CHAPTER 1

INTRODUCTION
The reaction rate expression of catalytic process provides the chemist with essential information on the performance of a catalyst understanding the full meaning of catalytic process, which requires a thorough knowledge of the molecular basis of reaction kinetics. Insight at this level is essential for the development of new catalytic reaction or the improvement of existing catalytic technology.

The elucidation of reaction mechanism for a process, besides being fascinating in itself is of great practical interest both in the laboratory and in industrial practice. Among the various tools employed for achieving this goal, kinetic study occupies a prominent place. Kinetic study may be concerned with describing the behaviour and properties of a system in terms of macroscopically observable quantities such as pressure, temperature and time. The widely used application of chemical kinetics in the study of rate changes produced by structural alterations in one or more of the reactants. A knowledge of the efforts of such changes on reactivity and on the rate equations of reactions is particularly useful in the study of organic reactions.

The interest in the study of the oxidation of amino acids is quite old. Oxidation of amino acids by a large number of oxidants has been extensively investigated from the mechanistic view point [1-5]. Amino acids are important compounds from biological point of view. Nadkarni et al. [6] examined the presence of radioactivity in blood glucose, muscle, liver, glycogen and respiratory carbon dioxide after administration of
serine [7] in rates. The uses of amino acids in biology, medicine and as reagents have been known. The free amino acids take part in numerous metabolic reactions. Specific metabolic role of amino acids includes the biosynthesis of polypeptides, proteins and synthesis of nucleotides etc. The kinetics of the oxidation of amino acids have been studied with various one-equivalent oxidants, such as Co (II), Mn (III), Ce (IV) and V(V) [8]. Of these V(V) is a versatile and potent oxidant and it has been used in kinetic investigations of the oxidation of many amino acids.

High oxidation state transition metals and their oxides are able to induce oxidative transformations. Furthermore, metal peroxides, which are obtained from the reaction of metal oxides (Cr, Mo, Ti, W, V etc.) with hydrogen peroxides or alkyl peroxides, serve as a useful oxidant.

The period over approximately last three decades has seen the development of the chemistry of aggregate of the molecules. The implications of such system are numerous. Even the life is associated with such aggregates as the living cell contains a large number of particles composed of aggregates of molecules. Complex biochemical process are all based on molecular organization viz. mitochondria, chloroplast etc. A knowledge of chemical behaviour inside molecular aggregates is essential for the understanding of biological processes. In an attempt to elucidate the mechanisms by which enzymes effects the catalysis. chemists have expended a great deal of efforts in studying mechanism of simpler, model chemical reactions [9].

Vanadium is biologically an essential element. Its inclusion in enzymes such as bromoperoxidase [10-11] and nitrogenase [12-16] reveals
the importance of its redox chemistry. A number of model complex system have been investigated in order to elucidate vanadium's redox mechanisms [17-23]. Some tunicates, marine sea squirts, selectively accumulate vanadium ions from the ocean [24-27]. This vanadium is incorporated into tunichromes, a class of reducing blood pigments which have been isolated and characterized. The metabolism, physiological role, and pharmacological effects of biologically active vanadium compounds have been reviewed [28-32].

QUINQUEVALENT VANADIUM AS AN OXIDANT

Vanadium (V) is a strong and very useful oxidizing agent for many organic and inorganic substrates. It works both as monodeelectronator and didelectronator. The simple one electron process of the oxidant may be written as

\[ \begin{align*}
V^{n+} + S & \longrightarrow V^{(n-1)+} + R^0 \\
R^0 + V^{n+} & \longrightarrow V^{(n-1)+} + P
\end{align*} \]

where \( S \) = Substrate
\( P \) = Product

An alternative two equivalent process may also be available

\[ \begin{align*}
V^{n+} + S & \longrightarrow V^{(n-2)+} + P \\
V^{n+} + V^{(n-2)+} & \longrightarrow 2V^{(n-1)+}
\end{align*} \]

Coryell and Yost [33] have studied the VO\(^{2+}\) ... VO\(^{4+}\) cell couple in HCl solution and gave following redox reactions:
\[ \text{VO}_2^+ + 2\text{H}^+ \rightarrow \text{VO}^{2+} + \text{H}_2\text{O} + \bar{\text{e}} \]

Vanadium (V) oxidation of organic compounds are investigated either in aqueous acetic acid or aqueous perchloric or sulphuric acid media.

