CHAPTER 1

INTRODUCTION
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1.0 INTRODUCTION

In recent years, compartmentalized liquids, viz., micelles, microemulsions, liposomes, vesicles, etc., have emerged as novel reaction media for investigating the reactivity, selectivity and catalysis of a number of chemical and biological phenomena. There appear numerous publications on micelles in English, in Russian, in German and in French. This worldwide interest in micelles originates from scientists with diverse specialities: organic chemistry, physical chemistry, biochemistry, pharmaceutical chemistry and polymer chemistry. Hundreds of patents on micelles and micelle forming compounds testify to the commercial importance of the subject. Surfactants and their micellar systems, have found their way into almost every chemical industry (food, textile, detergents, paints, cosmetics, pharmaceuticals, pesticides, fibres, plastics, petroleum, metal and paper processing. Many characteristics of molecules, e.g. absorption and fluorescence spectra, deprotonation and protonation equilibria etc., are changed drastically in micellar media. The unique presence of nonpolar and polar molecules under homogeneous and virtually isotropic conditions can simultaneously deal with both polar and nonpolar substrates separately in relation to reaction equilibria and reaction kinetics. Their normal characteristics are often appreciably affected in such solutions.

Recently vigorous interest has been shown in the kinetics and mechanism of organic reactions which occur in the presence of surfactants. In contrast with the wealth of information on the micellar catalysis of hydrolysis and solvolysis of carboxylic acid derivatives, and with the extensive and sophisticated research on micellar kinetics, comparatively little is known on the micellar hydrolysis of hydroxamic acids.

The goal of this present work to investigate the mechanistic studies of micellar catalysis of hydroxamic acids and the other factors which influence the rate and, hence, the magnitude of the catalysis. Hydroxamic acids still offer worthwhile scientific challenges for many physical organic chemists and at the same time have a potential for applications which is by no means exhausted.

It is necessary to know about surfactants and their action in brief before discussing their role in the present studies.
1.1 SURFACANT

Surfactants, sometimes called surface active agents or detergents, are amphiphilic materials which contain both non-polar, hydrophobic and polar, hydrophilic groups. The surface of amphiphilic aggregates consists of amphiphile head groups, counterions and water molecule while the interior mainly contains the hydrocarbon chains. It is essentially the balance between the hydrophobic and hydrophilic parts of the molecules (ion) which gives the special properties. In addition to the name surface active agents, these materials are often called by other names which include: surfactants, association colloids, colloidal electrolytes, amphipathic compounds, tensides etc. Most detergents are surface active agents but not all surfactants are detergents. In solvents which have a strong three-dimensional structure, for example water and sulphuric acid etc., this dual character of the amphiphile leads to self-association or micellization. All of them can be categorized as "self-assembling" or "self-organizing" in the sense that defined structures arise spontaneously owing to non-covalent forces among the component molecules. Such chemical systems are useful for many purposes, including decontamination of environmentally dangerous substances, drug delivery and organic compounds.

1.1.1 Classification of Surfactants

Surfactants are classified into four groups based on the nature of the head group, that is anionic, cationic, nonionic and zwitterionic. Some examples of these materials in common use are:

**Anionic**

Some representative micelle-forming anionic surfactants are as follows:

\[
\text{CH}_3(\text{CH}_2)_n\text{OSO}_3 \, \text{M}^+ \\
\text{CH}_3(\text{CH}_2)_n\text{SO}_3 \, \text{M}^- \\
\text{CH}_3(\text{CH}_2)_n\text{COO}^- \, \text{M}^- \\
\text{M}^- = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{NMe}_4^+; \, n = 8-18
\]

Out of these anionic surfactants sodium dodecyl sulphate \((\text{C}_{12}\text{H}_{25}\text{SO}_4\, \text{Na}^-)\) and sodium dodecanoate \((\text{C}_{11}\text{H}_{23}\text{COO}^- \, \text{Na}^+)\) are of much importance in chemical kinetics.

2
Cationic
The most common cationic surfactants are,

\[
\text{CH}_3(\text{CH}_2)_n \text{N}^+ (\text{CH}_3)_3 \times \text{CH}_3(\text{CH}_2)_n \text{N}^+ \times \times \times \times \times \times \times \times \text{X}^-, \text{Cl}^-, \text{Br}^-, \text{OH}^-, \text{etc.}
\]

\( n = 8-18 \)

Cetyltrimethyl ammonium bromide (CTAB) \( \text{C}_{16}\text{H}_{33}\text{NMe}_3\text{Br} \) and cetylpyridinium chloride (CPC) have been a preferred cationic surfactants because they are commercially available and can be easily purified.

