

CHAPTER I

General Introduction

1.1. Introduction

The interactions between dyes, surfactants, and polyelectrolytes have drawn a lot of attention lately in the fields of analytical chemistry, textiles, detergency, biochemistry, pharmaceuticals, photochemistry, and wastewater treatment ¹⁻³. The interaction of dyes with surfactants and polyelectrolytes (PE) is particularly intriguing since it can result in the creation of polymer/surfactant/dye complexes ⁴ due to electrostatic, hydrophobic, or both interactions ^{5,6}.

The nature and physicochemical characteristics of polyelectrolyte/surfactant, dye/surfactant, polyelectrolyte/dye, and surfactant/polyelectrolyte/dye systems are predominantly governed by the hydrophobic interactions ^{7,8}, in which molecules tend to aggregate due to their inherent lipophilic nature, and electrostatic interactions, wherein the presence of charges causes two particles to either attract or repel one another ⁹. Therefore, both solvent hydrophobicity and charges on component monomers, impact the stability and binding of the surfactant/polyelectrolyte, surfactant/dye, polyelectrolyte/dye, and PE/dye/surfactant complexes. Individual chemical and physical nature of the dye, surfactant, and polyelectrolyte, determine the nature and degree of hydrophilic/hydrophobic and electrostatic interaction in the mixed systems ^{10,11}.

For both basic understanding and potential applications, it is crucial to pay particular focus to the important physicochemical components of micelle formation and its reliance on environmental variables such as temperature and additives. Other important aspects include counterion binding, aggregation behavior, thermodynamics of formation, and catalyzing functions ¹². Variations in solvent standards offer the chance to investigate the function of the referred-to solvophobic effect ¹³. This kind of research is made more exciting by the growing use of surfactant/polyelectrolyte/dye complex in applications that call for water-poor or water-free media ¹⁴⁻¹⁸. By gradually substituting alternative polar solvents for water, a broad range of bulk phase polarity and its impact on micellization can be investigated. The majority of studies ¹⁹⁻²² concentrated primarily on two aspects: the structural characteristics of the aggregates produced in these

environments and the solvent needed for amphiphilic assembly. Elevated cohesive General Introduction energies, substantial hydrogen bonding, and extremely high dielectric constant capacity are characteristics of the solvents that cause surfactants to self-associate ¹³. According to Evans & Miller (1992), it is essential to be able to create hydrogen bonds for micellization to occur. In addition, the temperature sensitivity of surfactant micellar characteristics has drawn a lot of interest in the thermodynamics of micellization processes ²³. The micellization process can be better understood by conducting calorimetric studies that focus on the thermodynamic parameter's temperature dependency ^{19,24}. The critical aggregation concentration (CAC), dissociation degree (α), and critical micelle concentration (CMC) of surfactant the water-ethanol at various temperatures were determined using UV-Vis., conductivity, and tensiometry measurements. In the present work, variations in the solvent polarity and temperature lead to the change in the CAC, CMC, and α values which in turn causes the variations in various thermodynamic parameters and helped in the study of micellization process occurring in the micellar of surfactant in polyelectrolyte with and without dye.

1.1.1. Surfactants

Surface-active substances known as surfactants tend to gather at interfaces ^{11,25}. These substances exhibit ambivalence, having a tail hydrophobic group that despises water and a head with a hydrophilic group that is drawn to it ²⁶⁻²⁸. These groups exhibit varying proportions and patterns that ideally barrier at the interface involving liquid phases that have different polarity levels, like the interfaces between oil and water or air ²⁹.

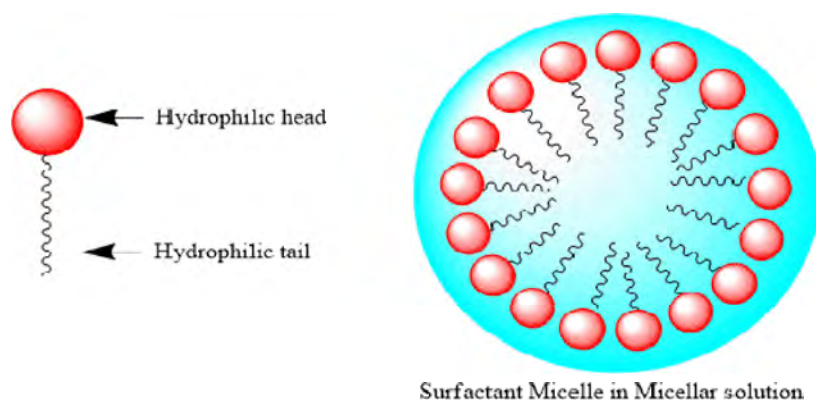


Figure 1.1: Formation of surfactant micelles in micellar solution with surfactant monomers.

The tail can be long or short, while the heads can be neutral, cationic, zwitterionic, or anionic. Amphiphiles, also known as surfactants, are commonly referred to as such due to their exceptional rheological features and capacity to stabilize the surface of liquids by lowering interfacial tension. The presence of both tail and head in the surfactant molecule activates, stabilizes, and reduces the interfacial tension and causes micelle formation ³⁰ (Figure 1.1). Above a specific concentration, this is the essential property that allows the surfactants to self-assemble into a range of micellar aggregations and be adsorbed at the interfaces ²⁹. To address the lack of readily available animal and vegetable fats during World War I, Germany produced the first surfactants for general application that are typically categorized as synthetic ³¹. In 2008, the expected global output of surfactants was 12 million tons annually, growing at a rate of two to three percent annually ³². According to market research institutes Ceresana Research, the worldwide surfactant market is predicted to produce over US\$41 billion in sales in 2018, which translates to a 4.5% yearly growth rate on average. Asia/Pacific is the major surfactant source, accounting for over 37% of global use, followed by North America and Western Europe ³³.

Many everyday items that we use, including detergents, cosmetics, shampoos, soaps, shower gels, foods, lotions, medications, and so on, include surfactants ³⁴. In addition to cleaning, surfactants have a wide range of other uses, including emulsification, wetting, solubilization, foaming, and dispersion. Occasionally, they are also highly helpful for enhancing penetration and having antimicrobial action ³⁵. High-tech uses are putting

increasing pressure on our ability to comprehend and control interfaces through the action of surfactants because of their outstanding functional versatility, which has led to their use in the manufacture and processing of foods, the recovery and purification of raw materials in the mining and petroleum industries, and the improvement of the quality of finished products like cosmetics, paints, pharmaceuticals, agrochemicals, lubricants, and mineral oils ³⁴. With the typical ups and downs that come with most businesses, surfactant technology, and applications are growing at a healthy rate overall today due to the needs of ecological, population growth, raw materials, fashion, and marketing appeal ^{26,34}.

1.1.1.1. Classification of surfactants

Surfactants exhibit a range of structural variations, which are closely associated with alterations in function. The hydrocarbon chain at the tail, which might be straight, branched, or aromatic, was previously described. It can also vary in length and size ³⁶. There are four types of hydrophilic heads: zwitterionic, neutral, anionic, and cationic. Surfactants are categorized as non-ionic, ionic (cationic or anionic), and amphoteric or zwitterionic according to the charge of the hydrophilic constituent charges ³⁰. If an ionic surfactant that is positively charged may split into an ordinary anion and a surface active cation in solution, it is referred to as a cationic surfactant ³⁷. A cationic surfactant's ability to strongly absorb onto most solid substrates is attributed to its positive head. Since they typically don't offer efficient cleaning, cationic surfactants aren't found in versatile detergents. The reason for this is that at high concentrations, cationic surfactants produce huge, worm-like micelles that have poor dirt transport ³². Since cationic surfactants with a positive charge are necessary for the keratin in hair, the cosmetics industry uses them extensively as antistatic agents and hair conditioners. Additionally, they work well as emulsifiers, fungicides, herbicides, fabric softeners, textile auxiliaries, antistatics, corrosion inhibitors, adhesion promoters, and flotation agents ³². Quaternary ammonium salts, such as N-Alkyltrimethylammonium bromides, are cationic surfactants that possess the benefit of maintaining a positive electrical charge in acidic, neutral, and alkaline conditions, despite pH fluctuations. In this study, we have employed a cationic surfactant CTAB or cetyltrimethylammonium bromide. In everyday life, CTAB is a highly potent cationic surfactant. As such, they find applications as antibacterial agents, hair conditioners, and fabric softeners ^{2,29}. Hexadecyltrimethylammonium bromide is the IUPAC designation for CTAB (with a

molecular weight of 364.45). If the negative-charged ionic surfactant's molecules split apart in solution to generate a surface-active anion and a regular cation, it is referred to as anionic. It consists of an anionic group that must be a part of a lengthy hydrocarbon chain, either directly or through intermediaries ^{32,38}. Since purity is frequently not essential for their effectiveness, the majority of commercial anionic surfactants are typically heterogeneous mixes in terms of composition and hydrocarbon chain length. Their proportion of the global soap market is over 75% ³⁹. To highlight their importance in cleaning products, anionics are frequently referred to as "detergents." Among the most distinctive qualities of anionic surfactants are their capacity for dispersion, strong foaming, sensitivity to water hardness, and denaturation of proteins ^{29,40}.