Waters and Co-workers [34] believe that vanadium (V) is completely converted into VO\(_2^+\) even in 0.10 M mineral acid. Quinquevalent vanadium in sulphuric acid solution has been found to form V(V) sulphate. A number of researchers listed different sulphates [35-36]. Lanford and Kieni [37] isolated the solids V\(_2\)O\(_5\).2SO\(_3\).8H\(_2\)O and V\(_2\)O\(_5\).2SO\(_3\).3H\(_2\)O from 120M H\(_2\)SO\(_4\) solution, on the other hand Gillespie et al. [38] and Zolotovin et al. [39] formulated some other sulphate complexes in moderately conc. H\(_2\)SO\(_4\) solution. The assumption that lower complexes of Vanadium(V) and bisulphate with the composition 1:1 or 1:2 are the active oxidising species is reasonable.

**SURFACTANTS**

Surfactants are among the most versatile products of chemical industry, appearing in such diverse products as motor oils used in automobiles, lubricants in high speed engines to micro level in pharmaceuticals and other biological applications. They also continue to prove remarkable fruitful for pure sciences. The range and complexity of the phenomena influenced or controlled by surfactants inevitable requires a rich subtlety in the basic properties at work. Subtlety is perhaps a good word to describe the remarkable maneuverability of the properties of surfactant systems and to explain the difficulties in reproducing measurements and defining adequately both the exact composition and
precise circumstances accompanying particular phenomena. Thus inspite of a wealth of experience in the field, the utilization of surfactants for a particular purpose remains more of an art than a science.

Surfactant is a most commonly and widely used term for surface active agents. It is a substance, when present at low concentrations in a systems, has the property of adsorbing on to the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surfaces or interfaces. Here the term interface indicates a boundary between any two immiscible phases and the term surface denotes mostly an interface where one phase is a gas, usually air.

Molecules which are strongly surface active at two interfaces have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as lyophobic [lyo-liquid; phobic-hating] group together with the group that has strong attraction for the solvent called the lyophilic [lyo-liquid; philic-loving] group. This is known as an “amphipathic” structure [40-43] . When a surface active agent is dissolved in a solvent, the presence of a lyophobic group in the interior of the solvent causes a distortion of the solvent liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant, this distortion of the water structure by the lyophobic (hydrophobic) group of the surfactant, and resulting increase in the free energy of the system, when it is dissolved, means that less work is needed to bring surfactant molecule to the surface resulting in increased concentration of the surfactant at the surface or interface. Due to presence of surfactant on the surface, the work needed to create unit area of surface (the surface free energy or surface
tension) is decreased. On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require desolvation of the lyophilic group and also responsible for the proper orientation of the surfactant molecule at the surface with lyophilic group in the liquid phase and the lyophobic group oriented away from it. For the same reason they aggregate in water to form “micelles” and again in aggregate state, the lyophobic portion of the surfactant attains a more favourable environment than it would otherwise [44].

There are certain substances whose molecules undergo spontaneous aggregation in a given solvent to form thermodynamically stable particles of colloidal dimensions, these substances are named as association colloids classified as amphiphiles, soaps, surfactants, detergents and tensides [45].

James W. McBain, in 1913, classified colloidal electrolytes as a special class, with low osmotic activity and high electrical conductivity. Synthetic detergents sometime called “Syndents” or “Surfactants” are generally regarded as man-made products intended to combine with water to wash out dirt. It contains 10 – 30% surfactant with builders, optical brighteners etc. [46].