Non ionic
Many of these are based on polyoxyethylene and a typical example is,

\[
\text{C}_{12}\text{H}_{26}[\text{OCH}_2\text{CH}_2]_x\text{OH}
\]

Non ionic surfactants will small head-groups also exist, some example being,

\[
\begin{align*}
\text{C}_{12}\text{H}_{25}\text{SOCH}_2\text{CH}_2\text{OH} & \quad \text{C}_{10}\text{H}_{21}\text{N-Me} \\
\text{Dodecyl sulphonyl ethanol} & \quad \text{Decyl(dimethylamine oxide}
\end{align*}
\]

The following two non-ionic surfactants are usually used for kinetics:

\[
\begin{align*}
\text{C}_{12}\text{H}_{26}(\text{OCH}_2\text{CH}_2)_x\text{OH} & \quad \text{C}_{12}\text{H}_{25}(\text{OCH}_2\text{CH}_2)_{25}\text{OH} \\
\text{x} = 9-10 & \quad \text{x} = 9-10 \\
\text{TX - 100} & \quad \text{Brij - 35}
\end{align*}
\]

Zwitterionic
A simple example of this type of material is

\[
\text{C}_{12}\text{H}_{26}\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-SO}_3^- \\
\text{Me}_2
\]

3-dimethyl dodecylamine propane sulphonate
N-dimethyl-N-dodecylglycine, \( \text{C}_{12}\text{H}_{25}\text{N}^+\text{(CH}_3)_2\text{CH}_2\text{COO} \) (B 1-12) and sulfobetaine \( \text{C}_{18}\text{H}_{33}\text{N}^+\text{(CH}_3)_2\text{CH}_2\text{SO}_3^- \) (SB 3-16) are common zwitterionic surfactants.

Recently, there appears some work on hydrolysis reaction catalysed by twin tailed and bolaform surfactants. The bolaform surfactants are

\[
X^+ \text{Me}_3\text{N}^+(\text{CH}_2)_n\text{N}^+\text{Me}_3X^- \\
X^- = \text{Br}, \text{Cl}, \text{OH} \quad n = 12, 16, 22
\]

The twin-tailed surfactants are didodecyl and cetyl dimethylammonium salts with Br\(^-\), Cl\(^-\) or (SO\(_4\))\(^{2-}\) as counter ion.

\[
(\text{C}_{12}\text{H}_{25})_2\text{NMe}_2X; \ (\text{C}_{18}\text{H}_{33})_2\text{NMe}_2X \\
(\text{DDDAX}) \quad (\text{DCDAX})
\]

Most of all the surfactants are soluble in water. The unique property of these materials is their ability to adsorb strongly at various interfaces and to lower the interfacial surface energy.

1.2 MICELLIZATION

The basic principle involved in explaining all facts of surfactants behaviour is the clustering of monomeric units of surfactants to form micelles. The concentration at which the micelle appear is known as critical micelle concentration (CMC). The shape and the size of the micelles depend on different parameters (temperature, pressure, concentration, nature of the surfactant, etc.). Many thermodynamic, transport and spectroscopic properties show a distinct change in behaviour with concentration around a rather well defined (CMC). By assuming that the formation of the micelles corresponds to that of a new phase, in the micellar region the increase in surfactant concentration leads to the increase in the concentration of the micellized surfactant while that of unmicellized surfactant is constant and equal to the CMC. So, the CMC represents the solubility of monomeric surfactant in water and, therefore, it is easily correlated to the standard free energy of micellization. However, since micellization is not a true phase-transition, it occurs in a more or less wide range of concentration around the CMC and the uncertainties which affect
the CMC are reflected in the derived properties. In the pre-micellar region, the properties change almost linearly and give information on the solvent-monomer and monomer-monomer interactions. Just above the CMC, the properties change strongly with surfactant concentration owing to the transfer of the surfactant from water to the micelles. At high surfactant concentration, the properties tend to constant value and deviations reflect micelle-micelle and monomer-micelle interactions.

Micellization depends upon a balance between hydrophobic and vander walls interactions which bring monomers together and repulsions between the polar or ionic head groups. But repulsions between ionic head groups will be offset by attractions of the counterions to the micellar surface. The CMC decreases with increasing chain length of the polar groups, and is higher for ionic than for non-ionic or Zwitterionic micelles. For ionic micelles it is reduced by addition of electrolytes especially those having low charge density counterions. Added solutes or cosolvents which disrupt the three-dimensional structure of water break up micelles, unless the solute is sufficiently a polar to be micellar bound.

Although, the concept of micelle formation won quick acceptance, the size, shape and structure of the postuated aggregates became the subject of controversy. At surfactant concentrations not markedly above the CMC, micelles are approximately spherical and their radius is similar to that of the extended chain length of the surfactant. Micellar head groups and associated counterions are fully hydrated. and one widely accepted micellar model, the so called Hartley micelle, involved a hydrocarbon like interior surrounded by polar or ionic head groups.

