSA and SDS micelles. Sen \textit{et al.} studied the fluorescence anisotropy decay of two dyes \textit{viz}., merocyanine 540 and oxazine 1 in a system containing poly(vinylpyrrolidone) (PVP) and SDS aggregates.\textsuperscript{578} Their results indicated that the microscopic friction in PVP-SDS aggregates is greater than that in an SDS micelle alone. Bloor \textit{et al.} examined the binding of sodium alkylsulfates (C\textsubscript{8}-C\textsubscript{16}) to a copolymer of N-(vinylacryloyl) pyrrolidine and the covalently bonded chromophore 4-vinylpyridine dicyanomethylide by monitoring the wavelength shift of the chromophore band at 390 nm. They observed that the bound surfactant exists in the form of micellar type aggregates and the spectral data indicate that initially these aggregates preferentially bind to the chromophore on the polymer.\textsuperscript{579}

Nayak \textit{et al.} studied a polymer-surfactant micellar complex as a fluorescence resonance energy transfer donor to fluorescein-labeled DNA. From TEM microscopic study they showed the formation of a nanowire micellar complex of cationic poly(fluorene-co-phenylene) (c-PFP) and the surfactants.\textsuperscript{580} Pu \textit{et al.} examined the effect of surfactant on energy transfer between cationic conjugated polymer and dye-labeled oligonucleotide.\textsuperscript{581} Sahoo \textit{et al.} studied the interaction of SDS and amphiphilic block
copolymers polyethylene-b-polyethylene glycol by monitoring the sharp change of excited-state charge-transfer complex photophysics of 2-(4-(dimethylamino)styril)-1-methylpyridinium iodide (DASPMI). The enhancement of emission intensity of DASPMI incorporated inside of the nanostructure formed by micellar and polymeric chains indicates a completely different environment compared to that in the water and micellar system. Nath et al. studied the interaction of capsular polysaccharide (an integral component of gram-negative bacteria) isolated from Klebsiella K18, with cationic dyes and surfactants. Their studies provide an understanding on the effects of the surfactants on binding with the polymer (SPS). The binding was found to be electrostatic in origin and also hydrophobic in nature to a certain extent.

Iatridi et al. reported the interactions between anionic polyelectrolytes and the oppositely charged surfactant DTAC in dilute aqueous solution, exploiting the optical properties of nile red. They had observed that the formation of ternary polymer/surfactant/Cu$^{2+}$ complexes leads to a pronounced quenching of the luminescence of nile red. Bazylinska et al. investigated the influence of dicephalic ionic surfactant interactions with oppositely charged polyelectrolyte upon the in vitro dye release from oil core nanocapsules.

Saikia and Dutta studied the acid-base equilibrium of three anionic sulfonephthalein dyes, viz., bromothymol blue, thymol blue and cresol red in aqueous media containing the nonionic polymers, viz., polyvinyl alcohol (PVA) and PEG in the presence SDS. They successfully employed the partition equilibrium method to determine the interacting parameter between the surfactant and the polymers.

**I.E: Curcumin- surfactant interactions**

**I.E.1: Curcumin**

Curcumin is a yellow pigment present in the spice turmeric (*Curcuma longa* Linn) that belongs to the ginger (*Zingiberaceae*) family. Curcumin was first isolated in impure form in 1815 by Vogel and Pelletier and it was first prepared in pure and crystalline form by Daube in 1870 followed by Ivanov and Gajevsky almost three decades later. Its chemical structure was determined in 1910 by J. Milobedzka and V. Lampe. The use of curcumin in biliary diseases was first documented in 1937 (67 patients treated), then its antibacterial action in 1949 and its ability to decrease blood sugar levels in human subjects (i.e. its use as an antidiabetic) in 1972. It has been termed as C.I. Natural Yellow 3 and
WHO (World Health Organization) and FAO (Food and Agriculture Organization) committees have approved it as a food additive.\textsuperscript{586}

Chemically, curcumin is a bis-\(\alpha,\beta\)-unsaturated \(\beta\)-diketone, commonly known as diferuloylmethane \{((1E, 6E)-1,7-bis(4-hydroxy-3-methoxy phenyl)-1,6-heptadiene-3,5-dione)\} and it was suggested that under physiologic conditions exhibits keto-enol tautomerism, having a predominant keto form in acidic and neutral solutions and a stable enol form in alkaline media (\(pH > 8.00\)).\textsuperscript{589} It has a molecular weight (MW) of 368.38, a melting point of 179-183°C and chemical formula is \(C_{21}H_{20}O_6\). Commercially available curcumin is a mixture of curcuminoids, containing approximately 77\% diferuloylmethane, 18\% demethoxycurcumin and 5\% bisdemethoxycurcumin.\textsuperscript{587,588} Curcumin is practically insoluble in water at acidic and neutral \(pH\) condition (~11 ng/ml in plain aqueous buffer \(pH 5.00\)) and ether however it is moderately soluble in aqueous solutions of high \(pH\) and in both polar protic and polar aprotic solvents.\textsuperscript{592} In alkaline medium, the deprotonation of curcumin occurs first as a result of hydrolysis and produces \textit{trans}-6-(4'-hydroxy-3'-methoxypenyl)-2,4-dioxo-5-hexenal.\textsuperscript{593} The hydrolysed product then further degraded to smaller molecular components such as vanillin, feruloyl methane and ferulic acid.\textsuperscript{593} Acidic conditions result in slower degradation of curcumin, with \(\sim 20\%\) of total curcumin decomposed at 1 hour.\textsuperscript{593}