Depending on the pH of the relevant solution, amphoteric or zwitterionic surfactants (such as sodium cocoamphoacetate and cocoamidopropyl betaine) exhibit either a positive or negative charge until they reach the isoelectric point. The cationic property is more prevalent in acidic pH values, while the anionic property is more prevalent in basic pH values. These types of surfactants are often helpful in stabilizing foam and thickening liquids; the only substances that decrease their activity are acidic substances ³⁵.

In an aqueous solution, non-ionic surfactants do not dissociate. Due to the non-dissociable nature of their hydrophilic portion, which includes ester, alcohol, ether, phenol, and amide, these surfactants do not ionize in water ³⁰. Their polyethylene glycol chain, which is produced by polycondensing ethylene oxide, is what gives them their hydrophilic quality. These surfactants have high compatibility with the skin and eyes because they are less foamy by nature. When combined with anionic surfactants, they can be utilized as washing agents because they foam less ⁴¹. Nonetheless, they are generally effective emulsifying agents in cosmetics for routine skin care, particularly for infant skin.

Menger and Littau (1991) discovered another category of new surfactant known as Gemini surfactant, which is composed of several hydrophilic groups connected by spacers ^{34,42}. The spacer group could be flexible, rigid, nonpolar, or polar. Since Gemini surfactants have higher surface activity, peculiar aggregation action, micelle formation, intriguing rheological features, and a higher solubilization capacity than monomeric surfactants, they have been the focus of increased attention for many years for a variety

of applications, including cosmetics, genetics, paints, oil recovery and mostly textile industries ^{26,34}. Gemini surfactants have a substantially lower craft temperature (the temperature at which the formation of micelle occurs) than ordinary monomeric surfactants.

Natural or biosurfactant surfactants are another type of surfactant, that must only come from natural sources, such as plant or animal organs ⁴¹. Any one of the hydrophilic or hydrophobic components of natural surfactants could originate from a natural source. Bio-surfactants exhibit a range of physiologically varied actions, including antiviral, antimicrobial, and hemolytic activity, along with reduced CMC, less toxicity, improved biodegradability, increased environmental compatibility, and mildly altered activity at a high pH or temperature. Because they are less dangerous, different biosurfactants are highly helpful in the production of personal hygiene products ^{43,44}.

1.1.1.2. Micellization and phase behavior of surfactants

The explanation for the behavior of micellization is dependent on the well-organized framework of surfactant molecules in aqueous solution above a certain concentration called micelles. They are made up of a hydrophilic portion that faces the aqueous medium and a lipophilic portion that associates with the interior of the aggregate ⁴⁰. Micelle formation is a crucial property of surfactant molecules, and the process of forming micelles is known as micellization. Because there is less interaction between the hydrophobic part of surfactants and water, the micellization process occurs, which reduces the free energy of the system ⁴⁵.

Micellization in the presence of additives is being investigated since additives offer a broad range of potential uses, such as solubilization, improved oil recovery, detergency, pharmaceutical formulations, biochemical investigation, etc. ^{10,46,47}. The way various amphiphiles aggregate in ethanol-water mixed solvent media is thought to be significant because these polar solvents, when combined with surfactants, may be used in cleaning and lubricating processes that necessitate a water-poor or free environment. Furthermore, research on surfactant micellization in non-aqueous polar solvents is crucial for comprehending the principles that will help foresee the advancement of these systems' technological applications ^{48,49}.

Additionally, researchers find this research useful in their understanding of the solvophobic effect. In this instance, the surfactant and polyelectrolyte are combined

with the dye to generate a mixture that frequently works better than either of the parts alone. This motivated us to investigate surfactant micellization behavior in the presence of additives due to the above point of interest. Despite a century of intensive research on the micellization of surfactants with additives in various mixture solvent environments, the findings are still regarded as incomplete ⁵⁰. Since micelle formation is a temperature-dependent phenomenon, the temperature at which micelle formation begins is called Krafft temperature ^{40,51,52}.

The micellization process is thermodynamically characterized by describing the corresponding hydrophobic and electrostatic aspects to the total Gibbs energy of the system. Water and hydrocarbons are incompatible; due to the hydrophobic effect and the restricted solubility of hydrophobic substances in water ⁵³. The transfer Gibbs energy (or the hydrophobic Gibbs energy) is the variation in Gibbs energy when hydrocarbon solute is shifted from the organic solvent to water. When analyzing the entropic and enthalpic contributions to the Gibbs energy transfer, a noteworthy feature of the hydrophobic effect is the dominance of the entropy term. This means that when the tail part moves from the organic solvent to water, the Gibbs transfer energy increases along with it ¹⁷. The breaking of water's typical hydrogen-bonded structure and the creation of differentially structured often referred to as icebergs around the hydrocarbon chain are what cause the drop in entropy. In the area around the hydrocarbon chain, the presence of the hydrophobic species encourages an ordering of water molecules. The "icebergs" tend to group to decrease the enormous entropy effect and the number of water molecules involved; this behavior is entropically unfavorable but enthalpically advantageous. The hydrophobic interaction is the propensity of the entire process to draw the hydrocarbon molecules together. Even at low surfactant concentrations, surfactant molecules adsorb at interfaces because of the hydrophobic effect. Since micelleization is opposed by electrostatic and thermal forces, it is influenced by several variables, such as the nature of the surfactant additive, temperature, pH, solvent, pressure, ionic strength, etc.⁵⁴.

1.1.2. Shape of micelle

Multiple forms of micelles exist, including spherical, cylindrical, lamellar, elongated, reverse, and vesicle forms. The form of a micelle is influenced by the surfactant's structure as well as the ionic strength, temperature, and concentration of the solution.

Large headgroups, which impede orderly packing, prefer spherical micelles, which are produced by many common surfactants at mild concentrations.

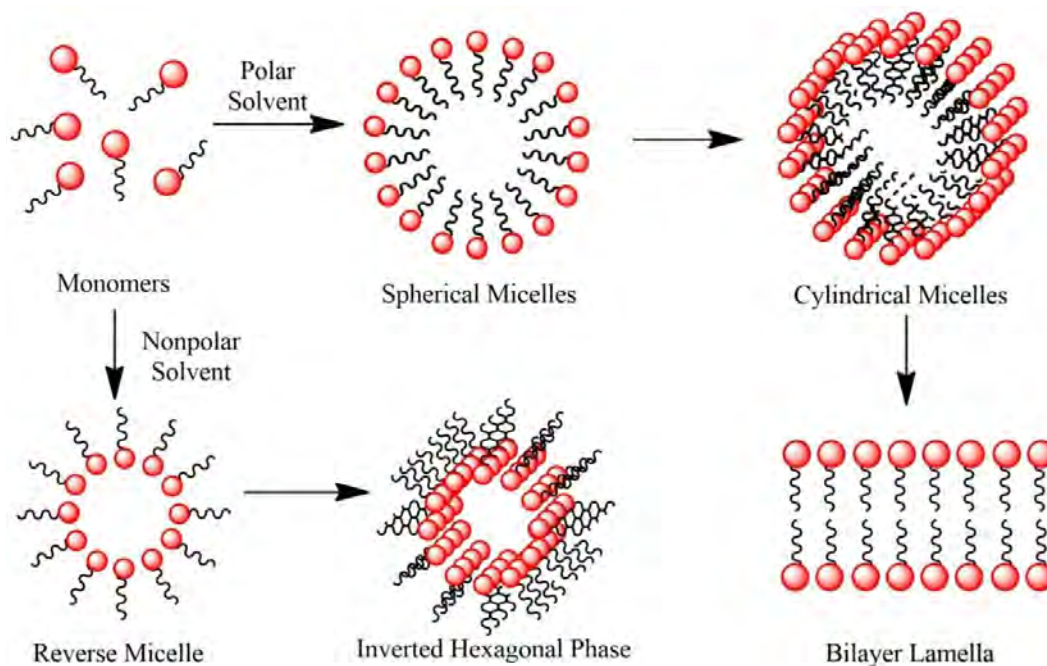


Figure 1.2: Various shapes of micelle in non-polar and polar solvents.

