Chapter 1 - Introduction

Kinetics of Organic Reactions in Micelles

The special properties of surfactants are important in a wide variety of applications in chemistry, biology, engineering, and other areas. These molecules are said to be amphipathic; i.e., they have distinct hydrophilic (polar) and hydrophobic (non-polar) regions. The polar region, called the head group, may be neutral, cationic, anionic, or zwitterionic. The hydrophobic tail has one or more chains of varying length, composed usually of a hydrocarbon. Common examples are:

- Polyoxyethylene (6) octanol, CH₃(CH₂)₇(OCH₂CH₂)₆OH (neutral)
- Cetyltrimethylammonium bromide, CH₃(CH₂)₁₅(CH₃)₃N⁺Br⁻ (C₁₆TAB, cationic)
- Sodium dodecyl sulfate, CH₃(CH₂)₁₁OSO₃⁻Na⁺ (SDS, anionic)
- N-dodecyl-N,N-dimethylglycine, CH₃(CH₂)₁₁(CH₃)₂N⁺CH₂COO⁻ (zwitterions).

Surfactants dissolve completely in water at very low concentrations, but above a certain level, the critical micelle concentration (CMC), the molecules form globular aggregates, called micelles. The hydrophobic tails group together to create a non-polar interior with the head groups located at the surface of the glob in contact with the aqueous environment. Micelles vary in size and shape, commonly rough surfaced spheres with aggregation numbers on the order of 50-100.

Surfactants are widely used and found a large number of applications because of their remarkable ability to influence the property of surface and interfaces. The widespread importance of surfactant in general and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject. In the years that have passed, micellar solutions have proven to be an extremely versatile topic of research. The catalytic potential of micellar aggregates has received special attention. This thesis
focuses on micellar catalysis of reactions and will provide, for the first time, a link between micellar catalysis and Lewis-acid catalysis. Before elaborating on this, the physical properties and catalytic potential of micellar solutions will be briefly reviewed. Surfactants are best known to us as detergents. Grease on skin, dishes, clothes, etc. is attracted to the hydrophobic micelle interior and is subsequently rinsed away. This ability to solubilize non-polar materials has made aqueous surfactant systems increasingly popular alternatives to organic solvents in various applications. An example is emulsion polymerization, in which water-insoluble molecules are polymerized in an aqueous micellar environment. This procedure alleviates problems due to high viscosities and removal of solvent and monomer. The presence of micelles can have marked effects on chemical reactions. The thermodynamic favorability such as an acid dissociation can be shifted significantly. Reaction rates can be either accelerated or decelerated, depending on the chemical system, the type and concentration of the surfactant, and other factors, such as pH, ionic strength, etc. The effect of surfactants on reaction kinetics is often called micellar catalysis.

**General Classification of Surface Active Agents**

Usually the classification used is one which puts surface active agents into various groups depending on the nature of head groups, that is anionic, cationic, nonionic and zwitterionic or amphoteric (ottewill and Greek).

1. **Anionic Surfactant:** The effective ion is negatively charged, e.g. \( \text{CH}_3(\text{CH}_2)\text{OSO}_3\text{OM}^+ \) where \( \text{M}^+ = \text{Li}^+, \text{Na}^+, \text{Ca}^{2+}, \text{Mg}^{2+} \) etc.

![Surface in active ions](image)

\( \text{M}^+ = \text{Li}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^+ \) etc.}
A number of anionic surfactants with oxyethylene units adjacent to the hydrophillic head group have also been reported as having industrial importance (Dahayanake 1986).

2. **Cationic surfactants:** The effective ion is positively charged eg. \( \text{CH}_3\text{CH}_2\text{N}^+\text{Me}_3\text{X}^- \) where \( \text{X}^- = \text{F}^-, \text{Cl}^-, \text{OH}^-, \text{NO}_3^- \) etc. Surface in active ions \( \text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{OH}^-, \text{NO}_3^- \)

3. **Nonionic Surfactant:**

The water soluble moiety of this type contains a polyoxyethylene chain and ethylene oxide chain length. The head group is larger than the hydrocarbon chain. For ex. Dodecyl hexoethylene glycol monoether \( \text{C}_{12}\text{H}_{25}[\text{OCH}_2\text{CH}_2]_6\text{OH} \). Nonionic surfactant with small head group also exists, such as, Docetyl sulphinyl ethanol \( \text{C}_{12}\text{H}_{25}\text{SOCH}_2\text{CH}_2\text{OH} \). A Homologous series of nonionic surfactants, N-alkanoyl-N-methylglucamines have also been synthesized by Hildreth.

\[ \text{CH}_3\ldots(\text{CH}_2)\ldots(\text{CH}_2)\ldots\text{N}^+\ldots(\text{CH}_2)\ldots(\text{CH}_2)\ldots\text{O} \]

\[ \text{CH}_3\ldots(\text{CH}_2)\ldots(\text{CH}_2)\ldots\text{N}^+\ldots(\text{CH}_2)\ldots(\text{CH}_2)\ldots\text{O} \]

\[ \text{N-alkanoyl-N-methylglucamines} \]
Most of the commercially available polymeric nonionic surfactants have also been reported. Their wetting and detergency is much inferior to simpler non ionic, the poly ether types which are not too degradable. The formulae and chemical structure of the polymeric surfactants are illustrated in figure1.

4. Amphoterics: This type of surfactant can behave as anionic, cationic or nonionic species, depending upon the pH of the solution eg. Zwitterionic form of N-dodecyl betaine C_{12}H_{25}N(CH_{3})_{2}CH_{2}COO-. Table 1.1 lists the above four major groups of surfactants. Recently a series of amphoteric oligomeric and amphoteric polymeric surfactants have been studied. Both contain a 2-Carboxyethyl group and a 2-hydroxyalyl (C12-HA or C14-HA) group. Other groups of surfactant include, Naturally occurring Compounds: Within this group there are numbers of important naturally occurring materials, known as triglycerides, a good example being lecithin, which occurs in the membrane of many cells.
Table 1.1 Classification of major chemical groups of surfactants (after greek)

<table>
<thead>
<tr>
<th>ANIONICS</th>
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<tbody>
<tr>
<td>Carboxylates (soaps)</td>
<td>R—CH₂—C—O⁻—Na⁺</td>
<td>R = C₁₅₁₈</td>
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<tr>
<td>Alkylbenzene sulfonates</td>
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<tr>
<td></td>
<td>R—CH₃—SO₃Na</td>
<td>n = C₁₀₁₃</td>
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<tr>
<td>Alkane sulfonates</td>
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<td></td>
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<tr>
<td></td>
<td>R₁—CH₂—SO₃Na</td>
<td>R₁ + R₂ = C₁₁₁₇</td>
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<tr>
<td>α-Olefin sulfonates</td>
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<tr>
<td></td>
<td>H₃C—(CH₂)ₙ—CH₃—CH—(CH₂)ₙ—SO₃Na</td>
<td>n + m = 9—15</td>
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<tr>
<td>Fatty alcohol sulfates</td>
<td></td>
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<tr>
<td></td>
<td>R—CH₂—O—SO₃Na</td>
<td>R = C₁₄₁₇</td>
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<tr>
<td>Oxo-alcohol ether sulfates</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R—CH—CH₂—O—(CH₂—CH₂—O)ₙ—SO₃Na</td>
<td>n + n' = C₁₁₄₃, n = 1—4</td>
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<tr>
<th>CATIONICS</th>
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<tr>
<td>Quaternary ammonium salts</td>
<td>[R¹⁺, R²⁺]Cl⁻</td>
<td>R¹⁺, R²⁺ = C₁₆₁₈</td>
</tr>
<tr>
<td>(quats)</td>
<td></td>
<td>R²⁺, R³⁺ = C₁²³</td>
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<tr>
<td>Amine oxides</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>RN⁺—(CH₃)ₙ</td>
<td>R = C₁₇₁₅</td>
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<tr>
<th>NONIONICS</th>
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KINETIC STUDIES OF SOME ESTERS AND AMIDES IN PRESENCE OF MICELLES

Alkylphenol ethoxylates

Fatty or oxo-alcohol polyethylene glycol ethers

Ethylene oxide-propylene oxide polymers

Fatty alcohol polyglycol ethers

AMPHOTERICS

Alkyl betaines (also sulfonated)