Surface-active agents are mainly classified into three categories. “Detergents. Wetting agents and Emulsifiers”, all with same basic chemical mechanism and differ chiefly in the nature of surface involved. Thus surfactant is a general word used to describe all the classes of surface active agents.
Depending upon their chemical structures surfactants can be divided into four groups [47]:

(i) **Neutral Surfactant** :

- Poly oxyethylene alcohol
  \[ \text{CH}_2(\text{CH}_2)_7(\text{OCH}_2\text{CH}_2)_6\text{OH} \]
- Poly oxyethylenated alkyl phenol
  \[ \text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH} \]

(ii) **Anionic Surfactant** :

- Sodium dodecyl sulphate (NaDS or SDS) Sodium lauryl sulfate.
  \[ \text{CH}_3(\text{CH}_2)_{10} \text{OSO}_3\text{Na}^+ \]
- Alkyl benzene sulphonate
  \[ \text{RC}_6\text{H}_4\text{SO}_3\text{Na}^+ \]

(iii) **Cationic Surfactant** :

- Cetyl trimethyl ammonium bromide (CTAB)
  \[ [\text{CH}_3(\text{CH}_2)_{15}]\text{N}^+ (\text{CH}_3)_{3}\text{Br}^- \]

(iv) **Zwitterionic Surfactant** :

- 3-(Dimethyl dodecyl ammonia)-propane-l-sulfonate

**Critical Micelle Concentration (CMC):**

At low concentration in water, detergents exist mostly as monomers [48-49]. If the concentration of surfactant in water increases continuously then above a characteristic concentration the surfactant molecules (normally 50-100) dynamically and spontaneously associate to form molecular aggregates of colloidal dimension called micelle [50]. This concentration is known as Critical Micelle Concentration (CMC). The
aqueous micelle formation is a co-operative process. When the surfactants are dissolved in solvent they distort the structure of the solvent and, therefore, increase the free energy of the system. They, therefore, concentrate at the surface, where by orienting, so that their hydrophobic groups are away from the solvent (water), the free energy of the solution is minimized. However, the free energy of the system is also minimized when the surfactant molecules aggregate in such a manner that the lyophobic groups directed towards the interior of the clusters called micelle and in this way they remain away from contact with solvent.

Generally the length of hydrocarbon chain is inversely proportional to the CMC value of the surfactant [51]. Above CMC, monomers and micelles exist in dynamic equilibrium [52].

The CMC values depend upon various factors some of which are hydrophobicity of the hydrocarbon chain, on the net charge of the surfactant, the nature of polar head groups and counterions, and also on the nature and concentration of added electrolytes [53], temperature [54] and pressure [55] of the whole system. The CMC is also affected by the addition of both ionic and non-ionic solutes. Despite many attempts [56] there is still no corrosion theory of these effects.

The determination of the value of the CMC can be made by the use of any of these physical properties, but most commonly the breaks in the electrical conductivity, surface tension, light scattering or refractive index-concentration curves are used for this purpose.

Although the question of micellar shapes has still not been completely settled, a considerable amount of data is available on micellar
aggregation numbers and the factors that govern them. As a general rule in aqueous media, the greater the “dissimilarity” between surfactant and solvent, the greater the aggregation number.

**Micelles and Their Structure:**

According to Bunton, “Micelles of non functional surfactants (detergents) can catalyze bimolecular reactions by bringing reactants together in an environment conductive to reaction and they inhibit reactions by keeping reactants apart, but they affect rates of unimolecular reactions by providing a submicroscopic medium”. The relation between the rate and surfactant concentration can be explained in terms of the distribution of reactants between the aqueous and micellar pseudo phases which can also be perturbed by added solutes. Catalysis depends upon the charge, type of the reaction and reactant hydrophobicity.”