Even single-chained surfactant can form nonspherical micelles; cetyltrimethylammonium bromide (CTAB) is assembled into elongated micelles above 0.2 m, for example. Depending on the aggregation number (N), different-sized and shaped micelles are formed³⁸. Viscosity and solubilization are two solution properties of surfactants that can be influenced by the size and form of the micelles. The geometry of the surfactants is the primary determinant of the micelle's shape. One relevant quantity to forecast the aggregate structure is the critical packing parameter (P), which provides a geometrical characterization of a molecule of surfactant^{32,38}.

$$P = \frac{v}{a_0 l_c} \quad (1.1)$$

In this case, a_0 is the measure of the area of cross-section occupied by the polar head part at the interface of micelle-solution, v denotes the volume occupied by the hydrophobic tail, and l_c measures the alkyl chain length. Broadly speaking, spherical

micelles are produced by P values less than $1/3$, rod-like micelles are produced by values between $1/3$ and $1/2$, and vesicles are formed when the P values become close to unity^{32,55}.

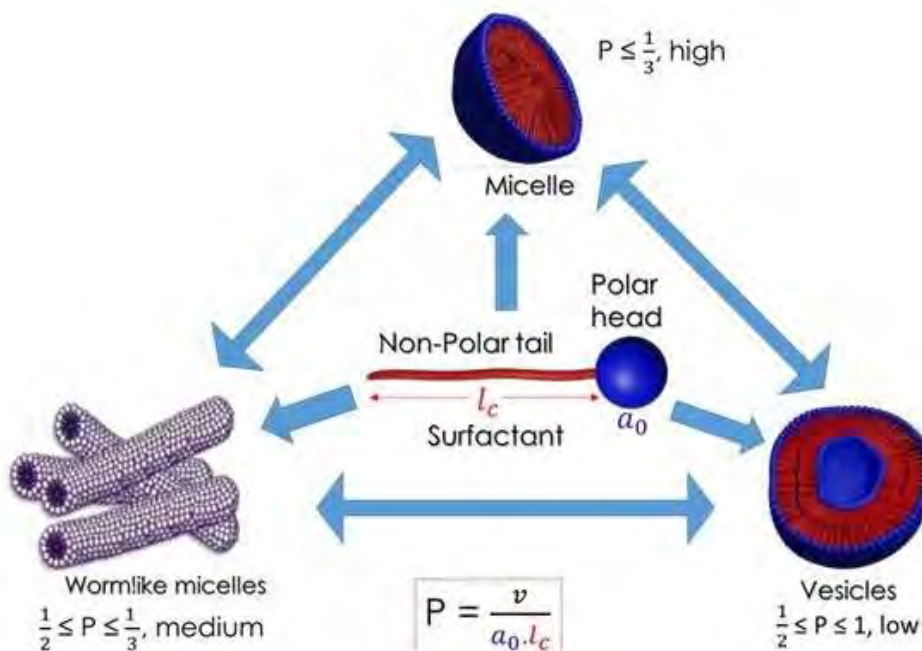


Figure 1.3: Morphologically variant nanoaggregates as a function of packing parameter.

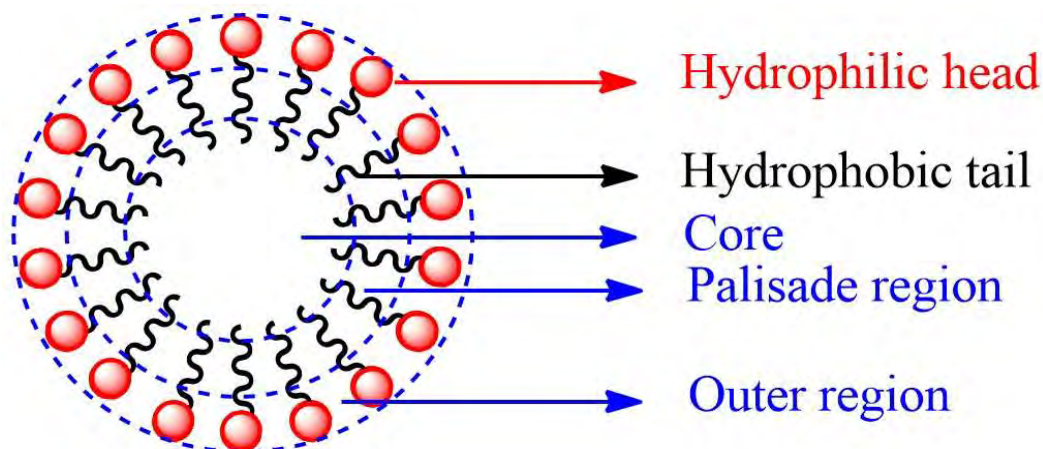


Figure 1.4: Different regions of a surfactant micelle.

1.1.3. Critical micelle concentration (CMC)

The CMC illustrates the specific concentration at which surfactant, or amphiphilic molecules, combine to form bigger, spherical aggregates known as micelles.^{35,56–58}. A

lower CMC corresponds to greater stability ⁵⁹. The CMC value decreases when hydrophobic species' solubilization properties increase in the solutions ⁶⁰. A key method of surfactant characterization is the determination of the CMC for a surfactant in a given solvent since it is utilized to evaluate and contrast the efficacy of surfactants for their intended purposes ^{54,61–64}. To find the CMC value of a surfactant micelle, one common method is to graph some relevant physicochemical parameters against the concentration of the surfactant. The CMC is then found by identifying the break in the plot.

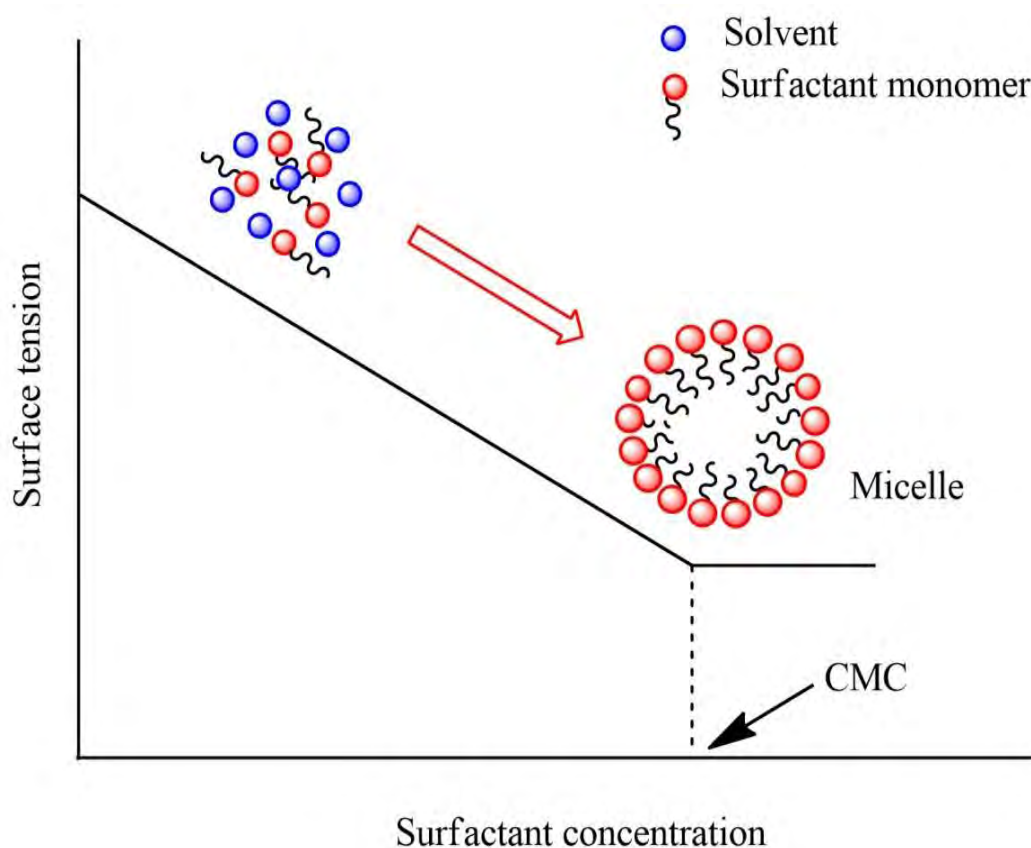


Figure 1.5: Representative plot of Surface tension against surface concentration indicating micelle formation at CMC.