Lecthin
Micellar aggregates: structure and dynamics

Surfactant molecules (also called amphiphiles or detergents) unite a polar or ionic head and a nonpolar tail within the same molecule. The nonpolar part, which is typically made up of one or more alkyl chains, causes these compounds to be sparingly soluble in water, whereas the polar or ionic part interacts strongly with water. Upon increasing the concentration of the amphiphilic compound in water, at a certain point the solubility limit will be reached and phase separation will set in. Due to the efficient interactions between the polar head groups and the surrounding water molecules, a complete phase separation is usually unfavorable. Instead, the process will be arrested in an intermediate stage with concomitant formation of aggregates of amphiphilic material, where in the non-polar parts stick together and are shielded from water, whereas the headgroups are located in the outer regions of the aggregate. A multitude of different aggregates can be formed in this way. The morphology of these assemblies is mainly determined by the shape of the individual surfactant molecules. Ninham and Israelachvili have introduced the concept of the packing parameter, allowing prediction of the type of aggregate formed by considering the cross sectional headgroup area and the length and volume of the nonpolar part of the amphiphile molecules.
Surfactants containing a single alkyl chain usually form micelles when dissolved in water. A schematic representation of a spherical micelle is given in Figure 1.1. The formation of micelles sets in after a certain critical concentration of surfactant (the critical micelle concentration, CMC) has been reached. Beyond this concentration the addition of more surfactant molecules will result in an increase in the number of micelles, while the concentration of monomeric surfactant remains almost constant. Micellization is usually driven by an increase in entropy, resulting from the liberation of the water molecules from the hydrophobic hydration shells of the monomeric amphiphile molecules, whereas the enthalpy change is generally close to zero (Corkhill 1973). Micelles are extremely dynamic aggregates. Ultrasonic, temperature and pressure jump techniques have been employed to study the rate constants, associated with the different equilibria involved. Rates of uptake of monomers into micellar aggregates are close to diffusion controlled. The residence times of the individual surfactant molecules in the aggregate are typically in the order of $10^{-5} - 10^{-6}$ second (Tanford 1972, Oakenfull 1974), whereas the lifetime of the micellar entity is about $10^{-3} - 10^{-1}$ second (Tanford 1972, Oakenfull 1974). Factors that lower the CMC usually increases the lifetime of the micelles as well as the residence times of the surfactant molecules in the micelle. Due to this dynamic character, the size and shape of micelles are subject to appreciable structural fluctuations. Hence, micellar aggregates are polydisperse, as is demonstrated by small-angle neutron scattering data (Ford 1966). Average aggregation numbers are typically in the range of 40 – 100 (Mukerjee 1966). The highly dynamic character for a long time successfully in their conception of the structure of a micelle. Extensive discussions have focused on the conformation of the alkyl chains in the interior (Turner 1968). It has been demonstrated that the alkyl chains of micellized surfactant. Starting from the head group, the first two or three carbon-carbon bonds are usually trans, whereas gauche conformations are likely to be encountered near the centre of the chain (Gitler). As a result, the methyl termini of the surfactant molecules can be located near the surface of the micelle, and have even been suggested to be able to protrude into the
aqueous phase (Kurz 1962). They are definitely not all gathered in the centre of the micelle as is often suggested in pictorial representations. NMR studies have indicated that the hydrocarbon chains in a micelle are highly mobile, comparable to the mobility of a liquid alkane (Menger). Another topic of heated debate comprised the extent of water penetration into the hydrocarbon interior (Turner 1968). Small-angle neutron scattering studies have resolved this matter by indicating that significant water penetration into the micellar core is unlikely (Albrizzio). However, at the interface, extensive contact between water and the hydrocarbon chain segments definitely occurs. The headgroups of the micelle are extensively hydrated. For ionic micelles, a large fraction of the counterions are located in the vicinity of the headgroups. These counterions normally retain their first hydration shell (Bunton 1972). The part of the surfactant that contains the headgroups and a variable fraction of the counterions is called the Stern region. This region comprises an appreciable electric field and a high concentration of ions (several molar) at the interface between the non-polar interior and the aqueous exterior of the micelle and can be expected to exhibit unique properties. For pyridinium iodides, the polarity of this region has been probed with the aid of the interionic charge transfer band characteristic, for these species. The results indicate a somewhat reduced polarity of the Stern region compared to bulk water (Gustavsson 1975). The important role of this region in solubilization and micellar catalysis is reviewed in the next sections. Some compounds like short chain fatty acids are amphiphilic or amphipathic i.e. they have one part that has affinity for non polar media and one part that has affinity for polar media. The interface formed at the polar head groups of micelles in the presence of a surrounding aqueous environment provides an unusual micro environment in which chemical reactions may occur. During the past decade, there have been a number of studies concerned specifically with the characteristics of reactions occurring at the micellar surface. Gruen has described a realistic model for a micelle (Figure 1) (Bunton et al). This model involves a rather sharp interface between a dry (Bunton and Cordes) hydrophobic hydrocarbon core and a region filled with surfactant headgroups,
part of the counter ions and water, viz. the Stern region. This model has been validated using molecular dynamics simulations (Cordes 1973, Mukerjee 1977, 1978) and is valid for both ionic and nonionic micelles. In micellar solutions, reactions can be both accelerated and inhibited compared to the reaction in water without added cosolutes (Israelachvili 1976, Sams 1972). Continuous interest have developed in micellar catalysis of both organic and inorganic reactions. Remarkable success in enhancing reaction rates (Oakenfull 1974) by the introduction of catalytic moieties in surfactants has been achieved (Schrier 1964). However, we limit our discussion to “medium effects” as they occur in solutions of unfunctionalised micelle forming amphiphiles. The distinction between medium effects and surfactants equipped with catalytic moieties may not always be clear, as for example in the case of micelles with catalytic counterions (Ford 1966). The aim of the present study was to investigate mechanistic aspects of micellar effects on pH-independent hydrolytic reactions and to develop a satisfactory description of the micellar pseudo phase as a reaction medium. A prerequisite for understanding the reaction medium offered by micelles is to know where the reaction is taking place. A micelle offers several binding sites for relatively polar molecules. These include the hydrophobic core and hydrophobic binding sites located in the Stern region. The latter region is particularly flexible in binding molecules as it contains highly hydrophilic surfactant head groups and hydrophobic domains in part due to back folding of the surfactant tails (Bunton, Cordes 1973; Mukhejee 1978)) as well as water molecules. A number of techniques is suitable for the study of binding locations inside micelles. Typically, these methods include Aromatic Ring Current effects which induce changes of (NMR) chemical shifts (Mukerjee 1963, 1968, Turner, 1968) paramagnetic relaxation enhancement experiments, (Kurz (1963), Menger) fluorescence probing experiments (Bunton and Huang 1978) and fluorescence lifetime experiments (Gustavsson et al. 1975) From the results of numerous studies applied, among others, the techniques mentioned above, s commonly assumed that polar molecules preferably bind to micelles in the Stern region(Oakes, Robb, Shinitzky, Khuanga, Faraday, Williams
(1957), Kunitake(1977) and Okahata 1971-76). Moreover, it is also commonly assumed that, up to a critical concentration, aromatic molecules also bind in the Stern region(Mukerjee, Kunitake and Klotz). However, for benzene the binding depends on surfactant structure with the preference for binding in the Stern region being higher for trimethylammonium headgroups (DTAB and CTAB) than for sulfate headgroups (SDS) (Yatsimirskii, Martinek et al 1973).

In combination with our results (vide infra), we contend that the reactions under study take place in the Stern region. One of the key factors in the medium offered by the micellar Stern region is the concentration of headgroups and counterions. It has been estimated (Okahata et al 1977, Jenecks 1975, Bunton 1971) that the concentration of headgroups in the Stern region lies in between of 3 to 5 mol dm$^{-3}$, though recent work also suggested lower values( Bunton et al 1970, 1973). The concentration of counterions is slightly less due to incomplete counterions binding, creating an electrically non-neutral environment. In order to study the nature of the micellar Stern region, two approaches were followed. One approach involved kinetic measurements of the rates of the water catalyzed hydrolysis of activated amides and an activated ester in micelles and in solutions mimicking the local environment in the Stern region. The second approach involved spectroscopic studies employing the solvatochromic ET(30) micropolarity indicator(Kemp and Paul 1975).

**Thermodynamics of Micellization**

The main concern of thermodynamics that are applied to micellar systems is the behavior of the chemical potentials (or activities) of the various solute species when the temperature and the composition of the solution are altered. During the past years, thorough ways to calculate changes in thermodynamic parameters that accompany micelle formation from experimental data. Hall and Pethica paid considerable attention to the thermodynamics of micellization, and in particular to the merits and demerits of the various approaches which have been made to this problem. Different
basic approaches that has been made to explain the thermodynamics of micelle formation which are:

**Phase Separation Model**

This approach treats micelle as a separate but soluble phase which begins to form at the CMC. Hence, the CMC is the saturation concentration for monomers and the concentration of activity of monomers should not exceed above it. This model could be formulated by assuming that the chemical potential of the surfactant in the micellar state is constant at a given temperature and may be adopted as the standard chemical potential, $\mu_m^0$, analogous to the standard chemical potential of pure liquid or solid. Equilibrium with the surfactant in solution is then represented by

$$\mu^m = \mu_1^0 + RT \ln a_1$$ (1.1)

where $\mu_1^0$ is the standard chemical potential in solution and $a_1$ is the activity of the surfactant monomer in solution. Putting $a_1 = x_1 F_1$, the standard free energy of micellisation per mol. Of monomer, $\Delta G_m^0$, is given by

$$\Delta G_m^0 = \mu_m^0 - \mu_1^0 = RT \ln X_1$$ (1.2)

where $X_1$ is the mole fraction of monomers and the activity coefficient $f_1$ is taken as unity. The CMC, may be identified with $X_1$.

The phase separation approach is, however, consistent with the facts that the activity of monomer decreases above the CMC and around the CMC. The properties of the solution changes rapidly and continuously. The phase separation model makes no provision for possible variation in the activity of surfactant as total concentration of surfactant in the solution and an equation of state analogous to those used to describe films is required to refine the model.
Mass Action Model

This approach consistent with the fact that the properties of the solutions change continuously at the CMC and predicts correctly that the activity of monomer changes above the CMC. Good estimates has been obtained between thermodynamic and spectroscopic estimates of the monomer concentration and its dependence on total concentration.

Figure 1.2. Distribution of surfactants between monomers and micelles
(After Lindman and Wenner-strom)

The small system/multiple equilibrium approach gives a clear statement of the approximation involved in treating the micelles as separate phase and regarding the micelle/monomer equilibria between a solution and its vapor. The treatment of micelle formation by the small system thermodynamic approach constitutes a general theory which partly includes treatments of both mass action and phase separation models and could be used to clarify the thermodynamically meaning of the application of both models. The factors for micelle formation include thermodynamic parameters such as the difference in standard free energy enthalpy, and volume per surfactant molecule in micellar and monomeric states of micellization. The larger the micelle, the greater the translational freedom of the monomer in it, and hence, a free energy which
decrease resulted from the order to disorder change. The overall decrease in free energy and changes in hydration of head independent of temperature.

The proportion of an increase in total concentration $X^*$ which is incorporated in the micelle and $\frac{dX_n}{dX_T}$ are shown as a function of the ratio of total concentration to the CMC. $X_T/X^*$.