The micelle is composed of three regions, a liquid-like core containing the surfactant tails, the Stern-layer containing the surfactant head-groups and a large fraction of the counterions, and the Gouy-Chapmen layer which extends radially out in to the aqueous phase and contains the remaining counterions. The Stern layer is an extremely anisotropic region with properties intermediate between those of water and hydrocarbon. Thermal motion creates a diffuse electrical double layer, called the Gouy-Chapmen layer, which extends out in to the aqueous phase and contains the remaining counterions.

In spite of the great amount of research that has been carried out in the field of surfactants, there remains much to be learnt about the micellization process. There are unanswered questions regarding micellar size and shape. The size of an
approximately spherical micelle is geometrically constrained, but based on a variety of measurements it appears that micelles grow with increasing concentrations of amphiphile or added electrolyte, and therefore become ellipsoidal. Growth of an ionic micelle depends very much upon the properties of counterions; for example for a C, quaternary ammonium ion (C,33H33N’Me) there is extensive growth with an increase in concentration of surfactant and counterion for the bromide, much less growth for the chloride, and very little growth for the hydroxide. But fortunately for a kineticist it seems that micellar size, is not a dominant factor in determining chemical reactivity, probably because it does not markedly affect the nature of the micelle-water interface.

1.3 MICELLAR CATALYSIS

The micellar catalysis of organic reactions has been widely studied in recent years. The study of both unimolecular and bimolecular reactions has received extensive coverage. In particular, ester hydrolysis and nucleophilic aromatic substitution have been particularly popular reactions. Traditionally both of these reactions have been favourite proving grounds for kinetic and mechanistic studies.

In attempting to understand the mechanism by which enzyme catalyze reaction, chemists have expended much effort in the study of catalysis in simpler, chemical systems. Catalysis of reactions within micelles has been studied from this point of view. Although the analogy between micelle-catalysed reactions and enzyme-catalyzed reactions is far from perfect, there are important similarities. The structure of both micelles and enzymes are similar in that they have hydrophobic cores with polar groups on their surface. Both catalytic micelles and enzymes bind substrates in a noncovalent manner. The kinetics of micellar catalysis resemble that of enzymatic catalysis in that the micelle may be saturated by the substrate, and conversely, the substrate may be saturated by the micelle. Micellar catalysis is generally attributed to the concentration of reagents within the smaller volume of the micelle. Micelles, on the other hand, may be reasonable models for reactions occurring between reagents incorporated within membranes provided covalent bond formation to the membrane is not involved.

The micellar catalysis of hydrolysis and solvolysis of carboxylic acid derivatives can occur through acid-catalyzed, pH-independent, and base-catalyzed mechanisms. These reactions can be classified further according to the type of bond fission and the molecularity of the rate-determining step.
The kinetic and mechanistic studies of micellar hydrolysis of hydroxamic acids have received remarkably little attention.\textsuperscript{81-87} The area of micellar catalysis of hydroxamic acids still full of challenging problems with potentials of rewarding solutions. The presentation of chemistry of hydroxamic acid in this chapter is by no means complete or exhaustive. The subject is simply too large to be covered in brief.

1.4 HYDROXAMIC ACID

The study of N-oxygenated compounds has recently become an area of active interest because several molecules containing this functionality display toxic properties while others, such as hydroxamic acids, have been shown to be growth factors for microbial species.\textsuperscript{91} The latter is in part because the hydroxamic acid grouping (I), forms highly stable,

\[
\begin{align*}
- & C = O \\
& \| \\
- & N - OH
\end{align*}
\]

stereospecific chelate compounds (siderophores) with Fe (III).\textsuperscript{92-98} While much needs to be learned about the application of hydroxamic acid derivatives to these and related biological and biochemical problems. Current interest has emphasized the study of hydroxamic acids, and especially siderophores, for their metal ion transport properties and possible use for the development of either broad-spectrum or species-selective antibiotics.\textsuperscript{99-100} Further synthetic and biological studies are certain to reveal extremely interesting aspects of iron metabolism as well as new modes of chemotherapy. A complete review of the chemistry and biologic activity of hydroxamic acids is beyond the scope of this work. Consequently, only major aspects related to micellar catalysis, have been discussed.