Certain solution properties of surfactants, such as conductivity, UV-visible, and surface tension, with concentration, undergo sudden changes because of micelle formation at the CMC point ⁶⁵. For numerous uses, including stabilization, isolation, solubilization, crystallization, etc., the CMC value of surfactants is important to know. Consequently, it is essential to determine the CMC as a crucial surfactant property. There are several methods for figuring out the CMC of surfactant solution ^{40,56,65–67}.

Table 1.1: Different techniques of CMC determination.

Different methods of CMC determination	References
UV-vis. spectrophotometry	(Noor et al., 2021)
Infrared spectroscopy	(Tran & Yu 2005)
Conductivity	(Salem et al., 2019)
Sound velocity	(Zielinski et al. 1987)
Surface tension	(Bhattarai, 2020)
Calorimetry	(Pan et al., 2013)
Chromatography	(Lin & Lin 2000)
NMR spectrophotometry	(Szutkowski et al., 2018)
Electrochemical techniques	(Racaud et al. 2010)
Surface Plasmon Resonance (SPR)	(Amendola et al. 2010)
Fluorimetry	(Zhu et al. 2014)
Light scattering	(Topel et al. 2013)

1.1.4. Factors influencing CMC

The temperature, cosolvents, salt addition, and surfactant chemical structure, among other parameters, are the most significant determinants of CMC value.

1.1.4.1. Temperature

The CMC value is significantly impacted by temperature. In comparison to water/cosolvent mixtures, the impact of temperature is less noticeable when the pure water case. Usually, two opposing variables are employed to show how micellization is affected by temperature. Micellization is hindered by the temperature rise because it breaks down the water structure around the hydrophobic sites and lowers the head groups' degree of hydration, which promotes micellization ⁶⁸. The results suggest that the second influence is more prevalent in the investigated range of temperature. The temperature rise causes a drop in the viscosity of the solution, which raises the CMC.

Figure 1.7 illustrates how the CMC for each surfactant first drops and then rises at rising temperatures. The first fall in CMC with temperature is a result of the surfactant molecules' reduced hydrophilicity, which is caused by a lesser possibility of forming hydrogen bonds at higher temperatures. From another perspective, the hydrophilic oxyethylene group becomes less hydrated as the temperature rises, favoring micellization¹⁹. Therefore, the commencement of micellization happens at lower concentrations as the temperature rises. However, when the surfactant molecules dissolve in water, the hydrophobic group causes the water's structure to be distorted. Moreover, micellization is adversely affected by rising temperatures because it accelerates the rupturing of the water around the hydrophobic parts ⁶⁹. Because of this, micellization typically begins at larger concentrations as temperature rises. Thus, on further increasing temperature, the hydrophobic groups' action starts to become more pronounced and eventually takes over as the CMC hits a minimal value and then rises with temperature. It is discovered that the lowest CMC temperatures for Polysorbate 20, 40, and 80 are 43, 42, and 40 °C, respectively ^{54,57}.

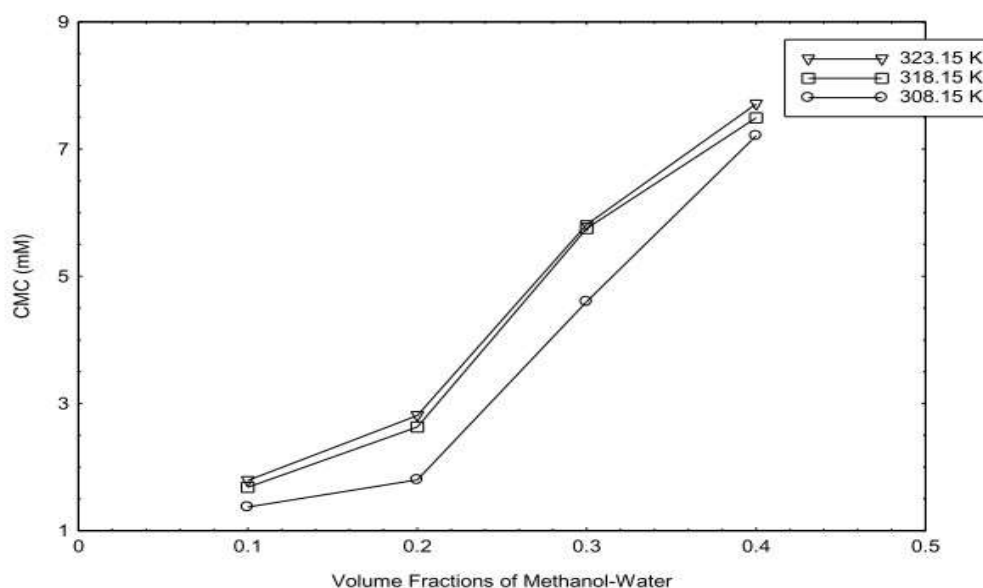


Figure 1.6: Variation of CMC with different V.F. of methanol-water at 308.15, 318.15, and 323.15 K ⁷⁰.

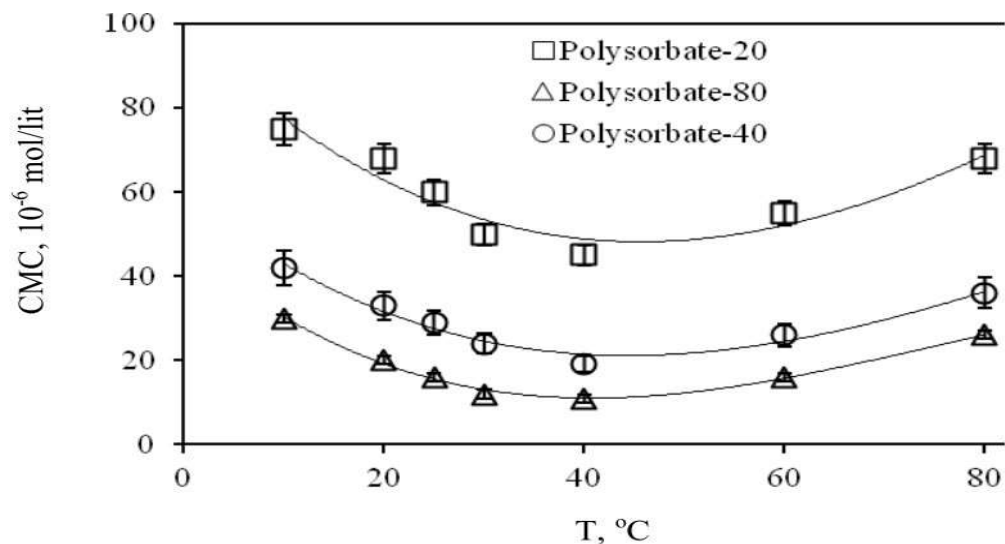


Figure 1.7: Change in CMC for various surfactants with temperature.

1.1.4.2. Cosolvents

Micelle formation and its dependency on organic co-solvents are significant physicochemical components that require in-depth research for both basic knowledge and practical applications. Water-soluble organic additives, such as formamide, polyhydric alcohols, and monohydric alcohols, modify the structure and dielectric constant of the media, altering the hydrophobicity of the medium and hence the micellization process ^{14,71}. Additives that resemble alcohol and glycerol have a high value of dielectric constant and cohesive energy and a stronger hydrogen bonding capacity. These factors make the organic additives under study significant. Based on the roles they play, the various organic compounds can be divided into two categories: cosurfactants and co-solvents. While co-solvents are not always amphiphilic, cosurfactants are often weakly amphiphilic molecules that are thought to be concentrated in the layer of surfactant aggregates generated by main surfactants ¹⁹. When combined with surfactants, the aggregation tendency of many amphiphiles in polar or non-polar solvents is thought to be significant. It might have significant uses in cleaning and lubricating processes that call for a water-poor or water-free environment. Furthermore, research on surfactant micellization in non-aqueous polar solvents is crucial for comprehending the principles that will help foresee the advancement of these systems' technological applications. Additionally, experimentalists find these findings useful in their knowledge of the solvophobic effect ^{12,72}.