**Small System / Multiple Equilibrium Model**

The observation of small system thermodynamics and essentially equivalent multiple-equilibrium approaches provides a powerful tool for discussing well defined single and multi-component, non-interacting, non-ionized surfactant system.

Good agreement has been obtained between thermodynamic and spectroscopic estimates of the monomer concentration and its dependence on total concentration.

The small-system/ multiple equilibrium approach gives a clear statement of the approximation involved in treating the micelles as separate phase and regarding the micelle monomer equilibria as equilibria between a solution and its vapor (Hall et al 1981).

The treatment of micelle formation by the small-system thermodynamic approach constitutes a general theory which partly includes treatments of both mass action and phase separation models and could be used to clarify the thermodynamically meaning of the application of the above models (Okawauch et al 1987).

The answer to “why do micelles form” could be explained on the thermodynamic parameters such as the difference in standard free energy, enthalpy and volume per surfactant molecule in micellar and monomeric states of micellization (Hall et al 1981) The larger the micelle, the greater the translational freedom of the monomer in it, and hence, a free energy decreases which resulted from the order to disorder change (Poland et al
1965,1966). The overall decrease in free energy and changes in hydration of head independent of temperature. At 25°C, the unique structural properties of water are evident, but at 166°C, those properties totally vanishes. This can be explained on the basis of the entropy and enthalpy changes on micellization. At 25°C the entropy change upon aggregation was large and positive (25 Cal K⁻¹mol⁻¹) whereas at 166°C it was large but negative (-13 Cal K⁻¹mol⁻¹). Negative entropy at the high temperature had little effect on water structure but it reflects the ordering and orientation, imposed on the hydrocarbon chain following its transfer from bulk water in monomer form to interior of a small micelle where it had less flexibility in movement. Evans suggested that at high temperatures aggregation was driven entirely by the energetic transfer of non-polar group from a polar solvent. However, at 25°C the same entropic and enthalpic factors were in operation and must be of same magnitude as they were nearly independent of liquid (hydrogen-bonding) structure. Hall (1987) has reviewed the work of Akisoda (1984), based on the thermodynamics of ionic surfactant micelle. The improvements were based on the thermodynamics of ionic surfactant micelle in Gibbs-Duhem equation, which is applicable to micellar solutions of ionic surfactants.

Structural Aspects of Surfactant Micellar Systems: Micelle Shape, size and Polydispersity

Micelles have a spherical or an ellipsoidal shape for small ionic amphiphiles in a dilute solution of surfactant (Murata et al 1973, 1974). In more concentrated solution, it changes to an elongated shape (Corkill et al 1963). However, micelles can also be lamellar, bilayer, rod or disc shaped and hemispherical shaped cylinder shaped (Mukerjee 1974, Menger 1979).

Various micellar shapes are suggested in figures 1.3 &1.4. Experiments which provide information regarding micellar shapes and size includes Viscosity (Mukerjee 1977), light scattering (Menger 1979), ultracentrifugation (Mukerjee 1977) low angle X-ray scattering, Laser-excited Raman spectra measurement technique (Kalyansundaram et al 1976) quase-elastic light
scattering (QULS), (Mazer et al. 1976). Nuclear Magnetic relaxation studies (Henriksson 1987), high-resolution NMR and small angle neutron scattering (SANS) techniques (Burns et al. 1980, 1982).

Figure 1.3: Various models of micelle structures, McBin spherical ionic micelle, McBain lamellar micelle, Hartley spherical micelle, Debye cylindrical micelle.
Figure 1.4: Diagrammatic representation of a cationic micelles curved arrows illustrate liquid like nature of the micelle core.

**Structure of Micelles**

The generalized structure of the cross-section of ionic micelles have liquid core formed by the associated hydrocarbon chains with fully ionized head groups projecting out into water.
The molecular structure of the micelle has been studied by different models. For example, Menger has contrasted the Hartley’s “Classical Oil Droplet Model” with his Porous Cluster Model that assumes the presence of water filled grooves allowing extensive water penetration beyond the surface of the micelle. Bonilha et al. differentiated the ‘larger, spherical model and a surfactant block model in terms of penetration of the solute. Bonilha further presumed that surfactant block model had greater resistance to penetration than larger model.

The main features of Dill-Flory lattice Model are

1. A smooth spherical surface in which head groups are closely packed as close to each other as are the chains.
2. A core centre with a “degree of order approaching” in a crystal.
3. Little terminal exposure to water when the chains are long but considerable exposure when chains are short.
Menger and Doll interpreted micellar structure in terms of coiling and disorder with chain placed chain termini in the water-rich stern regions. Figure 1.7 embodies the main characteristics of the Menger micelle: a large wet stern region, rough surface, looping, and disorder (i.e. non-radially distinguished, distributed chains).

Figure 1.6. Representation of DILL-FLORY Lattice model.

Figure 1.7. Schematic representation of Micelle embodying the main characteristics of the “Menger Micelle”.
Self-assembled surfactant aggregates

A surfactant at low concentration in aqueous solution exists as monomers (free or unassociated surfactant molecules). These monomers pack together at the interface, form monolayer and contribute to surface and interfacial tension lowering. Although this phenomenon is highly dynamic (surfactant molecules arrive and leave the interface on a very rapid timescale), molecules at the interface interact with the neighbouring molecules very strongly, which enables measurement of the rheological properties of the monolayer. As the surfactant concentration increases, the available area at the surface for surfactant adsorption diminishes and surfactant monomers start accumulating in the solution. However, the hydrophobic tail of the surfactant molecules has extremely small solubility in water and the hydrophilic head has extremely small solubility in non-polar solvents. Hence, the hydrophobic effect will drive surfactant monomers to form self-assembled aggregates above certain aggregate concentration. These aggregates are micelles, vesicles, liquid crystals and reverse micelles and exist in equilibrium with the surfactant monomers. All of these structures are dynamic in nature and surfactant molecules constantly join and leave the microstructure on a time scale of microseconds. As a result, these microstructures have a limited lifetime. For example, the lifetime of spherically shaped micelle is about milliseconds. Furthermore, the difference in energy between various microstructures is small so that the physical forces of the interaction become dominant. As a result, surfactant molecules can be transformed between several types of aggregates by small changes in temperature, concentration, pH or electrolyte strength. Also, the properties of the solution show sharp changes around the critical aggregation concentration. As shown in Figure 1.1, formation of self-assembled aggregates are evidenced by an increase in turbidity and organic dye solubility, a decrease in electrical conductivity (ionic surfactants only) and stability in surface tension, interfacial tension and osmotic pressure around the critical aggregation concentration.
Micelles and Critical Micelle Concentration

The properties of surfactant at low concentration in water are similar to those of simple electrolytes except that the surface tension decreases sharply with increase in concentration. At a certain concentration, surfactant monomers assemble to form a closed aggregate (micelle) in which the hydrophobic tails shielded from water while the hydrophilic heads face water. The critical aggregation concentration is called the Critical Micelle Concentration (CMC), when micelles form in an aqueous medium. The CMC is a property of the surfactant. It indicates the point at which monolayer absorption completes and the surface active properties are at an optimum. Above the CMC, the concentrations of monomers are nearly constant. Hence, there are no significant changes in the surfactant properties of the solution, since the monomers are the cause of the surface activity. Micelles have no surface activity and any increase in the surfactant concentration does not affect the number of monomers in the solution but affects the structure of micelles. The typical CMC values at room temperature are $10^{-3}$ to $10^{-2}$M for anionic surfactants, $10^{-3}$ to $10^{-1}$M for amphoteric and cationic surfactants and $10^{-5}$ to $10^{-4}$M for non-ionic surfactants. The CMC of several surfactants in aqueous media can be found. Surfactant structure, temperature, the presence of electrolyte, existence of organic compounds and the presence of a second liquid have an effect on the CMC. The following factors contribute to CMC decrease: (a) an increase in the number of carbon atoms in the hydrophobic tails (b) the existence of polyoxypropylene group (c) fluorocarbon structure (d) an increased degree of binding of the counterions (e) addition of electrolyte to ionic surfactants (f) the existence of polar organic compounds (such as alcohols and amides) (g) addition of xylose and fructose The following factors contribute to CMC increase: (a) branch of hydrophobic structure (b) Double bonds between carbon atoms (c) Polar groups (O or OH) in hydrophobic tail (d) Strongly ionised polar groups (sulphates and quaternaries) (e) Hydrophilic groups placed in the surfactant molecule centre
(f) Increase in the number of hydrophilic head 
(g) Trifluoromethyl groups 
(h) An increase in the effective size of hydrophilic head 
(i) An increase in the pH of weak acids (such as soap) 
(j) A decrease in pH from isoelectric region and increase in pH from isoelectric region for amphoteric surfactants (low CMC at the isoelectric region and high CMC outside the isoelectric region) (k) addition of urea, formamide, and guanidinium salts, dioxane, ethylene glycol and water soluble esters 
The CMC decreases with temperature to a minimum and then increases with further increase in temperature. The minimum appears to be around 25°C for ionic surfactants and 50°C for non-ionic surfactants. Several empirical correlations are available for the estimation of CMC values. For straight and saturated single tail ionic surfactants, the CMC can be calculated from:

$$\log \text{CMC} = A - Bn$$  \hspace{1cm} (1.3)

Where, $n$ is the number of carbon atoms in the hydrophobic tail, and $A$ and $B$ are temperature dependent constants for a given type of surfactant. The value of $B$ is around 0.3($= \log 2$) for the ionic surfactants because the CMC of the ionic surfactants is halved for each carbon atom added to the hydrophobic tail. $B$ value is about 0.5 ($\log 10$) for the non-ionic and amphoteric surfactants because the CMC will decrease by a factor of 10 for each of the two methylene groups added to the hydrophobic tail. The values of $A$ and $B$ for some surfactants can be found. The effect of electrolyte concentration on the CMC of ionic surfactant is given by:

$$\log \text{CMC} = a - b \log C$$  \hspace{1cm} (1.4)

Where $a$ and $b$ are constants for a given ionic hydrophilic head at a certain temperature and $C$ is the total counter ion concentration in equivalent per litre. The effect of electrolyte concentration on the CMC of non-ionic and amphoteric surfactants is given by:

$$\log \text{CMC} = x - yC_e$$  \hspace{1cm} (1.5)

Where $x$ and $y$ are constants for a given surfactant, electrolyte and temperature, and $C_e$ is the concentration of electrolyte in moles per litre. Further discussion of the theoretical CMC equations can be found.
Micellar Kinetics and The Pseudo-Phase Model

Exemplified by some hydrolytic reactions like water-catalysed, pH-independent hydrolysis reactions of 1-benzoyl-3-phenyl-1,2,4-triazole as shown in Scheme-1.