Hydroxamic acids can exists in two forms, i.e. the N-acyl derivative (II) or the O-acyl derivative (III).

\[
\begin{align*}
\text{O} & \\
\| & \\
\text{R} - \text{C} - \text{NHOH} & \quad \text{O} \\
\| & \\
\text{R} - \text{C} - \text{ONH}_2
\end{align*}
\]

(II) \quad (III)
N-acyl hydroxamic acids can exist following possible three tautomeric forms (IIa-IIc).

\[
\begin{align*}
\text{O} & \quad \text{OH} & \quad \text{OH} \\
\text{IIa} & \quad \begin{array}{c}
R - C - \text{NHOH} \\
\leftrightarrow
\end{array} & \quad \begin{array}{c}
R - C - \text{NOH} \\
\leftrightarrow
\end{array} & \quad \begin{array}{c}
R - C = \text{N} - \text{O} - \\
\end{array}
\end{align*}
\]

Possibilities of geometrical isomerism and internal hydrogen bonding have added to the complexity. Substitution of hydrogen atom bound to nitrogen atom in (II) by alkyl, aryl or cyclic group produces N-substituted hydroxamic acids (IV).

\[
\begin{align*}
\text{R} & - \text{N} - \text{OH} \\
\text{R} & - \text{C} = \text{O}
\end{align*}
\]

Some of the N-substituted hydroxamic acids used in the present investigation are as follows (V-VIII).

\[
\begin{align*}
\text{CH}_3 & - \text{N} - \text{OH} & \begin{array}{c}
\text{O} - \text{N} - \text{OH} \\
\end{array} & \begin{array}{c}
\text{CH}_2 & - \text{N} - \text{OH} \\
\end{array} & \begin{array}{c}
\text{O} - \text{C} = \text{O} \\
\end{array} & \begin{array}{c}
\text{O} - \text{C} = \text{O} \\
\end{array} & \begin{array}{c}
\text{O} - \text{C} = \text{O} \\
\end{array} & \begin{array}{c}
\text{O} - \text{C} = \text{O} \\
\end{array}
\end{align*}
\]

(V) N-Methylbenzo hydroxamic acid

(VI) N-phenylbenzo hydroxamic acid

(VII) N-p-chlorophenyl benzohydroxamic acid

(VIII) N-Benzylbenzo hydroxamic acid

These are weak proton donors which have numerous applications in such diverse fields as extractive metallurgy, corrosion inhibition, nuclear fuel processing, pharmaceuticals, medicinals, fungicides and analytical reagents. In recent years the hydroxamic acids have been the source of much biochemical interest. These are toxic metabolites of certain amines and amides. The carcinogenic properties of many aromatic nitrogenous compounds are the result of their conversion to hydroxamic acids in vivo. Undoubtedly the reactivity of hydroxamic acid in micellar system would serve as models for biological and biochemical applications.
N-acetyl hydroxamic acids can exist following possible three tautomeric forms (IIa-IIc).

\[ R - C - \text{N-OH} \leftrightarrow R - C - \text{NOH} \leftrightarrow R - C = \text{N} - \text{O} \]

(IIa)  (IIb)  (IIc)

Possibilities of geometrical isomerism and internal hydrogen bonding have added to the complexity. Substitution of hydrogen atom bound to nitrogen atom in (II) by alkyl, aryl or cyclic group produces N-substituted hydroxamic acids (IV).

\[ R - N - \text{OH} \]
\[ R - C = \text{O} \]

(IV)

Some of the N-substituted hydroxamic acids used in the present investigation are as follows (V-VIII).

\[ \text{CH}_3 - \text{N} - \text{OH} \]
\[ \text{Cl} - \text{C} = \text{O} \]

(V)  (VI)  (VII)  (VIII)

N-Methylbenzo hydroxamic acid  N-phenylbenzo hydroxamic acid  N-p-chlorophenyl benzohydroxamic acid  N-Benzylbenzo hydroxamic acid

These are weak proton donors which have numerous applications in such diverse fields as extractive metallurgy, corrosion inhibition, nuclear fuel processing, pharmaceuticals, medicinals, fungicides and analytical reagents. In recent years the hydroxamic acids have been the source of much biochemical interest. These are toxic metabolites of certain amines and amides. The carcinogenic properties of many aromatic nitrogeneous compounds are the result of their conversion to hydroxamic acids in vivo. Undoubtedly the reactivity of hydroxamic acid in micellar system would serve as models for biological and biochemical applications.
The overall objective is to unravel and understand the kinetic and mechanistic aspects of acidic and alkaline hydrolysis of hydroxamic acids in the presence of micelles. Micelles have long been recognized to be simplistic models of biological membranes. Thus, a study of hydrolysis in micellar environment may be a better model than studies in acid or base. In addition, the prevalence in biological systems of hydroxamic acid hydrolyses catalyzed by nucleophiles and by enzymes renders the investigation of micelle-catalyzed hydroxamic acid hydrolyses of obvious importance. We envisage that a detailed investigation of micellar hydrolysis of hydroxamic acids is opportune. The scope of these studies is to investigate the magnitude and the direction of the effects of cationic, anionic and non-ionic micelles on the acidic and alkaline hydrolysis of hydroxamic acids.