For every solvent system under investigation, the CMC value rises when the cosolvent/alcohol proportion increases at a given temperature. This results from the cosolvent's influence on electrostatic and hydrophobic interactions as well as an alteration in the degree of structuring. When the medium's alcohol content rises, the dielectric constant decreases ^{19,73}. Consequently, micelle production happens at slightly greater levels whenever hydrophobic surfactant chains experience more water structure disruption than hydrophilic moieties. The methanol-water plot's volume fraction and CMC* at varying temperatures are plotted against each other in Figure 1.7. The medium becomes less polar and the micelles enlarge in rising methanol's concentration. This intensifies the forces of electrostatic attraction between the ionic head parts in the micelle and progressively decreases the hydrophobic interaction between the surfactant's hydrophobic groups, consequently, the micellization tendencies are dropped ^{10,19,74,75}. It is well recognized that the dielectric constant of a medium, in particular its hydrophobicity, plays a critical role in determining its micellization behaviors. The CMC values rise as the volume of methanol in the solution increases because the hydrophobic tail of the surfactant binds more effectively with methanol compared to water ^{21,76,77}. To break down water structures, methanol functions as both a cosolvent and a hydrophobic solute ⁷². Consequently, the solubility of the surfactant rises, delaying the micellization process. Here, the micellization is induced by hydrophobic

interactions

78,79

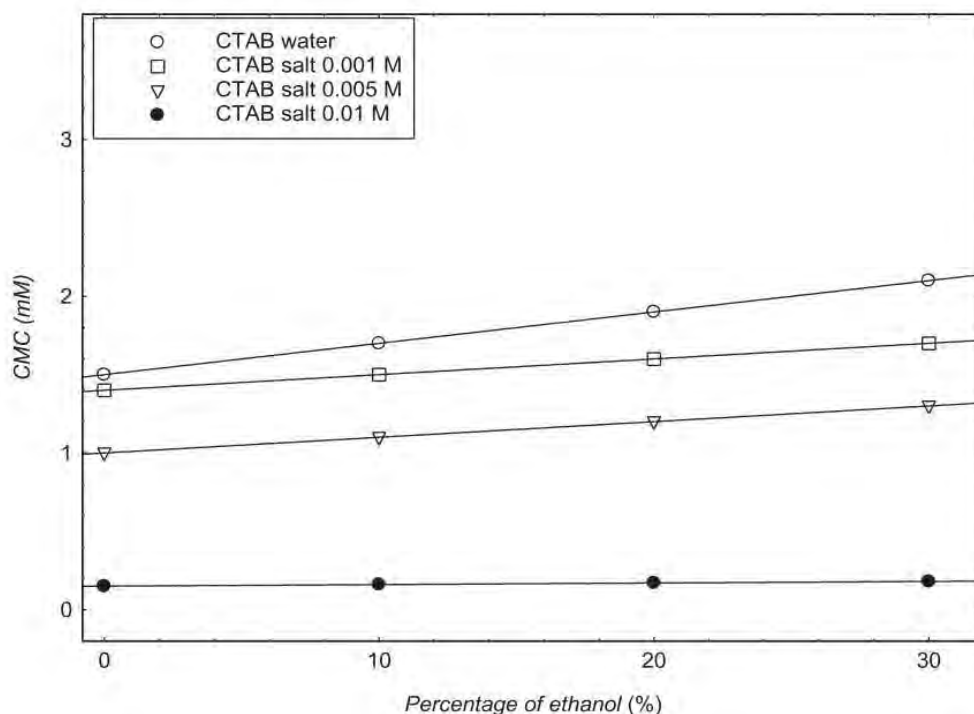


Figure 1.8: Changes in CMC with ethanol percentage at different salt concentrations ⁶⁹.

1.1.4.3. Addition of salts

The addition of salt results in a significant drop in CMC. Accordingly, the CMC values are significantly impacted by the valency of the added salt ions ³⁴. The phase behavior of the surfactant solution and other solution parameters, such as the CMC, are altered when salts are added to the surfactant solution. Most surfactants' CMC typically decreases when the electrolyte is present. Due to the screening impact that electrolyte has (by shielding the micellar charge), it lessens the repulsive forces between identical charged head parts of ions inside a micelle. As a result, the CMC is decreased as the surfactant monomers can pack closely. Since salt removes the hydrophobic alkyl chain from an aqueous solution and reduces electrostatic repulsion between polar head groups, it requires less electrical energy to form micelles, which lowers the CMC. Furthermore, because a more conspicuous charge screens more effectively and because the individual trivalent ion is more easily pulled into a total, the trivalent ion reduces surfactant headgroup territories and screens electrostatic interactions more efficiently than the di or monovalent counterions.

The "iceberg structure" of liquid water surrounding the monomer separates at varying speeds depending on the type of metal ions present in the surfactant mixture. This variation in hydration effectively determines the degree of entropy rise ³⁴. Because trivalent metal ions have larger effects on hydration than divalent metal ions, the entropy-driving effect for trivalent metal ions is more potent than that of divalent or monovalent metal ions. This results in a stronger impact of lowering the surfactant's CMC. One of the most significant characteristics of surfactants in micellar solutions is the formation of foam, which is crucial for many consumer applications including cleaning and washing. Here the salt significantly reduces the amount of foam and slows down the rate at which foam collapses ⁸⁰. Thus, Surfactants' CMC is lowered and their surface activities are increased when electrolytes are added, which promotes their practical use because surfactants' capacity to form micelles is a key component of many industrial applications.

1.1.4.4. Counterions

The ionic micelle surface is stabilized by counterions adhering to it; the degree of adsorption is influenced by the micellar charge density. The CMC falls with increasing counterion adsorption. The CMC falls with a rise in the counterion's valency. In contrast, a rise in the hydrated radius raises the CMC ⁸¹.

1.1.5. Polyelectrolyte and its classification

Polyelectrolytes (PEs) are a fascinating class of macromolecules that split into many charged groups and associated counterions in polar liquids ³. The electro-neutrality is maintained and repeated charged groups are neutralized by the smaller counterions. PEs behave like regular macromolecules when they're not charged, but even a slight ionic group dissociation can have a significant impact on the physicochemical characteristics of the material ^{82,83}. Because of this, polyelectrolytes display the characteristics of both electrolytes and polymers, which is useful for their interactions with different kinds of dye or surfactant molecules. The partial or total breakdown of the ionic portions can modify the behavior of the polymer by changing the electrostatic interactions, which in turn can cause variations in the polymeric characteristics ⁸³. Through the addition of ionic moieties to the polyelectrolyte atmosphere, PEs' physical properties, including solubility, viscosity, pH, diffusion coefficient, ionic strength, and ionization constant, can be altered ⁸⁴.

Polyelectrolytes have found widespread applications in a wide range of sectors, including biophysics, materials science, and colloids, due to their remarkable stability in water and ability to interact with surfaces and macromolecules that are negatively charged. Their main uses are in rheology modifiers, solar cells, adsorbents, colloidal stabilizers, coatings, suspending agents, optoelectronic devices, biomedical implants, drug delivery, and medicinal uses ^{85–90}.

Based on their origin, shape, charge, location of ionizable sites, pH dependency, and composition, polyelectrolytes are divided into several types ^{91,92}. Some polyelectrolytes that are synthetic like poly(vinyl amine), poly(acrylic acid), poly(vinylsulfonic acid), polyvinylpyridine, and polystyrene sulfonate, are frequently seen, while natural polyelectrolytes include polysaccharides, chitosan, alginates, pectin, carrageenan, and nucleic acids. The most prevalent functional groups in anionic polyelectrolytes are phosphonate ($-\text{PO}_3\text{H}^-$, PO_3^{3-}), carboxylate ($-\text{COO}^-$), and sulfonate ($-\text{SO}_3^-$), while primary or secondary or quaternary amino ($-\text{NH}_2$, $=\text{NH}$, and $=\text{N}^+$) groups are usually found in cationic polyelectrolytes ³. The structure of the repeating units, the kinds of ionic parts, and their counter ions impact the properties of polyelectrolytes ⁸⁴. In contrast to nonionic polymers, these characteristics are highly dependent on the ion content, solvent permittivity, and pH ⁸³.

It has been suggested that the electrostatic forces among charges on the monomeric units of polyelectrolytes are responsible for their diverse range of physicochemical properties. As an example, significant chain elongation can be caused by the electrostatic repulsion between identically charged monomer segments of a macromolecule in the absence of extra salts (ions), and this varies roughly linearly with the polymerization extent ^{3,93}. Compared to nonionizable polymers, the transition to the ionizable polyelectrolyte solution system might be achieved at notably lower polymer concentrations due to the substantial influence of polymerization extent on the transition of chain morphologies (coiling to elongation), increasing chain length ⁹⁴.