Extensive research have been carried out about the medicinal properties of curcumin which indicated that curcumin possesses remarkable therapeutic properties including antioxidant, anti-inflammatory, antimicrobial,\textsuperscript{594-597} antitumor,\textsuperscript{598-600} anticancer,\textsuperscript{597,599,601-603} etc. In addition to this the hepato- and nephro-protective,\textsuperscript{604,605} thrombosis suppressing,\textsuperscript{606} myocardial infarction protective hypoglycaemic,\textsuperscript{606-609} antirheumatic\textsuperscript{610} effects of curcumin are also well established.\textsuperscript{587} From the studies on different animal models or human bodies\textsuperscript{613-615} it has been established that curcumin is safe even at very high doses.\textsuperscript{587}

**I.E.2: Interaction of curcumin with surfactants**

It has been showed that, micellar systems potentially play an important role in leading improved aqueous solubility and bioavailability of curcumin. Tønnesen studied the stabilisation of curcumin at \(pH\) 5.00 and \(pH\) 8.00 in different types of surfactant micelles including SDS, TX-100 and TTAB.\textsuperscript{97} They observed that SDS and TX-100 micelles are
highly effective in stabilizing curcumin, while TTAB micelles are not as effective as SDS and TX-100 micelles at pH 8.00.97

Iwunze reported the thermodynamic stability of curcumin solubilised in cationic CTAB micellar medium with a free energy of transfer from the aqueous phase to micellar pseudophase of $-13.74$ kJ/mol.98 Wang et al. showed that SDS, SDBS and protein can enhance the resonance light scattering (RLS) and also fluorescence intensity of curcumin.616-618 They observed that the enhanced RLS is in proportion to the concentration of proteins. The same group also reported the nucleic acid enhancement of the RLS of curcumin in presence of CTAB.619

Leung et.al showed that curcumin can be encapsulated in cationic micelles of DTAB and CTAB surfactants which suppress the alkaline degradation of curcumin at pH 13.00.99 The attractive electrostatic interactions between the cationic head groups of the surfactants and the deprotonated curcumin (Cur$^{3-}$) play the key role in stabilising Cur$^{1-}$ in alkaline medium. The same research group investigated the interactions of curcumin with negatively and positively charged micelles and vesicles at different pH conditions.100 There is a strong interaction between the Cur$^{-1}$ phenoxy ion and the positively charged surfactants results in a change in the acidity of the phenolic hydrogen and a lowering of the apparent lowest pK$_a$ value for curcumin. However, in anionic micellar medium or negatively charged bilayers, they observed that curcumin partitions as the Cur$^{0}$ species. From femtosecond fluorescence upconversion experiments, Adhikary et al. reported that micelle-captured curcumin undergoes excited-state intramolecular hydrogen atom transfer.620

Recently, Ke et al. spectroscopically investigated the interaction of curcumin with cationic DTAB surfactant at pH 5.00.621 From their results they suggested that at low surfactant concentrations the DTAB/curcumin complex is formed, while, at intermediate concentration of the surfactant the dye induced premicellar aggregates of DTAB are formed. At high surfactant concentrations, DTAB micelles are formed and curcumin solubilised in the micellar core predominantly as enol curcumin.

**I.F: Lacuna and rational**

Despite many investigations of dye-surfactant systems and on the behaviour of surfactant and dye mixtures, there are limited numbers of studies on the dye-surfactant interactions in the presence of polymers. Most of the studies have examined the nature and strength of
polymer-surfactant interactions as well as the nature of the aggregation phenomena and acid-base equilibrium of dyes in the polymer-surfactant systems. The existing interpretation, both in submicellar and postmicellar concentration of surfactants seems to be unable to give a clear picture about the mechanism underlying the interaction of dyes with surfactants and with both polymers and surfactants together. The interactive forces which facilitates the dye binding to surfactants and to both polymers and surfactants together are not yet clearly understood, which may be due to limited choice of dye-polymer-surfactant systems in the reported studies. Moreover, there is no report regarding the interaction of dye and surfactants of same charge in the presence of polymers. There is also hardly any literature available on the subject of the natural dye curcumin-polymer-surfactant system. It would be of interest, from both practical and academic perspectives, to investigate the interactive forces operative in these systems explicitly.