1.5 REVIEW OF STATUS AND DEVELOPMENT IN THE FIELD

Micellar catalysis has attracted considerable interest with regard to fundamental studies of catalysis and mechanism and for its relationship to enzymatic processes. The hydrolysis of amide like substances is of interest because of their relationship to peptides. Considerable modification of the leaving group in the hydrolysis reaction results from substitution hydroxamic acid (X) for an amide (IX). The electronegative hydroxyl in place of hydrogen will result in a better leaving group, i.e., the expelled species is a weaker base.

\[
\begin{align*}
\text{Benzamide} & \quad H-N-H \\
\text{(IX)} & \quad C=O \\
\text{Benzohydroxamic Acid} & \quad H-N-OH \\
\text{(X)} & \quad C=O
\end{align*}
\]

Such substitution might lead to a significant change in reactivity in a micellar system. It is very unusual and surprising that hydroxamic acids escaped the attention of physical organic chemists for any systematic study of their micellar hydrolysis reaction till 1977. The available data on the micellar hydrolysis of hydroxamic acids are compiled in Tables 1.01 & 1.02. The first investigation of micellar catalysis of hydroxamic acid hydrolysis was reported by Berndt and Sendelbach in 1977. They studied the acidic hydrolysis (0.203 N HCl) of octanohydroxamic acid \([\text{CH}_3(\text{CH}_2)_6 \text{CONHOH}]\) and phenyl-acetohydroxamic acids \([\text{C}_6\text{H}_5\text{CH}_2\text{CONHOH}]\) in the presence of sodium dodecyl sulphate. Rate enhance-
| S | R1 | R2 | R3 | Formula | Reference | Molecular Weight | Temperature | Catalyst | Surfactant | Medium | Reaction | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | CH₃(CH₂)₆ | CH₃ | CH₃ | CH₃(CH₂)₆NO₂ | 81 | CH₃(CH₂)₆ | 0.001 M | SDS | Aqueous | HCl | Acid | 50.0 |
| 2 | CH₃(CH₂)₈ | CH₃ | CH₃ | CH₃(CH₂)₈NO₂ | 83 | CH₃(CH₂)₈ | 0.0006-0.06 M | SDS | Aqueous | HCl | Acid | 50.0 |
| 3 | CH₃(CH₂)₁₀ | CH₃ | CH₃ | CH₃(CH₂)₁₀NO₂ | 86 | CH₃(CH₂)₁₀ | 0.003-0.07 M | SDS | Aqueous | HCl | Acid | 50.0 |
| 4 | CH₃(CH₂)₁₂ | CH₃ | CH₃ | CH₃(CH₂)₁₂NO₂ | 87 | CH₃(CH₂)₁₂ | 0.0006-0.06 M | SDS | Aqueous | HCl | Acid | 50.0 |
| 5 | CH₃(CH₂)₁₄ | CH₃ | CH₃ | CH₃(CH₂)₁₄NO₂ | 88 | CH₃(CH₂)₁₄ | 0.0019-0.06 M | SDS | Aqueous | HCl | Acid | 50.0 |
| 6 | CH₃(CH₂)₁₆ | CH₃ | CH₃ | CH₃(CH₂)₁₆NO₂ | 89 | CH₃(CH₂)₁₆ | 0.0002-0.06 M | SDS | Aqueous | HCl | Acid | 50.0 |