[X = MeO]  [X = Me]  [X = CF₃O, X = NO₂]

Scheme 1

Kinetic data for reactions occurring in micellar solutions are generally analysed using the Menger–Portnoy equation (Kunitake et al 1977) (Equation 1.6).

Here $K_{\text{obsd}}$ is the observed rate constant at a surfactant concentration $[\text{surf}]$, $k(m_c=0)$ is the rate constant in water without added cosolute (pH = 4.0) and $k_{\text{mic}}$ is the rate constant under conditions of complete binding of the substrate to the micelles. $N$ is the aggregation number of the micelle, $K_m$ is the binding constant of the kinetic probe to the micelle, and CMC is the critical micelle concentration of the surfactant. This equation follows from an analysis in terms of the pseudophase model in which the micelle and bulk water are treated as different phases. The final equation is the linearised form of Equation 1.6 Kunitake et al 1977).

$$k_{\text{obsd}} = \frac{k(m_c=0) + k_{\text{mic}} \cdot K_m \cdot ([\text{surf}] - \text{cmc})/N}{1 + K_m \cdot ([\text{surf}] - \text{cmc})/N}$$

(1.6)

According to Equation, a plot of $(k(m_c=0)-k_{\text{obsd}})^{-1}$ versus $([\text{surf}]-\text{cmc})^{-1}$ yields $(k(m_c=0)-k_{\text{mic}})^{-1}$ as the intercept, and therefore $k_{\text{mic}}$ can be calculated if
\( k(mc=0) \) is known. From the intercept and the slope of the Menger–Portnoy plot, the micellar binding constant \( K_m \) can be calculated. Alternatively, Equation 2 can be used in a non-linear least-squares fitting procedure. In both the treatments, \( k(mc=0) \) is set equal to the rate constant in water without added cosolute. However, the monomeric surfactant concentration in the bulk water phase equals the CMC so that there is a possibility that hydrophobic interactions between probe molecules and monomeric surfactant molecules could exert an effect on the rate of hydrolysis in bulk water. This has been shown to occur for a surfactant with a CMC of 24.8 mmol dm\(^{-3}\). For the present reactions, the minor decrease in rate constant before the CMC indicates that these effects are small. In addition, the CMC of the surfactants used here is (significantly) lower than 24.8 mmol dm\(^{-3}\). Moreover, the Menger–Portnoy treatment is not particularly sensitive to the precise value of \( k(mc=0) \), because \( k_{\text{mic}} \) is determined from the intercept, \( i.e. \), mainly from the kinetic data at high surfactant concentrations. Furthermore, micellar rate constants for substrates bound to spherical micelles can be determined as long as the surfactant concentration is below the concentration at which wormlike micelles start to form. A refinement of Equation 1.6 includes the possibility of different reaction domains within the micelle. The pseudo-phase model, only distinguishes between a micellar phase and an aqueous phase. However, a three (Bunton 1968, or multiple (Bunton 1970, Duynstee et al 1959) domain model can be explored, for example, the Stern region and the hydrophobic micellar core are treated as separate regions. Hydrolysis in the first domain, \( i.e. \) the core of the micelle, then occurs with a rate constant \( k_c \), hydrolysis in the Stern region, a second domain, occurs with a rate constant \( k_s \) and the hydrolysis in bulk water, the third domain, has rate constant \( k(mc=0) \). In the limit of an infinite number of domains this model yields the “true” rate constant as integral over the domains with their local rate constant of hydrolysis. If we use the three domain model and assume that in the anhydrous, hydrophobic core no hydrolysis takes place (setting \( k_c \) to zero), \( k_{\text{obsd}} \) is given by Equation 1.7. (Note that here partition coefficients - concentration in one (pseudo)
phase divided by concentration in another phase - and volumes are used instead of equilibrium constants and concentrations.

\[
k_{\text{obsd}} = \frac{k_{m=0} + k_{\text{mic}} \cdot P_m \cdot \frac{V_m}{V_w}}{1 + P_m \cdot \frac{V_m}{V_w}}
\]  \hspace{1cm} (1.7)

The extensive literature generated has been the subject of several detailed reviews. The purposes of the present review are the following. First, to review those aspects of the chemistry of the micellar surface which are particularly important for the understanding of organic reactions occurring thereon? Second, to outline Here, \( V_m, V_w, \) and \( P_m \) are the micellar volume, the bulk water volume and the partition coefficient of the hydrolytic probe over the micellar phase with respect to the water phase, respectively, this relation still resembles the ordinary Menger–Portnoy equation, but \( k_{\text{mic}} \) is now given by Equation 1.8.

\[
k_{\text{mic}} = k_s \cdot \left( \frac{V_m \cdot P_m - V_c \cdot P_{ws} \cdot P_{sc}}{V_m \cdot P_m} \right) = k_s \cdot \left( \frac{V_s \cdot P_{ws}}{V_m \cdot P_m} \right)
\]  \hspace{1cm} (1.8)

Here, \( V_c \) is the micellar core volume, \( P_{ws} \) is the water–Stern region partition coefficient, \( P_{sc} \) is the partition coefficient for the Stern region–core equilibrium and \( V_s \) is the Stern region volume. It turns out that the micellar rate constant is, under the above conditions, given by the rate constant for the hydrolysis in the Stern region multiplied by a factor which represents the fraction of the total amount of micellar bound probe that resides in the Stern region. In addition to the determination of the micellar rate constants and the micellar binding constants \( K_m \), as outlined above, transition state pseudo-equilibrium constants \( K_{\text{TS}} \) can be determined (Bunton 1970). Transition state pseudo-
equilibrium constants $K^{TS}$ are the hypothetical binding constants of the activated complex to the micellar pseudophase. For the system under study, $K^{TS}$ is given by Equation 1.9.

$$K^{TS} = \frac{k_{\text{mic}} \cdot K_m}{k(m_c=0)} = \frac{k^3_{\text{mic}} \cdot [H_2O]^2_{\text{mic}} \cdot K_m}{k^3_w \cdot [H_2O]^2_w}$$

(1.9)

In Equation 1.9, $k^3_w$ and $k^3_{\text{mic}}$ are the third-order rate constants (rate of reaction of $P$: $d[P]/dt = k x^3 f[P] \cdot [H_2O]_w^2$) in the aqueous and the micellar pseudophase, respectively, $[H_2O]_w$ the water concentration in bulk water and $[H2O]_m$ the water concentration in the Stern region.

Salient features of the kinetics of organic reactions at the micelle surface, with particular emphasis on the source of the rate enhancements are observed. Third, to provide a theoretical picture which accounts for these features. Finally, to relate, where possible, the chemistry of reactions at the micellar surface to those of reactions occurring in related microenvironments.

**Kinetic Studies of Micellar Systems**

Reactions and product distributions have previously been used to investigate micellar properties. Kinetic studies aimed at identifying the non-covalent interactions. Determining micellar catalysis and inhibition by medium effects have been performed not only on purely micellar medium (Muller 1972, Corkhill et al 1972, Bunton et al 1971, Menger 1968) but also on, e.g., mixtures of both polymers and surfactant (to study the effect of bound polymer on micellar inhibition. In particular, the work involving arenediazonium probe by Romsted’s group was applicable and can be used to determine concentrations of a wide range of reactive (towards arenediazonium) compounds (Bunton 1970, 1973, Romsted, Bunton 1973). In another kinetic study, the sensitivity of hydrolysis reactions towards the charge of the micelle’s Stern region has been exploited, in order to estimate the relative
importance of hydrophobic and ionic interactions. The polarity as a description of the medium offered by the micellar Stern region was also studied kinetically, viz. by a Hammett type analysis yielding Hammett $\rho$ values. In addition, a discussion of the effects that determine the rate of hydrolysis of phenyl chloroformate in different micellar systems has been published recently. The kinetic approach used in the present study is less common. We compare the rate of reaction of a hydrolytic probe in the micelle with the rate of reactions in a model solution. Aqueous model solutions have been used before in order to estimate the polarity and water content of the micellar Stern region. However, only binary mixtures, containing either a salt or a polar non-ionic molecule have been used, thus modeling only one type of interaction. Here, it is shown that the Stern region can be accurately modelled in different ways depending on the sensitivity of the probe. The most elaborate model, containing both salt, mimicking ionic interactions, and 1-propanol, mimicking hydrophobic interactions, separates the effect of the ionic headgroups and of the hydrophobic tails and accurately reproduces the behaviour of all tested probes.