It has been shown recently that aqueous micelles have a dynamic structure such that the monomers are exchanging extremely rapidly with micelles in the micro second time range and vice versa. Since, equilibrium between micelles and monomers in dilute solutions is usually established very rapidly, micellar solutions of pure materials can be regarded justifiable as being in thermodynamic equilibrium and their properties are readily reproducible. This is a comparatively rare situation in colloidal science. It also enables equilibrium thermodynamics to be applied to micellar systems with confidence [57].

Fisher and Oakenfull [58], Merger [59] has published reviews on the structure and properties of micelles. Large amount of work has been done on the study of structures of aqueous micelles. Among that Hartley’s
structure is a classical micelle structure which is pictured as a roughly spherical aggregate of 50–200 monomers. The radius of the sphere corresponds to the length of the hydrocarbon chain of the surfactant, the micelle has a hydrocarbon core and a polar surface. The head groups and the associated counter ions of ionic micelles are found in the compact stern layer [60].

In 1979, Menger [61] deduced a micellar model with little empty space within the micellar core and it allows for the considerable water penetration into the micellar interior. In this model the micellar surface is more rugged and the stern layer is more poorly defined than in the Hartley model.

Structure of micelle has also been discussed in terms of statistical theory using lattice model [62-63].

Structures of micelles have also been rationalized in terms of the surfactant block model by Fromherz in 1980.

1. **Piszkiewicz Model:**

A kinetic model similar to Hill model [64] has been used by Piszkiewicz [65] to explain the catalysis of bimolecular reactions by surfactants. It begins with the assumption that a substrate “S” and a number “n” of detergent molecules D aggregate to form catalytic micelles DnS which may then react to yield product.

\[
\begin{array}{c}
\text{nD+S} \xrightarrow{K_D} \text{D}_n\text{S} \\
\text{D}_n\text{S} \xrightarrow{k_m} \text{Product}
\end{array}
\]
\[
S \xrightarrow{k_0} \text{Product}
\]

The actual reaction undoubtedly involves multiple sequential equilibrium steps in which detergents and substrate molecules aggregate to form catalytic micelles DnS. They are presented here as a single association step for the sake of convenience.

For this reaction scheme the observed rate constant is expressed as a function of the concentration of detergent D, by

\[
K_p = \frac{k'_m [D]^n + k_0 K_D}{K_D^+ [D]^n}
\]

.............................. (1)

This equation may be rearranged and its log taken to give:

\[
\log \left( \frac{k_p - k_0}{k_m - k_p} \right) = n \log[D] - \log K_D \quad .............. ...
\]

(2)

According to this equation plot of \( \log \left( \frac{k_p - k_0}{k_m - k_p} \right) \) versus \( \log [D] \) for a micelle catalysed reaction is linear with a slope of ‘n’ and at

\[
\log \left( \frac{k_p - k_0}{k_m - k_p} \right) = 0
\]

\[n \log[D] = \log K_D\]

.................................(3)
Also at \( \log \left( \frac{k_w k_0}{k_m - k_w} \right) = 0 \), catalysis by detergent shows one half of its maximum effect on rate constant. For convenience the value of \( \log[D] \) at this point is designated as \( \log[D]_{50} \) and it is equal to \( \log K_D/n \).

2. **Berezin Model**:

Phase separation approach of Berezin et al., [66] for one reactant being bound to micelle be given as:

\[
\begin{align*}
O_w & \xrightarrow{k_w} \text{Products} \\
\text{[S]} & \quad k_m \\
O_m & \xrightarrow{k_m} \text{Products}
\end{align*}
\]

Where \( O_w \) is reactant species in aqueous phase and \( O_m \) in micellar phase. The rate equation for above scheme is:

\[
k_1 = \frac{k_w + k_m K_B C}{1 + K_B C}
\]

(1)

Berezin et al. derived the rate of a bimolecular reaction in presence of dilute surfactant solution above CMC as:

\[
k_w = \frac{k_m K_A K_B C + k_w}{(1 + K_A[C])(1 + K_B[C])}
\]

(2)

where \( C = [D] - \text{CMC} \).
$K_A$ and $K_B$ are the binding constants of the two reactants with the micellar phase. If above CMC, reaction rate decreases monotonically, $k_m$ can be neglected in equation (2).