**Table 1.01**

**Micellar Catalyzed Reaction of Hydroxamic Acids: Acidic Hydrolysis**
<table>
<thead>
<tr>
<th>S. No.</th>
<th>R1</th>
<th>R2</th>
<th>Molecular Formula</th>
<th>Catalyst</th>
<th>Medium</th>
<th>Surfactant</th>
<th>Temperature °C</th>
<th>Reference</th>
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<tr>
<td>1</td>
<td>H</td>
<td>C7H5</td>
<td>C6H5CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
<td>0.160 N(HCl)</td>
</tr>
<tr>
<td>2</td>
<td>3-CH3C6H4</td>
<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
<td>0.160 N(HCl)</td>
</tr>
<tr>
<td>3</td>
<td>4-CH3C6H4</td>
<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
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</tr>
<tr>
<td>4</td>
<td>3-CH3C6H4</td>
<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
<td>0.160 N(HCl)</td>
</tr>
<tr>
<td>5</td>
<td>4-CH3C6H4</td>
<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
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<tr>
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<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
<td>0.160 N(HCl)</td>
</tr>
<tr>
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<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
<td>0.160 N(HCl)</td>
</tr>
<tr>
<td>8</td>
<td>3-CH3C6H4</td>
<td>-</td>
<td>C6H4CH2HCH3NO2</td>
<td>-</td>
<td>H</td>
<td>C7H5NO2</td>
<td>67.9±6.3°</td>
<td>0.160 N(HCl)</td>
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<tr>
<td>9</td>
<td>4-CH3C6H4</td>
<td>-</td>
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<td>H</td>
<td>C7H5NO2</td>
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<th>S. No.</th>
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<th>MOLECULAR FORMULA</th>
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<td>Acetonitrile (0.001 - 0.12M)</td>
<td>6.0 ± 0.2</td>
<td>19.0 ± 0.25</td>
</tr>
<tr>
<td>2</td>
<td>4-CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Acetonitrile (0.001 - 0.12M)</td>
<td>6.0 ± 0.2</td>
<td>19.0 ± 0.25</td>
</tr>
<tr>
<td>3</td>
<td>6-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Acetonitrile (0.001 - 0.12M)</td>
<td>6.0 ± 0.2</td>
<td>19.0 ± 0.25</td>
</tr>
<tr>
<td>4</td>
<td>4-B&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Acetonitrile (0.001 - 0.12M)</td>
<td>6.0 ± 0.2</td>
<td>19.0 ± 0.25</td>
</tr>
<tr>
<td>5</td>
<td>5-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;N&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Acetonitrile (0.001 - 0.12M)</td>
<td>6.0 ± 0.2</td>
<td>19.0 ± 0.25</td>
</tr>
</tbody>
</table>

**Medium**
- Acetonitrile
- Aqueous Solution
- Aqueous (0.001 - 0.12M) Sodium Acetate
- Aqueous (0.001 - 0.12M) Sodium Phosphate
- Aqueous (0.3 - 1.2M) SDS (104 - 0.02M)
ments in $10^{-4}$ to $0.16$ M surfactant solutions were observed. The detailed mechanism is lacking. Micellar catalysis with sodium 1-dodecanesulfonate has been demonstrated\(^{82}\) for the acidic hydrolysis of a series of substituted phenylaceto-hydroxamic acids. Sodium dodecanesulfonate is much more stable than the sodium dodecyl sulphate in aqueous acid. The catalytic effect has been found similar. The substrate-micelle association constants for the series of compounds correlates well with the empirical lipophilicity substituent constants $\pi$. Continuous efforts have been made by Professor Berndt and his group at Western Michigan University, USA towards a better understanding of substituent effects and mechanism in the micellar hydrolysis of hydroxamic acids.\(^{83-87}\) The rates of hydrolysis of octanohydroxamic and N-methyloctanohydroxamic acids under acidic conditions with sodium-1-dodecanesulfonate as surfactant and under alkaline conditions with cetyltrimethylammonium bromide as surfactant had been measured.\(^{83}\) Normal reaction rate orders were obtained. The effect of anionic surfactant on the acidic hydrolysis of a series of meta- and para-substituted benzo-hydroxamic acids were also studied. The substituent effects indicated specific micellar influences on the rates and a difference in mechanism between the bulk aqueous phase and the micellar phase.

Further Berndt et al.\(^{84}\) investigated the reaction parameters for the alkaline hydrolysis of various hydroxamic acids in the presence of CTAB. Empirical reaction orders of zero, one-half, and one were found for the hydroxamic acids depending upon reaction conditions and substrate structure. Their results were consistent with the Michaelis-Menten rate equation. Propano, hexano, octano and phenylaceto-hydroxamic acids were taken.

Recently Berndt\(^{86}\) and his group investigated octano and phenylaceto-hydroxamic acids with perfluorooctanic acid as a reactive counterion surfactant and also with sodium sulfonate surfactants and HCl in both water and aqueous acetonitrile solvents. The pseudo phase ion exchange model satisfactorily explains the micellar effects for both the reactive and non-reactive counterion surfactants in both solvents systems. In order to examine the influence of structural parameters in the environment of a perfluoro aggregate Berndt et al.\(^{87}\) reinvestigated substrate-structural effects in micellar catalysis of hydroxamic acids with perfluoroctanoic acid. Variation in the structure of the hydrophobic-moiety of the hydroxamic acid substrate was obtained by the incorporation of different chain lengths and differently substituted aryl groups into the substrate. The major influence of the change in substrate structure is on the binding constant for binding of the substrate to the
<table>
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<th>No.</th>
<th>R&lt;sub&gt;1&lt;/sub&gt;</th>
<th>R&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Molecular Formula</th>
<th>Catalyst</th>
<th>Surfactant</th>
<th>Medium</th>
<th>Reference</th>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CTAB</td>
<td>Aqueous</td>
<td>60.0 ± 0.1</td>
<td>0.11 M (NaOH)</td>
</tr>
<tr>
<td>2</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CTAB</td>
<td>Aqueous</td>
<td>60.0 ± 0.1</td>
<td>0.1 M (NaOH)</td>
</tr>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CTAB</td>
<td>Aqueous</td>
<td>60.0 ± 0.1</td>
<td>0.11 M (NaOH)</td>
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<tr>
<td>4</td>
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<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CTAB</td>
<td>Aqueous</td>
<td>60.0 ± 0.1</td>
<td>0.1 M (NaOH)</td>
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<td>5</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>CTAB</td>
<td>Aqueous</td>
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<td>0.11 M (NaOH)</td>
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<tr>
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<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CTAB</td>
<td>Aqueous</td>
<td>60.0 ± 0.1</td>
<td>0.1 M (NaOH)</td>
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surfactant aggregate. The number of substituents on the aryl ring appears to be more important than the total number of carbon atoms in the substrate. Typical surfactant kinetic effects consistent with their previous studies were observed for all the compounds.