Properties of The Micelle—Water Interface

Above the Critical Micelle Concentration, ionic surfactants in water form aggregates of various sizes, shapes, and dispersity. The simplest micelles, formed from ordinary surfactants such as sodium dodecyl sulfate or hexadecyltrimethylammonium chloride, contain 50—100 molecules of surfactant. Such small micelles are nearly monodisperse (Mukerjee, 1972, Muller 1975); other micellar systems have been shown to be polydisperse (Mukerjee, 1972, Muller 1975, Corkhill 1972). Small micelles are frequently considered to be spherical in shape. However, geometrical considerations associated with micelle formation require that they be ellipsoids of revolution. Several lines of evidence, however, suffice to indicate that the axial ratio of micelles is ordinarily not greater than 6:1 (Oakenfull 1974, Schrier 1954, Ford 1966). Certain micelles undergo a transition to large rod shaped structures at sufficiently high concentrations of certain salts. Most reactions of interest in
this review occur at the interface between the micelles and the surrounding water solvent. Consequently, the properties of that interface are of importance to us. Number of related systems in aqueous solution also possesses interfaces which may provide a microenvironment for chemical reactions, related in some respects to that of the micellar surface. Included in this category are the surfaces of polysoaps, globular proteins, microemulsions and inverted micelles, liposomes, and biological membranes. Where pertinent, comparisons between properties of these surfaces and of chemical reactions occurring on them will be developed.

The crucial aspects of the chemistry of the interface, formed between micelles and water, and the related interfaces mentioned above, are the following: hydrophobic, hydrophilicity, polarity, charge, water activity, segmental and rotational mobilities of groups located at the surface, and the presence of functional groups which may participate directly in chemical reactions, for example, nucleophiles. Needless to say, these properties are interdependent but each shows up in one or more facts of reaction kinetics at the micellar surface. One of the most salient and important features of the micellar surface is amphipathic. Just as a surfactant molecule can be considered to be a one—dimensional amphipathic construct, the micellar surface can be viewed as a two—dimensional amphipathic structure. This shows up in the fact that both hydrophobic organic molecules and hydrophilic ions may associate with micelles and be localized at the micellar surface (Fendler 1975). In fact, a large number of reaction studies in micellar systems involve two substrates one, an organic molecule and the other an ion. Examples the acid catalyzed hydrolysis of acetate, the basic hydrolysis of esters, alkaline fading of triphenylmethyl dyes, and addition of ions to pyridinium ions. The amphipathicity of the micellar surface is a property, shared with the surfaces of proteins and membranes. For example, it is well known that serum albumin has high affinity for nonpolar molecules such as steroids and also interacts strongly with ions. Similarly, membranes have high affinity for both the classes of substances. The structural basis of the amphipathic character of the protein surface has been clearly defined as a consequence of extensive x—ray. The
surface is dotted with exposed cationic and anionic groups, which are separated, to some extent, by exposed hydrophobic side chains of amino acid residues. Consequently, a molecule may encounter quite distinct environments depending on what specific site, on the protein surface, it probes. The structural basis of the amphipathic nature of the micellar surface is not so easy to understand. The surface is, in the simplest model, heavily occupied by the charged groups, their counterions, and solvating water molecules. It is not clear why an organic molecule should be attracted to such an environment. Most likely this uncertainty derives from the fact that this model is too simple. More realistically, one should view the micellar surface as rough so that a molecule absorbed on to the surface will be exposed to the first two or three methylene groups of the surfactant chains. This model is made attractive by the fact that micelles are highly dynamic structures, in rapid equilibrium with their monomeric constituent molecules. Moreover, as we shall see, individual molecules within the micelle have abundant freedom of motion. A dynamic, rough—surfaced, micelle provides a suitable structural model for accounting for the amphipathic character of the micellar surface. The polarity of the micellar surface has been probed by two means. Mukerjee and Ray employed the position of the charge transfer band between pyridinium ions and iodide as a measure of the dielectric constant of the ionic micellar surface (Mukerjee and Ray 1966). They derived a value near 35. Thus, the polarity of the micellar surface is considerably less than that of the aqueous environment and is more nearly comparable to that of ethanol. A second approach realise on the position of the fluorescence maxima of absorbed dyes such as amidino naphthalene-7-sulfonate. The position of the fluorescence maxima can be correlated with the Kosower Z values (Turner 1968); representative data is provided in Table 1.3 (Cordes 1973). This data is in essential agreement with the conclusions of Mukerjee and Ray: the micellar surface is significantly less polar than that of water but somewhat more polar than that of ethanol. Note specifically that the polarity of the micellar surface is comparable to that at the surface of simple globular proteins and the membrane of the erythrocyte. The surfaces of micelles
formed from ionic surfactants are highly charged. A simple arithmetical calculation suggests that the concentration of charged groups at the micellar surface is 3—5 M. About 80% of these charges are neutralized directly through the incorporation of counterions into the micellar surface, forming the Stern layer. The remainder of the counterions form the diffuse Gouy—Chapman layer. The existence of a substantial net charge at the micellar surface provides a large drop in electrical potential across the Stern layer and attracts ions of opposite charge, a conclusion of importance in understanding reaction kinetics at the micellar surface. There are three lines of evidence strongly suggests that the activity of water at the surface of ionic micelles is not very different from that in the bulk solvent. First, it was noted some years ago that the rate of pH—dependent hydrolysis of long—chain alkyl sulfates is unchanged when these substrates form micelles (Kurz 1963). Since this reaction involves the attack of water on the phosphate ester, the conclusion cited above follows. A related observation has been recently made by Menger. He has established that the. Estimation of the polarity of binding sites from the emission maximum of bound aminonaphthalene 7 sulfonate. (Table 1.3)
A direct effort was made to measure the activity of water at the micellar surface by comparing the extent of hydration of N alkyl 3 formylpyridinium ions in water and in the presence of micelles, into which it is incorporated. The results fail to indicate a significant difference in the extent of hydration in the two environments (Albrizzio), added support for a near normal water activity at the micellar surface. Finally, Bunton has observed that the rate of attack of water on triphenylmethyl cationic dyes was not uninfluenced by the presence of micelles (Bunton 1973). Our conclusion is also consistent with the results of several studies indicating that the extent of hydration of counterions incorporated into the Stern layer is same as that for the ions existing free in

### TABLE 1.3. Estimation of the polarity of binding sites from the emission Maximum of bound 1 aminonaphthalene 7 sulfonate

<table>
<thead>
<tr>
<th>1,7-ANS bound to</th>
<th>Protein Concentration (mg/ml)</th>
<th>ν_F X 10^4 (cm^-1)</th>
<th>Z (Estimated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glutamate dehydrogenase</td>
<td>1.20</td>
<td>2.193</td>
<td>84</td>
</tr>
<tr>
<td>Chymotrypsinogen</td>
<td>0.9</td>
<td>2.198</td>
<td>84</td>
</tr>
<tr>
<td>Hexokinase</td>
<td>0.19</td>
<td>2.193</td>
<td>84</td>
</tr>
<tr>
<td>Aldolase</td>
<td>3.0</td>
<td>2.212</td>
<td>82.5</td>
</tr>
<tr>
<td>Lysozyme</td>
<td>1.0</td>
<td>2.155</td>
<td>88</td>
</tr>
<tr>
<td>Hemoglobin-free erythrocyte membranes</td>
<td>1.0 – 2.0</td>
<td>2.214</td>
<td>82.5</td>
</tr>
<tr>
<td>Hexadecyltrimethylammonium</td>
<td>-</td>
<td>2.174</td>
<td>85.5</td>
</tr>
<tr>
<td>Tetradecyldimethylbenzy1</td>
<td>-</td>
<td>2.183</td>
<td>84.5</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>-</td>
<td>2.183</td>
<td>84.5</td>
</tr>
</tbody>
</table>
the bulk aqueous solvent (Gustavsson 1975, Oakes 1973, Robb 1974). The interior of a micelle is viewed as being much like a liquid hydrocarbon droplet. Fluorescence (Shinitzky 1971) and esr (Oakes 1973) measurements on the rate of rotational reorientation of probe molecules in micelles indicates that this is substantially true even though their motion is significantly restricted relative to that in pure organic solvents of low viscosity. This conclusion is consistent with results of measurements of spin lattice relaxation times for several carbon atoms of alkyltrimethylammonium surfactants in the monomeric and micellar states (Williams 1973). Upon micellization, significant restrictions on segmental and rotational mobilities for all carbon ions are observed. The restrictions are most marked for the carbon atoms, at the micellar surface and one moves down the chain away from the ionic head group. Despite the restrictions on mobilities, the values of the spin—lattice relaxation times indicates a rather fluid environment, both in the micellar interior and at the surface. The fluid nature of the micellar surface may provide an insight concerning the fact that there are relatively few well—defined examples of stereochemical control of organic reactions in micelles. Finally, large number of surfactants has been constructed through chemical synthesis which bears reactive functionalities. These frequently include nucleophilic groups which are active against esters. Such studies have been frequently undertaken in an effort to generate realistic models for enzymes, such as chymotrypsin, which carry out direct nucleophilic attack on their substrates. It is in fact true that micelles formed from surfactants containing nucleophilic functionalities are frequently exceptionally effective catalysts for the hydrolysis of esters (Kunitake 1976, Klotz 1971, Yatsimirskii 1970, Okahata 1977). This brings to the conclusion of our consideration of properties of the micellar surface. As noted above, it has been established that micelles are frequently catalytically active towards organic reactions. With this background in hand, it is now appropriate to turn to consideration of this catalytic action.
Contributing Factors in Micellar Catalysis

A side from inherent interest in micelles as catalytic entities, a good deal of consideration of micellar reactions as models for certain aspects of enzyme catalyzed reactions has been developed. The same statement is also true for catalysis of organic reactions by polystoaps. In many respects, micelles fail as models for enzyme catalyzed reactions. Functional micelles have been developed which match certain enzymatic reaction velocities but non-functional micelles are much less effective catalysts. Neither functional nor non-functional micelles exhibit the degree of specificity associated with enzymatic reactions and neither class of micellar reaction is subjected to the kind of control to which the enzymes are. Nonetheless. In one important respect, non-functional micelles are suitable models for enzymatic catalysis. Enzymes and micelles derive significant portion of their catalytic ability from the same sources. This matter has been discussed, in revealing detail by Jencks (Jencks 1975). The fact that micelles are catalysts for a number of reactions is equivalent to that there is a decrease in the standard free energy of the transition state relative to reactants in the aqueous phase. The question is: to what factor or factors may one attribute this diminution in standard free energy difference between reactants and transition state? In dealing with reactions in homogeneous systems, it is customary to discuss this question in terms of the Brönsted—Bjerrum equation:

\[ \delta \Delta G^* = RT \ln \frac{f^*}{f_A f_B} \]  