In the studies of acid-base equilibrium of dyes in micellized surfactants in the presence and absence of polymers, the spectroscopic properties of the dyes as a function of concentration of surfactants are expected to through some light on the mechanism underlying the dye binding to the surfactants in the presence of polymer, as well as nature of polymer-surfactant interactions. A study of the dimerization of a dye in an anionic surfactant-nonionic polymer system allows one to obtain precisely the critical concentration of surfactant that maximizes the dimer formation and the redissolution of the monomer in the polymer-surfactant complex. The investigations on the physicochemical properties of a natural dye in polymer-surfactant systems provide desirable information in solubilizing and stabilising of the dye. In addition, binding to a biopolymer can be used to monitor as a delivery system for administration of the dye as a drug, with implications on biological and medical applications.

Spectrophotometry is a commonly used technique for qualitative and quantitative determination of dye-polymer-surfactant interactions. It was therefore decided to carry out some systematic studies on various dye-surfactant-polymer interactions using UV-visible and fluorescence spectroscopic methods with different chosen synthetic and natural dyes. In case of the natural dye, for clear understanding of the physicochemical behaviour the dye in such systems, surfactant concentrations are chosen from submicellar to post micellar ranges.
I.G: **Aim and objectives**

The aim of the present work was to carry out a systematic study on the acid-base equilibrium of two synthetic dyes of different charge types, the dimerization of another synthetic dye and the physicochemical behaviour of a natural dye in different surfactants and in polymer-surfactant systems. The different polymers and surfactants were varied without a tremendous change in structures.

The chosen anionic dye was a sulphonephthalein dye *viz.*, phenol red (PR). The anionic surfactant chosen for using with the anionic dye was SDS. The nonionic polymers chosen were polyvinyl alcohol (PVA) (M.W. 14,000), PVA (M.W. 1,25,000), PEG 200, PEG 400 and PEG 600. For a system, a phanizine dye, *viz.*, neutral red (NR) was chosen as a neutral dye. The nonionic surfactants were polyoxyethylene(20) sorbitan monolaurate (Tween-20), polyoxyethylene(20) sorbitan monopalmitate (Tween-40), polyoxyethylene(20) sorbitan monostearate (Tween-60) and polyoxyethylene(20) sorbitan monoooleate (Tween-80). The nonionic polymers chosen for this system were PVA (M.W. 125,000), PEG 200, PEG 400 and PEG 600. The cationic dye chosen for surfactant-induced dimerization study was a thiazine dye, *viz.*, methylene blue (MB). The dimerization of MB was studied in the presence of an anionic surfactant *viz.*, SDS and a nonionic polymer, *viz.*, PVA (M.W. 14,000).

A natural dye of versatile medicinal activity, *viz.*, curcumin, was chosen for the study. We examined the interactions of the dye with surfactants of different charge types as there are only a few studies reported on the physicochemical properties of curcumin in micellar systems. In submicellar medium, only one report with cationic surfactant is available. The anionic surfactants chosen for using with curcumin were an alkylsulphate surfactant, *viz.*, SDS, an alkyl benzene sulfonate surfactant, *viz.*, SDBS and an alkyl sulfonate surfactant, *viz.*, sodium dodecylsulphonate (SDSN). The cationic surfactants chosen were some alkyltrimethylammonium halide surfactants of varying chain length, *viz.*, CTAB, TTAB and DTAB. The polymer chosen was a nonionic polymer, *viz.*, PVA (M.W 125,000). In a system of curcumin and a cationic biopolymer, the biopolymer chitosan was chosen along with TW80 and CTAB surfactants.

We have investigated the partition of the two chosen dyes between aqueous and micellar pseudophases to investigate the acid-base equilibrium of the dyes in polymer-surfactant medium using the partition equilibrium method based on UV-vis spectroscopy. The induced dimerization was also studied using a spectroscopic method.
method. For the study of the stabilisation of the natural dye in polymer-surfactant medium, the fluorescence spectroscopic technique has been used.

The work was planned as described below:

- Preparation of the aqueous solutions of dyes, surfactants and polymers and their mixtures.
- Recording of electronic spectra of the aqueous dye solutions as a function of concentration of surfactants ranging from below the CMC of the surfactant to above the CMC in polymer free medium as well as in presence of polymers.
- Recording of electronic spectra of the aqueous dyes as a function of concentration of polymers in presence of surfactants of fixed concentrations.
- Calculation of thermodynamic parameters.
- Recording of fluorescence spectra of the aqueous dye a function of concentration of surfactants in absence of polymers and in presence of polymers.

At the end of the chapter the author would like to acknowledge all the authors cited in this thesis. The author also apologizes for any lapse which might have occurred due to oversight or error in judgement.
References:


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