It is evident from literature that much of the existing evidence is fragmentary and vital important information for significant mechanistic details, remain largely unknown. Whatever little work that has been done on the micellar hydrolysis of hydroxamic acids deals primarily with unsubstituted hydroxamic acids.\textsuperscript{31-87} Only a few counted surfactants have been used. Besides these, comprehensive mechanistic framework has not been established. The quantitative description of the mechanism of solubilization, substrate specificity as well as the other factors which influence the rate are not available. The different diagnostic criteria, the effect of temperature, the kinetic solvent isotope effects, solvent effects, salt effects and product identification have not been studied extensively.

The analytical and complexation chemistry of hydroxamic acids have kept pace with the growth of interest in them. With the increasing demand for sensitive reagents, the use of N-substituted hydroxamic acids was explored as these form very stable chelates with metal ions. However, the use of surfactants for the analytical applications of hydroxamic acids have not been achieved. The addition of surfactant results intense, water soluble, highly coloured complexes with much greater molar absorptivity and solubility than the complex formed in the absence of surfactants. This increased sensitization of colour reactions of metal ions has come as a great help to analytical chemists. The selection of an appropriate surfactant is largely an empirical process. Little detailed guidance available.

During the last five years considerable efforts have been made by our group to obtain detailed mechanistic information of hydrolysis reaction of unsubstituted and N-substituted hydroxamic acids.\textsuperscript{111-120} Ghosh and his co-workers have investigated the kinetics of acidic and alkaline hydrolysis of hydroxamic acids.\textsuperscript{111-120} A rapid and reliable analytical method is developed for the determination of hydroxamic acids in the presence of micelles suited for kinetic investigation.

1.6 THE PRESENT INVESTIGATION

Since micellar catalysis of hydroxamic acid is a relatively unexploited area of research, systematic and careful collection of data is necessary in order to
<table>
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<th>S. No.</th>
<th>Surfactant Used in the Present Investigation</th>
<th>Molecular Formula</th>
<th>Structural Formula</th>
<th>Molecular Weight</th>
<th>Make</th>
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<tr>
<td>1</td>
<td>CTAB (Cetyltrimethylammonium bromide)</td>
<td>CnH2n+1NO3-</td>
<td></td>
<td>358.01</td>
<td>Sigma</td>
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<td>2</td>
<td>CPC (Cetylpyridinium chloride)</td>
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<td>Loba Chemie</td>
</tr>
<tr>
<td>3</td>
<td>CPB (Cetylpyridinium bromide)</td>
<td>CnH2n+1Br</td>
<td></td>
<td>304.38</td>
<td>Sigma</td>
</tr>
<tr>
<td>4</td>
<td>SDS (Sodium dodecylsulfate)</td>
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<td>288.38</td>
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</tr>
<tr>
<td>5</td>
<td>LLS (Lithium dodecylsulfate)</td>
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<td>272.35</td>
<td>Sigma</td>
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<tr>
<td>6</td>
<td>Tnn-100 (Polyoxyethylene dodecyl ether)</td>
<td>CnH2n+1OCH2CH2O(-O-CH2CH2O)nOH</td>
<td></td>
<td>646</td>
<td>E. Merck</td>
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</table>
observe and possibly predict the underlying trends in the effects of surfactants on the hydrolysis mechanism. The present investigation is divided into following parts:

(I) Micellar Catalysis of the Acidic and Alkaline Hydrolysis of Hydroxamic Acids

An attempt has been made to collect the kinetic and thermodynamic data on the influence of some cationic, anionic and non-ionic surfactants on the acidic and alkaline hydrolysis of some hydroxamic acids. In studying rate acceleration or inhibition in the effects of surfactants a reasonable range above and below the CMC has been covered. The surfactants used in the present investigation are given in Table 1.03. For comparative study four N-substituted hydroxamic acids MBHA(V), PBHA(VI), N-p-Cl PBHA(VII) and BBHA(VIII) which have a common substituent group \( \text{C} = \text{O} \) attached to four different N-substituted hydroxylamines.

\[
\begin{align*}
R &\quad N\quad OH \\
\text{O} &\quad \text{C} = \text{O}
\end{align*}
\]

\( R = \text{CH}_3 \) , N-Methylbenzohydroxamic Acid (MBHA)
\( R = \text{C}_6\text{H}_5 \) , N-Phenylbenzohydroxamic Acid (PBHA)
\( R = \text{p-Cl C}_6\text{H}_4 \) , N-p-Chloro phenylbenzohydroxamic Acid (N-p-Cl PBHA)
\( R = \text{C}_6\text{H}_5, \text{CH}_2 \) , N-Benzylbenzohydroxamic Acid (BBHA)

The acidic hydrolysis of some hydroxamic acids have also been investigated in the absence of surfactants.

(i) Salt Effects

Salt effects on the micellar catalysis are larger. They appear to be due to the specific competition among counterions for sites on the micelle rather than due to the increase in double layer shielding. Different salts have been used.

(ii) Substituent Effects

The use of substituent effects as a criteria of the mechanism has been of tremendous value on the development of physical organic chemistry as a distinct
field of study linear free energy relationships for various substituent groups, particularly at para position in the phenyl-substituted hydroxamic acids have been examined.

(iii) Solvent Effects

Solvent plays a major role in micellar catalysis reaction. In this study an attempt has been made to compare and correlate the kinetic effects of various solvents on rate with their properties.

(ii) Quantitative Treatment of Micellar Rate Effects

In the last few years, significant progress has been made in the quantitative treatment of the dependence of the rate of a particular reaction on the concentration of surfactant. It is generally agreed that micellar catalytic effects in bimolecular reactions are observed only when there is a favourable position of the substrate and the reactant between aqueous and micellar phases. Thus, the rate increase and or decrease observed is explained in terms of changes in concentration and rate constant in the two phases. Several methods for the correlation of micellar rate effects exist in the literature. These include Pseudophase model, Piszkiewicz\textsuperscript{121} cooperativity model, pseudophase ion-exchange model\textsuperscript{122-124} and Poisson-Boltzmann equation\textsuperscript{125-130} etc. In the present investigation both pseudophase and Piszkiewicz models have been successfully applied for the rate data.

(iii) Analytical Study

Hydroxamic acids are excellent analytical reagents for spectrophotometric determination of various metal ions. The selectivity and sensitivity of analytical reactions is increased with the addition of surfactants. A new, rapid and selective method for spectrophotometric determination of vanadium in steel and blood samples have been analysed.

1.7 THE ORDER OF PRESENTATION

The following order of presentation has been adopted.

Chapter-I of this thesis comprises the introductory part describing surfactants, their role, behaviour and classification micellization, micellar catalysis, hydroxamic acids and their importance, and review of the earlier work.
Chapter-II of this thesis includes experimental conditions. In this Chapter, the synethesis of hydroxamic acids and product identification of hydrolysis products have been given. The determination of CMC have also been discussed.

In Chapter III, the mechanism of acidic hydrolysis of some N-substituted hydroxamic acids was investigated in the absence of surfactants using all kinetic tools, such as Arrhenious parameters, kinetic solvent isotope effect, Bunnett \( \omega \) and \( \omega^* \) parameters, Yates-McClelland parameter and Cox-Yates excess acidity treatments. Based on these studies the most probable mechanism for the hydrolysis reaction has been proposed.

Chapter-IV of this thesis incorporates results obtained for the hydrolysis of hydroxamic acids in the presence of cationic, anionic, and non-ionic surfactants upon the acidic and alkaline conditions. Activation parameters have also been evaluated.

Chapter-V of this thesis deals with the effect of various factors viz., salt, solvent, and substituents on the reaction rates in the presence and absence of surfactants. This study has been found to be very useful for understanding of mechanisms of all the three hydroxamic acids used.

In Chapter VI all the results for acidic and alkaline hydrolysis of hydroxamic acids in surfactants have been summarized and applicability of different quantitative models of micelles i.e. pseudo-phase model and Piszkiewicz model has been examined.

Chapter-VII of this thesis deals with effect of surfactants upon spectrophotometric determination of vanadium (V) with hydroxamic acid. Highly satisfactory results have been obtained in applying the system to a variety of complex materials for the determination of V (V).
REFERENCES


100. V. Prelog, Pure Appl. Chem. 1963, 6, 327.