In terms of this equation, one analyzes rate changes in terms of effects on activity coefficients for substrate and transition state. While this is a straightforward procedure, for the most part, for homogeneous systems that there are two significant difficulties in carrying out such analysis for reactions occurring on the surface of a micelle or, for that matter, on the surface of an enzyme. First, an important contributor to catalysis in micellar or enzymatic systems for second order and higher order reactions derives from a decrease in entropy of the reactants by virtue of their binding to the catalyst surface.
That is to say, if the substrates are confined to the micellar surface the volume available to them is much decreased from that available in the bulk aqueous phase. This is equivalent to recognize that the two or more reactants will be much more concentrated with respect to each other as a consequence of the binding reactions. This entropic contribution to the reaction rate is not easily understood in terms of the Bronsted—Bjerrum equation. Second, the activity coefficient of a molecule in the micellar phase may not be revealing in attempting to account for an increase in reaction rates. This derives from the fact that there may be different microenvironments for different parts of the absorbed molecule. The fact that an organic substrate, for example, associates with micelles with an equilibrium constant, greater than unity, requires that its activity coefficient decreases on going from the aqueous phase to the micellar phase. However, the overall decrease in the activity coefficient of the reactant may be accompanied by an increase in the activity coefficient at the site of chemical reaction. This consideration is true for both enzymatic and micellar reactions. It, too, is not evident on the basis of the Bronsted—Bjerrum equation. Understanding of catalysis for organic reactions in the presence of micelles requires that one separate the two factors indicated above: the entropic contribution reflecting concentration effects and the effects on the relative activity coefficients at the site of reaction for substrates and transition states, a consequence of the nature of the microenvironment in which the reaction occurs. Perhaps the simplest means of accomplishing this end is to begin by considering unimolecular reactions for which the entropic contribution cannot be important. Rate changes, whether it be catalysis or inhibition, must necessarily reflects the changes in the nature of the medium in which the reaction occurs. If it is assumed that all of the substrate is in the micelle and those activity coefficients for both substrate and transition state in the aqueous phase is unity, the extent of catalysis is given by the simple equation:

$$\frac{K}{K_0} = f^A/f^#$$  \hspace{1cm} (1.11)
in which the activity coefficients refer to the micellar system. Clearly, catalysis may result from destabilization of the reactant, an increase in $f_A$, or stabilization of the transition state, reflected in a decrease in $f$. As a pertinent example of micellar catalysis for a unimolecular reaction, let us consider the decarboxylation of 5-nitrobenzisoxazole-3-carboxylate, a reaction probed in considerable detail by Bunton and his coworkers (Bunton 1970, 1971, 1973):

$$\text{5-nitrobenzisoxazole-3-carboxylate}$$

This reaction is catalyzed by cationic, nonionic, and zwitterionic surfactants. The decarboxylation of 5-nitrobenzisoxazole-3-carboxylate is a reaction in which a negatively charged localized in the substrate, is delocalized in the transition state. Consequently, it might be anticipated that the reaction would be accelerated in less polar environments. The work of Kemp and Paul, prior to the initiation of studies in micellar systems, established that this is the case (Kemp 1970). Consequently, the most logical explanation for the fact that micelles are effective catalysts for this reaction is substrate destabilization in the less polar environment, provided by the micellar surface. This destabilization is most probably electrostatic in nature, since, a consideration indicated above suggests that the carboxylate function is probably not significantly desolvated at the micellar surface. This reaction shows one additional notable feature. The rates are modestly increased upon the addition of certain salts. This is contrary to the observations made for many bimolecular reactions in micellar systems for which salts are almost uniformly inhibitory. In this particular case, the catalytic effect of added salts must reflect some alteration in the shape and properties of the micelles. (Kunitake et al 1977). have investigated the polysoap—catalyzed
decarboxylation of the same substrate (Kunitake 1977). Partially, laurylated poly(4—vinylpyridine) and poly(2—ethyl—l—vinylimidazoles) are more effective as catalysts for this reaction than simple cationic surfactants. The addition of hydrophilic salts elicits complex kinetic behavior. Such salts first diminishes then, at higher concentrations, increase the rate of the polysoap dependent decarboxylation. Like the micellar reaction, catalysis, observed in the presence of polysoaps probably reflects destabilization of the carboxylate moiety of the substrate in the nonpolar environment. Bovine serum albumin was observed by the same workers to be noncatalytic for this reaction (Kunitake 1977). Klotz and coworkers have observed that partially laurylated polyethyleneimines are even more potent catalysts for 5 nitrobenzisoxazole 3 carboxylate decarboxylation (Suk 1976). A maximum catalytic effect of 1300 fold was observed. The reaction obeys the Michaelis Menten kinetics pattern typical of enzymatic reactions. A second example of micellar catalysis which must derive from medium effects, as opposed to entropic ones, was provided by the unimolecular hydrolysis of phosphate esters.

\[
\begin{align*}
R-O-P-O^- + H_2O &\rightarrow R-O-H + PO_3^- \\
\text{(1.12)}
\end{align*}
\]

Although phosphate monoanions are readily incorporated into micelles, formed from cationic surfactants. This does not result in an appreciable alteration in the rate of hydrolysis (Bunton 1968). Those phosphate ester dianions in which the leaving group contains strong electron attracting groups also hydrolyze via unimolecular elimination of metaphosphate. In this case, however, cationic micelles are good catalysts for hydrolysis (Bunton 1968,70 , Buist 1970,). For example, the rate of hydrolysis of 2,5—dinitrophenyl phosphate dianion is approximately 25 times more rapid in the presence of an optimal concentration of hexadecyltrimethylanunonium bromide than in water. The loss of the metaphosphate anion from a phosphate ester dianion involves dispersal of two negative charges. Consequently one may argue that the
The catalytic driving force involves destabilization of the substrate relative to the transition state by the relatively nonpolar micellar surface, an explanation essentially the same as that invoked in the case of decarboxylation reactions. This conclusion is consistent with the fact that the rate of hydrolysis of phosphate ester dianions is significantly increased with a decrease in solvent polarity in the absence of micelles. These examples of catalysis by micelles for unimolecular reactions indicate that the utilization of binding forces between substrate and micelle can bring reactive functionalities of the substrate into an environment in which reactivity is augmented. We now turn attention to the case of bimolecular reactions in which not only medium effects but entropic effects resulting from concentration of reactants may be important. In one of the earliest thorough studies of micellar catalysis, Duynstee and Grunwald established that rate and equilibrium constants for addition of hydroxide ion to stable triphenyl methyl cationic dyes, such as Crystal Violet, is subjected to catalysis by cationic surfactants (Duynstee and Grunwald 1959). This conclusion has been confirmed and amplified in several subsequent investigations (Bunton 1972-1973, 1976, Albrizio 1972). Facilitation of this reaction may reflect (i) concentration of hydroxide ion in the presence of the cationic dye by the cationic micellar surface and (ii) destabilization of the cationic dye by the cationic micellar surface that the latter effect is important & suggested by two considerations. First, equilibrium constants for incorporation of the cationic dye and the corresponding alcohol into the micellar phase indicate a strong electrostatic effect in this process. The magnitude of the effect is about the same as that for the equilibrium constant for addition of hydroxide ion to the cationic dyes in the presence of micelles (Duynstee 1959). Second, Bunton has established that addition of amines to the trianisyl cation is catalyzed by surfactants (Bunton 1973). The former effect is important and strongly suggested by the observation that the addition of hydroxide ion to Crystal Violet in the presence of cationic surfactants is subject to strong inhibition by other anions, presumably the consequence of competition between hydroxide ion and these anions for binding sites at the micellar surface (Albrizzio 1972). Thus, the observed
catalysis may be ascribed to electrostatic substrate destabilization as well as to the concentration of the reactive nucleophiles in the presence of the substrate. A closely related example is provided by the case of catalysis of the addition of cyanide ion pyridinium ions:

As the data in Table 1.4 indicates, both rate and equilibrium constants, for this reaction, are markedly increased in the presence of cationic surfactants. Moreover, the extent of the increase in rate and equilibrium constants is magnified by increasing substrate hydrophobicity and surfactant hydrophobicity (Baumrucker 1972). Here, again catalysis may reflect the selective destabilization of the cationic head group by the cationic micelle as well as the concentration of cyanide ions in the vicinity of the substrate through electrostatic interactions with the micellar surface (TABLE 1.4.) Rate and association constants for the addition of cyanide ions to a series of N—substituted 3—carbamoylpyridinium ions in the presence of a series of n-alkyltrimethylammonium bromides in water at 25°C.
Table 1.4 Rate and association constants for the addition of cyanide ions to a series of N—substituted 3—carbamoylpyridinium ions in the presence of a series of n-alkyltrimethylammonium bromides in water at 25°C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Octyl</th>
<th>Decyl</th>
<th>Dodecyl</th>
<th>Tetradecyl</th>
<th>Hexadecyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.21; 135</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decyl</td>
<td></td>
<td></td>
<td>1.10; 530</td>
<td>1.35; 710</td>
<td></td>
</tr>
<tr>
<td>Dodecyl</td>
<td></td>
<td></td>
<td>2.5; 1100</td>
<td>5.8; 4000</td>
<td></td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>0.28; 330</td>
<td></td>
<td>6.6; 3600</td>
<td>10.4; 4500</td>
<td></td>
</tr>
<tr>
<td>Hexadecyl</td>
<td>6.4; 4500</td>
<td></td>
<td></td>
<td>13.3; 4800</td>
<td></td>
</tr>
</tbody>
</table>

A surfactant concentration of 0.02 M throughout. The entries in the Table 1.4 are second order rate constants in units of Min⁻¹ sec⁻¹ followed by association constants in units of (Baumrucker 1972). The effect of the hydrophobic character of substrate and surfactant is particularly noteworthy. Basically, what happens is that binding interactions between substrate and catalyst are employed to destabilize the substrate. In this respect, the catalysis strongly resembles that of enzymes. As the length of the chain of the substrate increases from 8 to 16 carbon atoms, the rate of the reaction increases 64 fold and the equilibrium constant 355 fold (Table 1.4). The former figure corresponds to utilization of 38% of the available binding energy to facilitate the reaction and the latter figure corresponds to utilization of 54% of the available binding energy to increase the affinity of substrate for cyanide (Jencks 1968). Finally, it has been established that this reaction is also subjected to catalysis by bilayers, formed from biological surfactants (Baumrucker 1973) and to marked catalysis by polyelectrolytes.