Thus the equation can be modified to:

$$k_w = \frac{k_w}{(1+K_A[C])(1+K_B[C])}$$

(3)

In order to compute $K_A$ and $K_B$ the graphical method was employed. The equation (3) can be rearranged to the form:

$$\frac{k_w}{k_w-1}/C = \alpha + \beta [C]$$

(4)

To test the validity of equation (4) $[k_w/k_w-1]/C$ was plotted against $[C]$. The slope and intercept $\alpha$ and $\beta$ of the linear plot, could be used to compute $K_A$ and $K_B$ values.

3. Menger–Portnoy Model

Micellar effects upon reaction rates and equilibria are generally analysed in terms of the pseudo phase ion exchange mode [67-77]. The pseudo phase model of micellar rate effects treats micelles and water as distinct reaction regions. So that the overall rate of reactions depend upon reactant concentration and rate constants in aqueous and micellar pseudo phases. The variation in the rate constant with addition of surfactant is generally treated on the assumption that substrate “S” is distributed between the aqueous and micellar pseudo phases, designated by W and M respectively and can react in each phase.
With first order rate constants being $k_w$ and $k_m$. The concentration of micellised surfactant (detergent $D_n$) is given by equation:

$$D_n = D - CMC$$  \hspace{1cm} (1)$$

Where $[D]$ is total concentration and CMC is critical micellar concentration of monomeric surfactant, under kinetic conditions. $K_s$ is the equilibrium constant of substrate binding. This relationship leads to the following equation:

$$\frac{1}{k_w - k_w} + \frac{1}{(k_w - k_m)} \frac{N}{(k_w - k_m)} = K_s([D] - CMC)$$

$k_w$ is the observed pseudo first order rate constant, and $N$ is micellar aggregation number. Values of $K_s/N$ and $k_w$ were obtained from slope and intercept of the linear relationship observed in the plot of $1/k_w - k_w$ versus $1/([D] - CMC)$.

**Vanadium (V) Oxidations:**

Among the various metal ion oxidants vanadium(V) is one of the most widely used versatile oxidant involving the d-block chemistry. The study related to reaction by V(V) involving various organic and inorganic substances have been described briefly.
Kinetic oxidation of quinol catachol and its derivatives [78-80] mcresol [81-85] and hydroquinone [86-87] by V(V) have been studied. Recently Os (VIII) catalysed oxidation of stilbene by V(V) in perchloric acid media has been studied. They discussed role of water molecule on the basis of Hammett’s and Bunnett’s plot [88].

In the oxidation of pentoses by V(V), the rate dependent on \([H^+]\) at lower acid concentration and on \([H^+]^2\) at higher acid concentration [89]. Many workers [90-94] reported the formulation of formic acid or formaldehyde in the oxidation of monosaccharides by V(V). Recently Ag\(^+\) catalyzed oxidation of D-galactose by vanadium(v) in aqueous sulphuric acid medium has been investigated. The inhibitory action of sulphuric and bisulphate ion are also explained [95].

Carbonyl compound bearing \(\alpha\)-hydrogens undergo facile oxidation with pentavalent venadyl ions in acidic media. Cyclic ketones undergo ring-opening catalytic oxygenation in the presence of an alkanol and molecular oxygen to give a ketoester or di-ester, depending on the \(\alpha\)-substituent [96]. \(\alpha\)-\(\beta\)-unsaturated ketones show different reactivities. 2-Cyclohexane-l-ones undergo dehydrogenative aromatization to yield the aryl alkyl ethers [97]. An oxo-vanadium species generated from VO(OR)Cl\(_2\) and AgOTf or Me\(_3\)SiOTF induces the aromatization more effectively and under the milder conditions than VO(OR)Cl\(_2\) alone [98]. 2-Cyclo pentanes and their substituents have been oxidized by V(V) [99].