1.1.6. Dye and its classification

Unsaturated organic compounds known as dyes bind to the surfaces they are applied on and absorb a portion of visible light. Because chromophores and auxochromes are present, dyes are the primary components of color ². They are used to add color to textiles, food items, clothes, and other items to make them stand out and look more

beautiful ³². Natural dyes are typically derived from plants, including their wood, roots, leaves, bark, and fruits. Common natural dyes include henna, indigo, jackfruits, turmeric, and onions. Once crude oil is cracked, petroleum products can be used to make synthetic hues ³. Perkin discovered the first synthetic dye on August 26, 1856, and it was called aniline purple or mauveine ³. Although some dyes may have negative consequences, dyes are widely utilized in the production of pharmaceutical, industrial, and personal hygiene items, as well as in the diagnosis of diseases, drug delivery, and wastewater treatment ³⁰. Studying these compounds and how they interact with oppositely charged particles, which may be non-binding, H-bonded, hydrophobic/hydrophilic, electrostatic, or a combination of these, is therefore crucial.

The features and chemical structure of the dyes determine the type and extent of these interactions. The way molecules interact with surfactant + dyes or polyelectrolyte + dyes can be either hydrophilic, where two particles attract or repel each other because of the existence of charges on the molecules in nature, or hydrophobic, where molecules pull apart because of their poor affinity with water ⁹⁵. Hydrophobic interactions, like those between hydrocarbon chains, are those between nonpolar molecules that are insoluble in water. Conversely, polar molecules that are soluble in water or other polar solvents engage in hydrophilic interactions with one another. Similar to this, H-bonding uses an H-atom as a bridge to form a bond between two electronegative components.

The complexation of dye with polyelectrolytes or surfactants is driven by molecular interactions, and the thermodynamic characteristics associated with these interactions can assess the stability of the complexes that are formed ⁹⁶. The properties of a solution, including viscosity, surface tension, conductivity, critical micellization concentration (CMC), phase behavior, spectral behavior, and solution rheology, can be altered by combining surfactant/polyelectrolytes with dyes ⁹⁷. The dye's monomer band may shift blue or red when interacting with surfactants or polyelectrolytes ⁹⁸.

Dyes are classified into four main classes according to the kinds of chromogens they contain: (a) polyene; (b) cyanine; (c) donor-acceptor; and (d) $n \rightarrow \pi$ transition, by theoretical models and our understanding of the electrical origins of color ³. Dyes are frequently categorized in several other ways. Dyes can be classified as natural or synthetic based on where they come from that is the origin ⁹⁵. Dyes can be classified as

azoic/acid/basic/vat/dispersed/direct/reactive/sulfur/solvent dyes, and mordant dyes based on their diverse commercial applications ³².

Depending on the composition of their chemicals or nuclear structure, several kinds of dyes can be categorized, such as triarylmethane, phthalocyanine, acridine, azo, anthraquinone, cyanine, nitro, diazonium, nitroso, euryhodin, aniline, safranin, and xanthene dyes ³. Other classes of dyes include fuel dyes, oxidation dyes, smoke dyes, fluorescent dyes, leather dyes, sublimation dyes, leuco dyes, inkjet dyes, solvent dyes, and optical brighteners, depending on several other parameters ^{32,99–101}. The charged groups carried by the water-soluble dyes might be either cationic or anionic. Typically, an anionic dye has a carboxylate or sulfonate component. Since sulfonic acids are highly acidic, dyes containing sulfonate groups remain anionic throughout the pH ranges. Conversely, a carboxylic acid is a weakened acid, a carboxylate-containing dye requires a rather elevated pH to be water-soluble and anionic ³⁰.

1.1.7. Dye solubilization

One technique for determining the CMC is dye solubilization ^{102,103}. The first step in figuring out a dye's solubility in water is to construct calibration curves of the dye in a mixture of water and an appropriate solvent (such as ethanol or acetone) across an interval of dye concentrations. The method most frequently employed for quantitative dye characterization is UV-Vis spectroscopy ^{30,38}. The linear variation of absorbance at the maximum wavelength (λ_{max}) to dye concentration can be utilized to calculate the molar extinction coefficient (ϵ) of the dye through the application of Beer-Lambert's law, which is relevant for lower dye concentrations:

$$A = \epsilon \times l \times c \quad (1.2)$$

where c represents the dye concentration, l is the length of the light path, and A is absorbance. The concentration of solubilized dye in surfactant or polyelectrolyte is obtained from the calibration curve by measuring the solution's absorbance in a UV-Vis. spectrophotometer. The amount of dye that is soluble in one mole of micellized surfactant equals the surfactant's molar solubilization capacity, also known as solubilization power (SP) ³²:

$$SP = (S_{\text{total}} - S_{\text{wat}}) / (C_{\text{surf}} - \text{CMC}) \quad (1.3)$$

where S_{total} and S_{wat} are respectively the solubilities of the dye (mol/L) in the aqueous as well as in water, and $C_{\text{surf.}}$, the surfactant concentration in mol/L. The solubility strengths of a surfactant can be ascertained by evaluating the slope of the solubilization curve that follows the CMC. If the solubilisate and surfactant molecular weights are known, another method to describe the SP is the solubilized weight per unit mass of the surfactant ¹⁰⁴. When dye solubilization does not affect $N_{\text{aggregation}}$, or the number of molecules of surfactant in every micelle—also known as the surfactant aggregation number—the solubilization capacity (Σ), or how many dye molecules are solubilized in every micelle, can be stated as follows ¹⁰⁵:

$$\Sigma = \text{SP} \times N_{\text{aggregation}} \quad (1.4)$$

The value of Σ becomes 1 if each micelle solubilizes only one molecule of the dye, which could happen with spherical micelles. Nonetheless, there is a great deal of ambiguity because the uptake of the dye may cause the micelles to grow into disc-like structures or elongate, and these big micelles may easily solubilize several molecules of dye ¹⁰⁴. However, For spherical micelles, the Σ values are usually significantly smaller than one. For a given surfactant concentration, the ratio of the dye concentration in the micelle to the surrounding water is known as the micelle-water partition coefficient ($R_{\text{mic/wat}}$), expressed as follows:

$$R_{\text{mic/wat}} = (S_{\text{total}} - S_{\text{wat}}) / S_{\text{water}} \quad (1.5)$$

$$\therefore R_{\text{mic/wat}} = \text{SP} \times (C_{\text{surf}} - \text{CMC}) / S_{\text{water}} \quad (1.6)$$

The solubilization (ΔG_{Sol}) free energy is then obtained by the following equation ³²:

$$\Delta G_{\text{Sol}} = RT \ln (R_{\text{mic/wat}}) \quad (1.7)$$

where T is the Kelvin temperature and R is the gas constant. Here the activity of the solute must be taken rather than the concentration to acquire thermodynamic data (such as ΔG_{Sol}) accurately. The solute-surfactant interaction in the micelles is represented by the activity coefficient, which gives the ideality deviations ³². The aforementioned values (i.e., Σ , SP , ΔG_{Sol} and $R_{\text{mic/wat}}$) can be utilized to compare different surfactants under various conditions, like temperature, salt content, and pH, and to quantitatively determine the solubilization effectiveness of a surfactant. Temperature, PH, the addition

of electrolyte or polyelectrolyte, surfactant content, dye structure, and other factors all influence the solubilization of the dye.

Solubilizing dye in a surfactant solution is a conventional wastewater treatment method, particularly in the textile sector, to remove color. The physicochemical properties of the surfactant molecule play a major role in the dye's adsorption and its location in the substrate ¹⁰⁶.

Through solubilization in a surfactant solution during the post-treatment washing procedure, the substrate's weakly bound dyes are removed. It is not observed that the dye solubilizes below the surfactant's CMC because it mostly solubilizes in the hydrophobic cores of the micelles. As surfactant concentration rises above the CMC, the amount of dye solubilized grows linearly.

1.1.8. Surfactant-Polyelectrolyte interaction

When a polyelectrolyte with an opposing charge is present, surfactant and polyelectrolyte begin to aggregate as surfactant concentration rises above a threshold value the critical called CAC ¹⁰⁷. The binding site of the polyelectrolyte and the surfactant produce a neutral ion pair during this process, where the surfactant ion replaces the counter ion of the polyelectrolyte. Binding is highly favorable and relies on the polyelectrolyte ions' charge density due to the strong electrostatic attraction in this association process. Therefore, binding takes place in these systems at extremely low free surfactant concentrations, frequently one to three orders of magnitude below the surfactant's CMC ¹⁰⁸. In the absence of polyelectrolytes, this cooperative process is comparable to the natural association of surfactant monomers in aqueous solution that occurs in the small concentration ranges when surfactant concentration surpasses the CMC ³⁷.