**A Kinetic Model For Micellar Catalysis**

It has been tempting to provide an explicit quantitative explanation to account for the principal features of micelle catalyzed reactions. These include the shape of rate concentration profiles, dependence of catalytic parameters on the nature of the surfactant, particularly on the length of the hydrocarbon.
chain which determines the cmc, dependence of catalytic parameters on the hydrophobicity of the substrate, and inhibition of the reaction by salts. The first kinetic model for micelle catalyzed reactions was proposed by Menger and Portnoy (1967):

\[
\text{products} \quad \text{products}
\]

\[\begin{align*}
D_n + S & \xrightarrow{K} D_n^* \quad & \xrightarrow{k_m} & \text{ products} \\
 & \xrightarrow{k_v} & \text{ products} & \text{(1.14)}
\end{align*}\]

employing certain simplifying assumptions, this kinetic scheme provides the following rate law: in which K is the equilibrium constant for association of substrate, S, with micelles, Dn and Km is the concentration of micelles: Cm(CD—cmc)/N, CD being the total surfactant concentration and is the micelle aggregation number. This equation predicts an increase in rate constant with increasing surfactant concentration. Such behavior is seen for unimolecular reactions in the presence of micelles and this simple equation gives a good account of the data. On the other hand, reactions which are second—order, or higher order, usually exhibit an optimal rate at some surfactant concentration above which the rates decrease with increasing concentration. This fact has led to a search for a more satisfactory kinetic treatment for these more complex cases. An important advance was made by Berezin and coworkers who treated the case of reaction of two uncharged organic molecules. The equation which they derived is:

\[
k_{\text{app}} = \frac{k_mPc_DV + k_\omega(1-c_DV)}{1 + c_DV(P-1)^n}
\]

(1.15)

in which V is the molar volume of the surfactant, P is the partition coefficient of the substrate between the two phases, and the other quantities have been identified earlier. This equation accounts well for data which was intended to explain. On the other hand, it is not readily applicable to understand some of the features of reactions between ions and organic molecules. Perhaps the most generally satisfactory theory was that developed by Romsted in the
author's laboratory (50). Romsted's theory depends on the following assumptions. First, one can write an equilibrium constant for the interaction of the substrate with the micelles. This assumption is common to all kinetic treatments of micellar catalysis but may fail in cases in which micelle structure and properties change as a function of some parameter in the reacting system. Second, and crucial, is the assumption that the Stern layer is always saturated with respect to counterions. In this respect, the Romsted treatment differs from all previous ones. This assumption is equivalent to the statement that the ground state for ions is the ion bound to the micellar surface, and not the ion free in the bulk phase. This assumption was introduced into the kinetic treatment in the form of an equilibrium constant describing counterion exchange on the micellar surface:

\[
\begin{align*}
I_m + X_v & \rightleftharpoons \frac{K}{k_m} \ I_w + X_m \\
\text{products} & \rightleftharpoons \text{products}
\end{align*}
\] (1.16)

in which I is taken to be a reactive and X an unreactive counterion. Mathematical analysis yields the following equation to describe the rate constants for second—order reactions in the micellar phase:

\[
k = \frac{k_m \delta k_a (C_m - cmc)}{[k_a (C_m - cmc) + 1][1 + X_c k]} + \frac{k_w}{[k_a (C_m - cmc) + 1]} \] (1.17)

in which the degree of binding of counterions to the Stern layer and S is the molar density of micellar phase. In the case of first order reactions, this simply reduces to the equation of Menger and Portnoy (eq. 1.14). The utility of (1.17), lies largely in the fact that it accounts quantitatively for the basic features of reaction kinetics in micellar systems. Let us briefly consider few examples, more detailed analyses are available (Romsted 1975, 1977). First, one of the repeated observations for second—order reactions in the presence
of micelles is that plots of observed rate constants against surfactant concentration pass through maxima. Computer—generated plots, based on eq. 10 mimic this behavior (Romsted 1975, 1977). This fact can be understood in terms of two competing effects, both of which are integrated into eq. 1.17. On the one hand, with increasing surfactant concentration, the relative concentrations of organic substrate and ionic reactant in the Stern layer increase rapidly; this tends to accelerate the reaction, accounting for the ascending limb of the curve. On the other hand, increasing surfactant concentration (for ionic surfactants) requires that the unreactive counterion concentration also increase while the reactive ion concentration remains constant. Since there are a limited number of ionic binding sites in the Stern layer, this requires that the concentration of the reactive ion in the vicinity of bound organic substrate decrease. This accounts for the descending limb observed at high surfactant concentrations. Second, it has been observed in a number of cases that increasing substrate hydrophobicity results in larger maximal rate increases which are attained at progressively lower surfactant concentrations (Table 1.4 for example). Computer—generated plots based on eq. 10 reproduce this behavior very nicely (Romsted 1975, 1977). The increase in substrate hydrophobicity is reflected in eq. 10 in terms of an increase in K, the equilibrium constant for incorporation of the organic substrate into the Stern layer. The greater the binding constant, the less surfactant required to incorporate the substrate into the micellar pseudophase. This leads to faster rate increases as a function of surfactant concentration. In turn, this means that less unreactive counterion will be present, accounting for the fact that greater maximal rate increases are observed. Third, it is frequently observed that increasing surfactant hydrophobicity also leads to greater maximal rate increases which are attained at lower surfactant concentrations (Table 1.4 for example). This is accounted for in just the same way as that employed above: increasing hydrophobicity (in substrate or surfactant) leads to increases in Ka and hence, to a greater concentration of reactive ion in the Stern layer. Hence, eq. 10 accounts well for this observation, too. Fourth, a particularly nice success of
eq. 10 is that it accords with the important observation of (Bunton and Wolfe) that second—order rate constants for specific acid catalyzed hydrolysis of nitrobenzaldehyde diethyl acetal in the presence of sodium dodecyl sulphate decrease with increasing acid concentration. Note that eq. 10 predicts that the observed second—order rate constants are inversely related to the reactive ion concentration, accounting for the observation. This realization was first stated by Berezin and his coworkers (Berezin 1973). Finally, there are many examples of inhibition of reactions in micellar systems through increasing concentrations of unreactive counterions; the extent of inhibition increases with increasing affinity of the unreactive counterions for the Stern layer. This phenomenon finds a ready explanation in terms of eq. 10 since a competition between reactive and unreactive ions for sites in the Stern layer, and hence in the vicinity of bound organic substrate, has been built into the model explicitly (eq. 9). These examples should suffice to indicate that the theory of Romsted, and to a significant extent that of Berezin, is adequate to account for the salient features of micellar catalysis in a qualitative way at least. No one would argue that the theoretical treatments available are the last word; quite the contrary, it seems certain that improvements will be forthcoming regularly. However, in addition to provide chemically rational explanations for the dependence of the kinetics of these reactions on a number of variables, the equations derived are of predictive value. Efforts to examine these predictions will certainly lead to additional insight into reaction kinetics in micellar systems.

**Solubilization**

One of the most important characteristics of micelles that is their ability to take up all kinds of substances. Binding of these compounds to micelles is generally driven by hydrophobic and electrostatic interactions. The dynamics of solubilisation into micelles are similar to those observed for entrance and exit of individual surfactant molecules. Their uptake into micelles is close to diffusion controlled, whereas the residence time depends on the structure of the molecule and the solubilization, and is usually in the order of $10^{-4}$ to $10^{-6}$.
seconds. Hence, these processes are fast on the NMR time scale. Solubilisation is usually treated in terms of the pseudophase model, in which the bulk aqueous phase is regarded as one phase and the micellar pseudophase as another. This allows the affinity of the soluble state for the micelle to be quantified by a partition coefficient $P$. Different definitions of $P$ can be found in the literature, differing in their description of the micellar phase. Frequently $P$ is expressed as a ratio of the mole fractions of soluble state in the micellar pseudophase and the aqueous phase. However, when dealing with catalysis by micellar aggregates it is more convenient to express $P$ as a ratio of concentrations.