The oxidation of cyclo butanone with more that 2-molar equivalent of VO(OEt)Cl\(_2\) in the presence of an olefin bearing an electron withdrawing group, results in random oxidative ring opening and addition to the olefin
Os(VIII) catalysed oxidation of phenyl esteryl ketones by V(V) has been studied in aqueous sulphuric acid medium [101]. The oxidation of 2',2'-di-Chloro-3-Cyclo buten-l-ones with VO(OR)Cl₂ results in the regioselective formation of alkyl 2,4,4 trichloro-3-butenoates with chlorination at the α-position [102]. 1,1.3.3, tetramethyl cyclobutane-2,4-dione undergoes VO(OR)Cl₂.

Oxidation kinetics of some aliphatic ketones by V(V) in aqueous medium has been explored by Sharma et al. [103-105]. Cu(II) [106] catalysed oxidation with V(V) of cyclo hexanone involve a complex formation. Virtanen et al. have studied the effect of pressure on oxidation of acetone and hydroxy acetone with V(V). Vanadium (V) oxidation of acetyl acetone and benzyl acetone shows first order with [oxidant] and [substrate] [107]. Recently oxidation of acetophenone oximes with V(V) have been studied. The two electron oxidation to the carbocation has been proposed [108].

The kinetics of oxidation of isopropyl alcohols and sorbital were investigated by Succubai and Santappa [109]. Oxidation of manitol [110] involves [VO₂(H₂SO₄)₂⁺] as active oxidant. A series of aliphatic [111-113] cyclic [114-115] and aromatic alcohols [116-117] were subjected to oxidation by V(V) in acid medium.

Lactic, maleic and mandelic acids oxidative decarboxylation with ammonium metavanadate (V) to give the corresponding aldehydes [118]. Likewise, D-galacturonic acid is oxidized to formic acid by sodium metavanadate (V) in aqueous HCl solution [119]. The aerobic oxidation of N-(Phosphonomethyl) iminodiacetic acid to N-Phosphonomethyl.
glycine is catalysed by vanadyl sulphite in a similar manner [120]. Either vanadyl trichloride or trichloro (aryl imino) V(V) also can induce oxidative decarboxylation of the -3-hydroxy carboxylic acids to give the olefin [121-122].

Oxidation of aliphatic aldehydes [123-124] can proceed in two ways: (i) terminal oxidation i.e. R-CHO$\rightarrow$ RCOOH or by (ii) attach at $\alpha$-position i.e. RCH$_2$CHO$\rightarrow$ RCH(OH)CHO. In the oxidation of pinacols [125], glycols and glycerol [126-128] V(V) acts as one electron oxidant.

Many workers studied the oxidation of hydroxy acids [129-130] atrolactic acid[131], tartaric acid [132], 2-hydroxy-2-methyl propionic acid [133] and glycolic acid by V(V)[134-135].

Oxidation of many inorganic compounds such as iodide ion [136-140] As(III) [141-142], phosphorous acid [143-145], Sn (II) [146-147]; Ti(III)[148], U(IV) [149], NP (IV), [150-151], ferrocyanide [152-153], oxalic acid catalysed oxidation of nitrous acid [154] and phenyl halides [155] by V(V) have also been reported.

**Oxidation of Amino Acids**

The chemical oxidation of amino has received considerable attention in recent years [156-157]. The oxidative decarboxylation of $\alpha$-amino acids can be achieved by using VO(OEt)Cl$_2$ but not VO(OEt)$_3$ [158].

Various oxidants have been used to explore the mechanism steps of the oxidation of amino acids.
OXIDATION BY METAL CATIONS

Metal cations act both one electron and two electron oxidants.