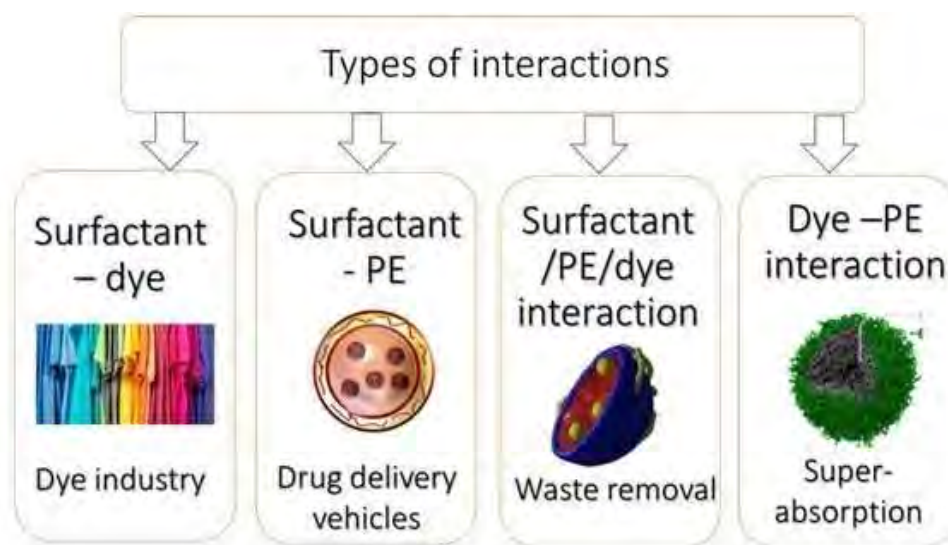


Figure 1.9: Applications of the various interactions occurring between surfactants, dye, and polyelectrolytes.

In polymer-surfactant systems, binding processes are primarily caused by the following interactions: (a) Hydrophobic interactions occur between polyelectrolyte molecules and surfactant, and even between the hydrophobic segments of surfactant molecules. (b) Electrostatic interactions between hydrophilic portions of surfactant-polyelectrolyte molecules, between surfactant molecules, and also between polyelectrolyte molecules; these interactions can be repulsive or attractive, depending on whether the molecules have comparable or opposite charge ^{37,81}. The micellization process of surfactant is severely adversely affected by these repulsive interactions. The primary cause of the association of polymer-surfactant systems generally, for the various interactions discussed, is the hydrophobic interactions between surfactant molecules ³. Due to sensitive energy balances, even minute contributions from the other interactions can significantly impact the self-assembly process and generate significant interactions between surfactant and polyelectrolyte. Owing to the electrostatic interactions, micellization of ionic surfactant will be especially susceptible to variations ^{37,107,108}.

1.1.9. Surfactant-Polyelectrolyte-Dye interaction

The substantial consequences of the molecular interaction between surfactants and polyelectrolytes with organic dyes in, industrial processes, materials science, pharmaceuticals, and environmental remediation make these interactions an area of great interest. The desired properties are obtained by combining surfactants with

different additives. Because numerous investigations have been published using water as a medium, interactions between polymers and surfactants, dyes and surfactants, and dyes and polymers are common issues of surface chemistry study.^{3,8,15,46,72,96,109–112} To date, such triple interactions give an interesting avenue for further research as they are still largely unexplored in ethanol-water solvent systems.

In contrast to conventional surfactant analogs, surfactant-polyelectrolyte complexes (PSCs) have shown outstanding dye removal capabilities and are frequently employed in polyelectrolyte-enhanced ultrafiltration of a variety of dyes. PE and surfactant charge play a major role in dye flocculation when employing surfactant-PE complexes⁵. Carefully observing the degree of copolymerization and polymerization of the charged segments with charged or neutral monomers regulates the charge density of the PE¹¹³. The way that dye interacts with surfactant is notably impacted by the hydrophobicity of the surfactant. Longer hydrocarbon chain surfactants are more effective at removing methyl orange (MO), according to studies on the anionic dye's interaction with a homologous sequence of quaternary ammonium bromide surfactants. The efficiency of removal of MO removal is $C_{10}TAB (15\%) < C_{12}TAB (37\%) < C_{14}TAB (90\%) < C_{16}TAB (>95\%)$ ¹¹⁴. In research, dye molecules have been used to interact with PSCs to create dye-loaded, thermosensitive surface films that include cationic quaternary ammonium surfactants and natural polyelectrolyte, such as right-handed double-stranded DNA¹¹⁵.

The different types of PE-surfactant and dye interactions and the resulting complexes are illustrated in Figure 1.10 (a-f).

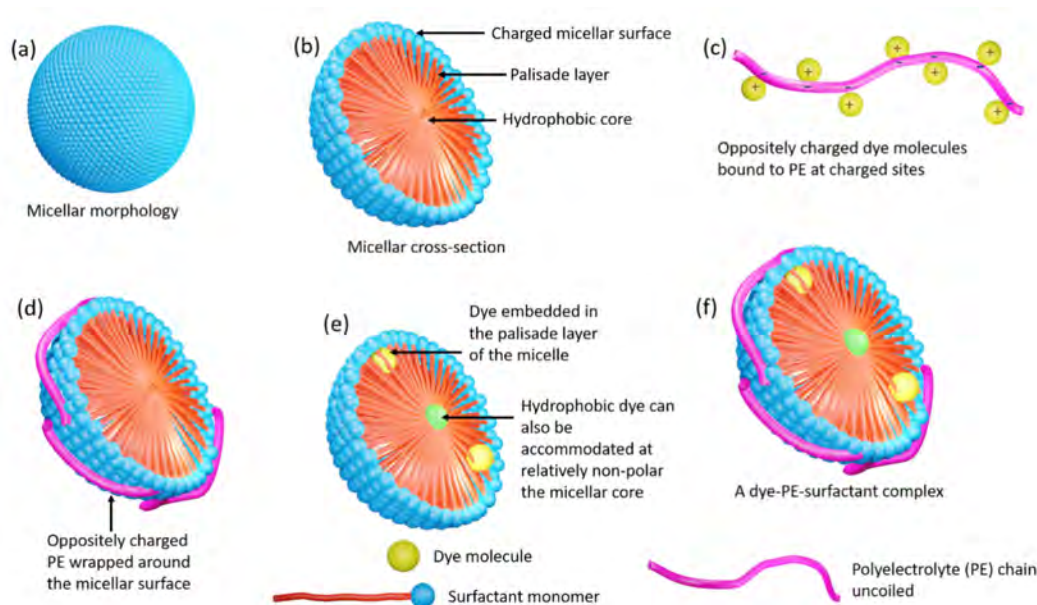


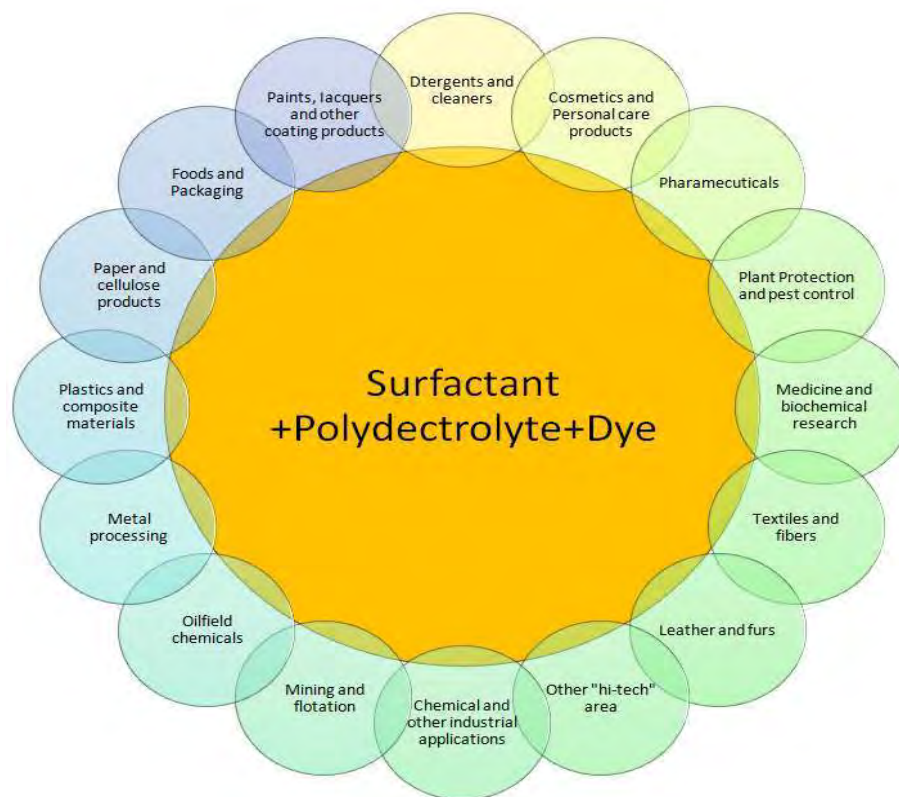
Figure 1.10: The different types of polyelectrolyte, surfactant and dye interactions and the resulting complexes.