The incorporation of nonionic solutes into micelles has recently been subjected to multi-parameter analysis. These studies attribute a dominant role to the volume of the soluble state in determining the partition coefficient. This suggestion was rationalised on the basis of hydrophobic interactions being more efficient for larger molecules. The hydrogen-bond acceptor capacity of the soluble state, on the other hand, counteracted the uptake by the micelles, suggesting that the micellar microenvironment is a less efficient hydrogen-bond donor than bulk water. Still, quantitative understanding of soluble state is far from complete. For instance, Hirose and Sepulveda have demonstrated that replacement of a proton in the benzene molecule with a hydrophilic group enhances its interaction with the micelle. The authors attribute this to a shift in the average binding location more towards the surface of the micelle where dipole-dipole interactions are more favourable. The time-averaged location of different solubilisates in or at the micelle has been a topic of concern. The nature of the solubilisate largely determines its position in the aggregate. Saturated hydrocarbons show a preference for the interior of the micelle. In contrast, solubilisates that contain hydrophilic substituents, such as alcohols or amines, prefer to stay at the surface, where the hydrophilic groups can remain largely hydrated. In the case that the solubilisate has an amphiphilic character itself, the polar parts are generally directed towards the centre of the micelle and its orientation in the aggregate resembles that of the surfactant molecules. The position of aromatic hydrocarbons has been
intensively debated. Investigations have focused on the distribution of benzene in aqueous solutions of cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (SDS). Some authors have claimed that this solubilisate resides mainly in the interior of these micelles, whereas others have reported data that it indicates binding at the interface or in both regions simultaneously. These seemingly contradictory data can be understood in terms of differences in the concentrations of solubilized benzene. At low concentrations these compounds prefer the outer regions of the micelle, whereas at higher concentrations, when the interfacial region is saturated, they penetrate deeper into the micelle with concomitant swelling of the aggregate. The unexpected preference for the interfacial region at lower concentrations of benzene has prompted speculation. It has been demonstrated that aromatic compounds are capable of forming weak hydrogen bonds with water. This ability favours uptake in the aqueous interface over solubilisation in the interior. Alternatively, some authors have attributed the binding behaviour of benzene to its weak surface activity that is amplified by the extremely high surface to volume ratio characteristic of micellar solutions. Likewise the high Laplace pressure of small aggregates has been frequently cited as cause. The high pressure in the interior of the small aggregates squeezes out the solubilisate, which can bind to the interface. However, as has been pointed out by Marqusee and Dill, the Laplace pressure cannot be the dominant factor, since worm-like and spherical micelles show comparable solubilisation behaviour, whereas the Laplace pressure of the former is half that of the latter. Also the large volume of the interfacial region as compared to the core of the micelle needs to be considered, favouring binding to the interfacial region on purely statistical grounds. The binding behaviour of benzene can be extrapolated to many other aromatic compounds such as naphthalene and benzene derivatives. Interestingly, a large number of probe molecules contain aromatic rings and many of them will prefer the outer regions of micelles, whereas in bilayer systems, the same molecules prefer the interior of the aggregate. Clearly these probes cannot be used to determine polarity of the micellar interior or
the extent of water penetration therein. For ammonium surfactants there is evidence for the existence of an additional specific interaction between the headgroups of the surfactant and the aromatic solubilisate. This is in line with the observation that partition coefficients for benzene in CTAB solutions are much higher than those for SDS solutions. These cation-pi interactions have been observed in many different fields in chemistry. The importance of these specific interactions for micellar systems has been questioned by de Schryver et al.

**Micellar Catalysis - Kinetic Models**

A micelle-bound substrate will experience a reaction environment different from bulk water, leading to a kinetic medium effect. Hence, micelles are able to catalyse or inhibit organic reactions. Research on micellar catalysis has focused on the kinetics of the organic reactions involved. An overview of the multitude of transformations that have been studied in micellar media is beyond the scope of this chapter. Instead, the reader refers to an extensive set of review articles and monographs. The kinetic data are always treated essentially using the pseudophase model, regarding the micellar solution as consisting of two separate phases. The simplest case of micellar catalysis applies to unimolecular reactions where the catalytic effect depends on the efficiency of binding of the reactant to the micelle (quantified by the partition coefficient, $P$) and the rate constant of the reaction in the micellar pseudophase ($k_m$) and in the aqueous phase ($k_w$). Menger and Portnoy have developed a model, treating micelles as enzyme-like particles. The catalytic effect on unimolecular reactions can be attributed exclusively to the *local medium effect*. For more complicated bimolecular or higher-order reactions, the rate of the reaction is affected by an additional parameter: the *local concentration* of the reacting species in or at the micelle. Also, for higher-order reactions the pseudophase model is usually adopted. However, in these systems the dependence of the rate on the concentration of surfactant does not allow direct estimation of all of the rate constants and partition coefficients involved. Generally independent assessment of at least one of the partition
Partition coefficients are usually determined using ultrafiltration or NMR or UV-vis spectroscopy. Kinetics of micelle-catalysed bimolecular reactions are generally, monitored spectrophotometrically under pseudo-first-order conditions. The decrease of the absorption of one of the reactants (A) is followed in time in the presence of a more than 20 fold excess of the other reactant (Bunton 1973).

\[
\text{Figure 1.8. Kinetic analysis of a bimolecular reaction } A + B \rightarrow C \text{ according to the pseudophase model.}
\]

In the absence of surfactant, the second-order rate constant \( k_2 \) follows from Equation 1.18:

\[
k_2 = \frac{k_{obs}}{[B]} \quad (1.18)
\]

Herein \( k_{obs} \) is the observed pseudo-first-order rate constant. In the presence of micelles, analogous treatment of the experimental data will only provide an apparent second-order rate constant, which is a weighted average of the second-order rate constants in the micellar pseudophase and in the aqueous phase (Equation 1.19).

\[
k_{app} = k_{obs} / [B] \quad (1.19)
\]

Berezin and co-workers have analysed in detail the kinetics of bimolecular micelle-catalysed reactions (Buist 1970, Bunton 1976). They have derived the
following equation, relating the apparent rate constant for the reaction of A with B to the concentration of surfactant:

$$k_{app} = \frac{k_m P_A P_B [S] V_{mol,S} k_w (1/ [S] V_{mol,S})}{(1) (P_A + 1) [S] V_{mol,S} (1) (P_B + 1) [S] V_{mol,S}}$$  \(1.20\)

Herein PA and PB are the micelle-water partition coefficients of A and B, respectively, defined as ratios of the concentrations in the micellar and aqueous phase; [S] is the concentration of surfactant; Vmol,S is the molar volume of the micellised surfactant and km and kw are the second-order rate constants for the reaction in the micellar pseudo phase and in the aqueous phase, respectively. The appearance of the molar volume of the surfactant in this equation is somewhat alarming. It is difficult to identify the volume of the micellar pseudo phase that can be regarded as the potential reaction volume. Moreover, the reactants are often not homogeneously distributed throughout the micelle and the average location of one reaction partner may differ from that of the other. Despite these serious complications, data analysis using eg 1.4. almost always produces reasonable results. Studies of micellar catalysis of bimolecular reactions of uncharged substrates have not been frequent (Duynstee 1959, Bunton 1976, Albrizzio 1972). Dougherty and Berg performed a detailed analysis of the kinetics of the reaction of 1-fluoro-2,4-dinitrobenzene with aniline in the presence of anionic and non ionic surfactants (Duynstee 1959). Micelle induces increase in the apparent rate constant of this reaction. In contrast, the second-order rate constant for reaction in the micellar pseudophase observed to be roughly equal to, or even lower than the rate constant in water. When one or more of the reaction partners of a bimolecular reaction are ionic, the kinetic analysis is further complicated. Particularly in the case when the ionic reactants are not identical to the counterions of the surfactant, estimation of the concentrations of reactive ions in the interfacial region requires a refinement of the model. There is now competition between the reactive counterions and the inert counterions with respect to binding to the micellar surface. Romsted et al.
developed the pseudophase ion-exchange (PPIE) model and applied it successfully to the description of the kinetics of micellar catalysis of ionic bimolecular reactions (Buist 1970). This model treats micellar surface as a selective ion exchanger and assumes that the total fractional occupation of the surface by the counterions is constant, irrespective of the nature of these ions. For ionic bimolecular reactions, the second-order rate constant for reaction in the micellar phase is remarkably similar to the second-order rate constant in the aqueous phase, suggesting a water-like medium for the majority of micelle-catalysed bimolecular reactions (Mukerjee 1966, Baumrucker 1972). Hence, the frequently encountered increase in the apparent rate constant by several orders of magnitude results largely from the increase in the local concentrations of the reactants in the micellar pseudophase.

Projected objectives and the objectives attained by this Thesis

This thesis can take pride of the fact that the work embodied in this thesis is the pioneering work in the field of kinetics. Probably it is among there very few work of this kind where a prominent organic reaction mediated by micellar environment was identified. Its manifestations and other aspects were studied in detail, and viability of the findings in various applications was also studied. The objectives projected in the beginning of the work and the objectives attained described briefly. Over all, this Thesis is the outcome of an intensive work on the various aspects of kinetic study of some esters in micellar environment. The major objectives of this thesis are as follows:
Table 1.5. Objectives projected and attained in the presented work

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Projected objectives</th>
<th>Objective attained and Title of the Chapter</th>
<th>Chapter concerned</th>
<th>Pages included</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Introduction</td>
<td>Outline of the Thesis and the Principles involving different processes projected in the research work</td>
<td>Chapter 1</td>
<td>1-50</td>
</tr>
<tr>
<td>2.</td>
<td>Chemical studies of surfactants</td>
<td>Critical Micelle concentration of surfactant, mixed surfactant and polymer by different method at room temperature and its importance.</td>
<td>Chapter 2</td>
<td>55-99</td>
</tr>
<tr>
<td>3</td>
<td>To establish the kinetic method and to elucidate the mechanism for the hydrolysis reactions of esters in micelles</td>
<td>Effect of PEG-4000 &amp; PEG – 8000 on the reactivity of Hydroxamate ion</td>
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<tr>
<td>4</td>
<td>To study the nucleophilic substitution reactions of carboxylic and phosphate esters in micellar media</td>
<td>Studies on Nucleophilic substitution reaction of Carboxylic esters in presence of Polymer/Surfactant</td>
<td>Chapter 4</td>
<td>115-143</td>
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<tr>
<td>5</td>
<td>To analyse the kinetic rate data quantitatively, using different micellar catalysis models</td>
<td>Kinetic Model Study Of The Effect of Nucleophilic on the $\alpha$-effect : Nuclophilic Substitution Reaction of p-Nitrophenyl Diphenyl Phosphinate with Butane-2,3-dione Monoximate and Substituted Phenoxides in Cationic Micelles</td>
<td>Chapter 5</td>
<td>149-167</td>
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</tbody>
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The Detailed works and findings are followed in the chapters there of ....
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