Cr (VI) Oxidations:

Kinetics and mechanism of Cr(VI) oxidation of L-cystine at neutral pH has been reported [159]. The results of studies in the kinetic of anation aquachromium (III) ion by amino acid in aqueous acidic medium show that the rates are insensitive towards the change in ionic strength of the medium [160]. The data on the oxidation of serine, methionine and cysteine by chromic acid [161] can be well interpreted on the basis of rate determining of hydride ion loss.

Mn (III) Oxidants:

Kamaluddin [162-164] studied the oxidation of some α-amino acids with Mn(III) sulphate. He also demonstrated that the reaction follows a path through deamination-accompanied by decarboxylation. Mn (III) perchlorate [165] has been employed for the Kinetic oxidation of amino acids. Catalytic effect of Mn$^{2+}$ on oxidative deamination and decarboxylation of L-isomers of amino acids by permanganate has been reported [166]. Kinetics of oxidation of some neutral amino acids (L-serine, DL-alanine, DL-threonine) by Mn (III) ions have been studied. The reactions shows first order dependence each in [Mn (III) and [A] [167]. Oxidation of L-glutamine by Mn (III) in aqueous sulphuric acid media has been studied by Rangappa et al. [168].
Co (III) and Co (II) Oxidations:

The Kinetics of the interaction of Co (III) with L-tyrosine was investigated [169] in the pH range 6.10 to 6.90. Waters [170] and Santappa [171] carried out the uncatalysed oxidation of some amino acids by Co(II) and found that rate of reaction is slow, they suggested an outer sphere mechanism. Navaneeth Rao et al. [172] explored the oxidation of amino acids by Co (II) in sulphuric acid medium.

Ce (IV) Oxidations:

Ceric oxidation of glycine in HNO₃ medium using Ag (I) as a catalyst has also been carried out [173]. Ir (III), Mn (II) system has been employed in the oxidative decarboxylation and deamination of amino acid by Ce(IV) [174]. Navaneeth Rao et al. reported that glycine and α-alanine were oxidised only in the presence of Ag⁺.

Polymerization of acrylonitrile and methyl methacrylate monomers (M), initiaed by Ce(IV)-glycine redox system catalysed by bromide ion was reported kinetically [175]. A Kinetic investigation of Ru (III) catalysed oxidation of alanine by ceric perchlorate in perchloric acid medium has been made and the results indicate first order dependence on each of [Ce (IV)], [alanine], [Ru (III)] and [H⁺] [176].

Vanadium (V) Oxidations

Kinetics of oxidative deamination-decarboxylation of L-proline and L-hydroxy-proline have been studied by V(V) in sulphuric acid medium [177]. Pandey et al. [178] made a systematic study of some amino acids in the presence of sulphuric acid. The reactions are first order in oxidant and
substrate each and are acid catalysed. Vanadium (V) oxidation of amino acids proceed through intermediate free radical [179] formation. Reactions are acid catalysed, participation of water molecules in the slow step has been suggested on the basis of ‘w’ value. A free radical mechanism has been proposed for the oxidation of cysteine [180].

**Oxidation by Haloamides and Imides**

Kinetics of oxidation of proline by acidic solution of N-bromo succinimide in the presence of Ir (III) chloride as a catalyst have been studied in the presence of mercuric acetate as Br Scavenger [181]. A recent study of oxidative decarboxylation and deamination of some amino acids i.e. proline, histidine, arginine, lysine and tyrosine by N-chloronicotinamide (NCN) have been reported in aqueous acetic acid medium in presence of HCl [182]. Kinetics and mechanism of oxidation of DL-methionine (met) by sodium alkaline medium in presence of O₃O₄ as catalyst have been reported [183]. Kinetics and mechanism of N-bromosuccinimide oxidation of L-arginine in aqueous acetic medium has been studied by Nandibewoor et al. [184]. The reaction is first order in (N-bromosuccinimide), fractional order in (L-arginine). Kinetics and mechanism of oxidation of amino acids have been carried out using various N-halo compounds [185-187]. N-bromoacetamide oxidation of serine, threonine, arginine, aspartic acid and glutamic acid in alkaline medium reported by Sundaram et al. [188-189]. The oxidation of histidine has been studied in H₂O\text{\textbar}M₃OH system [190-191]. Oxidation of amino acids [192-194] with N-bromo succinimide a potent imide oxidant, exhibits first order dependence in each of the reactant and inverse first order in [H⁺].
Oxidation by KMnO₄