- (a) Morphology of a spherical micelle, (b) Cross-sectional view of the micelle indicating regions of variable polarity. The complexes formed in the various interactions are represented as (c) polyelectrolyte-dye complex where charged dye particles interact with the oppositely charged segments in the polyelectrolytic chain via charged patch interaction; (d) micelle-polyelectrolyte complex, the charged polyelectrolyte interact with the opposite charges micellar head group via electrostatic interaction; (e) dye-micelle complex, where dye monomers are embedded in the palisade layer of the of micelles surfactant, the non-polar micellar core has room for accommodation of hydrophobic dye; (f) the dye-polyelectrolyte-surfactant complex, where the dye-micelle complex if further interacted upon by the polyelectrolytic chain.

The results of this study will help to clarify the thermodynamics, feasibility, and stability of these complex systems, with possible uses in environmental remediation to industrial formulation. It will also open the door for further investigations into the influence of many other co-solvents along with various additives in the interaction between surfactant, polyelectrolyte, and dye, to generate new, cutting-edge, inventive materials with enhanced quality products and economy that will be valuable to the community.

1.1.10. Present Investigation

It is clear from the above discussion that the issues surrounding polyion-counterion, polyion-surfactant, and surfactant-polyelectrolyte-dye interactions are fascinating. To get a firm conclusion, it is therefore desirable to investigate this matter utilizing several experimental methodologies. Additionally, compared to studies conducted in aqueous solutions, investigations conducted in mixed solvent media offer a broader perspective on how surfactant, polyelectrolyte-surfactant, and surfactant-polyelectrolyte-dye behave in micellar solutions. This is because the use of successive mixed solvents gradually alters the relative permittivity of the media and, consequently, the interactions that exist in these solutions. The mixed solvent ethanol-water (EtOH-water) is employed in this investigation. Water plus ethanol is a common combined solvent that has been thoroughly researched ^{19,68,96,116}. Despite being completely miscible at normal temperature, the two solvents in these combined solvents have rather diverse chemical composition, which makes them interesting. The most simple amphiphile is hydrogen-bonding liquid ethanol, which contains hydrophobic (-CH₃CH₂) and hydrophilic (-OH) groups. In the chemical and biological sciences, it is crucial to comprehend the solvation properties of ethanol about the distribution of hydrophobic and hydrophilic groups in polar or nonpolar solvents. This is because amphiphiles are crucial components of cell membranes and are also widely employed as micelles in chemical industries, such as in detergent action ^{19,68,96}. Numerous scientific studies and important technological uses have focused on the anomalous features of water-alcohol mixtures ^{1,117,118}. Consequently, it would be intriguing to gain insight into how CTAB-NaPSS or DTAB-NaCMC behaves in these mixture solvents both with and without MR or MO. Thus, in the current study, we studied the solution properties of CTAB, DTAB, CTAB/NaPSS, DTAB/NaCMC, CTAB/NaPSS/MR, and DTAB/NaCMC/MO in ethanol-water mixed solvent media at 298.15, 308.15 , and 318.15 K using conductometry, tensiometry, and UV-Vis spectrophotometry.



Scheme 1: Some important, high-impact areas of surfactant+polyelectrolyte+dye interactions.

1.1.11. Objectives of the present research work

Since surfactants are utilized together with a range of additives to acquire the desirable characteristics, interactions between surfactants in polyelectrolyte with the inclusion of dyes are of significant importance due to their broad applications in the fields of materials science, health, industry, and environmental restoration. Surfactant/Polymer, polymer/dye, and surfactant/dye/ interactions are commonly found in surface chemistry investigations since numerous studies have been published in aqueous medium. However such ternary systems in ethanol/water solvent media have not yet been investigated, providing an interesting area for investigation.

Hydrophilic and hydrophobic interactions have a significant impact on micelle formation, which is affected by the polarity of the medium, which can be altered by changing the solvent composition. Thus, the system containing surfactant/polyelectrolyte/dye in mixed solvent medium of varying dielectric constants can be used for investigation. Temperature also plays a significant role in almost all scientific investigations. In the case of our systems, the physicochemical properties are

greatly affected by temperature. Presumably, with the increase in temperature, the thermal energy of the system increases which ultimately leads to an increase in several physical properties of working solutions.

The objective of this work is related to the fundamental and applied aspects of interaction and micellization behavior of surfactant in polyelectrolyte solution containing dye in water and ethanol-water solvent media at 298.15, 308.15 , and 318.15 K temperatures. We calculated the thermodynamic variables like CAC, CMC, α , and others that provide important information about the interactions occurring in such systems. It is expected that the results of this research will clarify the thermodynamics, stability, and viability of these complex systems, with potential uses extending from environmental cleanup to industrial operations. Further investigation into the effects of various co-solvents and extra additives in the interaction between surfactant, dye, and polyelectrolyte will also be made possible by this, opening the door to the creation of novel, cutting-edge, inventive, and sustainable materials with enhanced yields and economy that will be useful to the community.

1.1.11.1. General Objectives

1. To measure the effect of surfactant concentration on surface tension, conductivity, and spectral behavior of (polyelectrolyte + surfactant + dye) solution.
2. To measure the effect of temperature, and solvent composition on conductivity, surface tension, and spectral behavior of (polyelectrolyte + surfactant + dye) solution.

1.1.11.2. Specific Objectives

1. To investigate the interaction and micellization behavior of CTAB in NaPSS with and without MR in aqueous and ethanol/water solvent media (0.1, 0.2, and 0.3 volume fractions) media at 298.15, 308.15 , and 318.15 K by conductivity method.
2. To investigate the effect of NaCMC on the interaction and micellization properties of DTAB in the presence and absence of MO in aqueous and ethanol/water mixture solvent media (0.1, 0.2, and 0.3 volume fractions) at three various temperatures (298.15, 308.15 , and 318.15 K) by conductivity technique.

3. To investigate the spectral and interaction tendencies of Methyl Red with Cetyltrimethylammonium bromide under the effect of Sodium polystyrene sulphonate in aqueous and ethanol/water (0.1, 0.2, and 0.3 volume fractions) solvent media at room temperature (298.15 K) by UV-visible spectroscopic method.
4. To investigate the spectral and interaction behavior of Methyl Orange with Dodecyltrimethylammonium bromide under the influence of Sodium Carboxy Methyl Cellulose in aqueous and ethanol-water (0.1, 0.2, and 0.3 volume fractions) mixed solvent media at room temperature (298.15 K) by UV-visible spectroscopic method.
5. To study the surface, micellization, and thermodynamic behavior of CTAB with NaPSS in the presence and absence of MR in ethanol-water mixed solvent media (0.1, 0.2, and 0.3 volume fractions) at three various temperatures 298.15, 308.15 , and 318.15 K by surface tension method.
6. To determine CAC, CMC, and α values, and thermodynamic parameters like the standard free energy of binding, standard free energy of micellization (ΔG_m^0), standard entropy of micellization (ΔS_m^0), the standard free energy of bound micelle, standard heat of micellization (ΔH_m^0), binding constant (K_b), and standard free energy of tail transfer (ΔG_{trans}^0), and surface properties: packing parameter (P), maximum excess surface concentration (Γ_{max}), area occupied per surfactant molecule (A_{min}), surface pressure at the CMC (π_{CMC}), and standard free energy of adsorption (ΔG_{ad}^0) from the above investigations to determine the spontaneity of the micellization phenomenon for the CTAB, CTAB/NaPSS, and MR/CTAB/NaPSS systems in ethanol/water solvent media (0, 0.1, 0.2, and 0.3 volume fractions) and three various temperatures (298.15, 308.15 , and 318.15 K).

The study has been limited to 0.3 volume fractions of EtOH-water solely because the formation of the cloudy solution in the system prevented us from continuing over this volume fraction, where micelle production is not expressly noticeable due to the medium's low dielectric constant ¹⁰.

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