The Kinetics of oxidation of L-aspartic acid in aqueous alkaline medium at a ionic strength of 2.0 mol dm⁻³ has been studied spectrophotometrically [195]. Nandibewoor and co-workers have oxidized amino acids by aqueous alkaline permanganate and proposed manganate ion MnO₄⁻² as the product [196-197].

Permanganate oxidation of amino acids are also studied by Tiwari et al. Oxidation of amino acids by KMnO₄ have been conducted in acidic medium [198-201]. In a current study of the Kinetics of oxidation of DL-serine by permanganate in aqueous alkaline medium, spectrophotometrically has been reported [202]. Kinetics of oxidative deamination and decarboxylation of dl-leucine by acidic permanganate in presence pf silver ion has been investigated [203]. The Kinetics of oxidation of L-isomer of amino acids viz, aspartic acid, asparagine, glutamine and glutamic acid have been studies in sulphuric acid media by KMnO₄ by Shastry et al. [204].

Oxidation by Ninhydrin:

Recently, Zaheer Khan and Co-workers [205-207] have reported the oxidation of glycine, alanine, phenylalanine and proline by ninhydrin. They suggested the formation of aldehyde, ammonia and CO₂ as products. Subramanian et al. [208] investigated the kinetic oxidation of a number of amino acids by potassium bromate in aqueous acetic acid medium in presence of Hg (II). Oxidation of glycine [209] with aqueous chlorine exhibits first order kinetics in oxidant and substrate each and inverse first order in [H⁺].
Oxidation by Potassium Persulphate

Ag⁺ catalysed [210-211] or uncatalysed [212] oxidation of amino acids by K₂S₂O₈ have been investigated by different co-workers. Cu (II) as a catalyst was employed in the peroxysulphate oxidation of amino acids [213]. Peroxomonosulphate, oxidation of serine and glutamic acid in the absence and the presence of CH₃CHO and C₂H₅CHO reported by Vivekanundam et al. [214]. Peroxomonosulphate has been used for the oxidation of some amino acids.

The formation of epoxide as an intermediate has been proposed [215] in the oxidation of α-amino acids viz, glycine, alanine, phenylalanine, valine, aspartic acid, serine and threonine by Fremy’s radical (potassium nitroso disulphonoate), (PNDS) in aqueous buffer solution. The order of reactivity has been found to be phenylalanine> alanine> serine> glycine> valine> threonine> aspartic acid [216].

Oxidation by N-Halogeno and N-Metallo Reagents

The role of α-substituent on the oxidation of α-amino acids by bromide ion in acid medium has been explored by Ramchandran et al. [217]. B. Thimme Gowda has been investigated the oxidation of six amino acids by t-butyl hypochlorite in aqueous acetic acid media. A comprehensive mechanism of oxidation is also suggested [218]. Mahadevappa and co-workers [219-223] employed chloramine-T in acid medium for the oxidation studies of amino acids. Kinetic oxidation of amino acids by chloramines-T in alkaline medium were conducted by Mushran et al. Recently, K.K. Banerjee and Co-workers [224] have studied
the oxidation methionine by pyridium bromochromate. Chloramine-T oxidation of a number of α-amino acids are studied by several workers [225-226].

**Oxidation by Periodates:**

Periodate was utilized to explore the kinetics of oxidation decarboxylation of some α-amino acids [227]. Clamp and Hough [228] suggested that the oxidation of glycine and N-substituted glycine by periodate proceed by an electrophilic attack of the oxidant on nitrogen atom. Oxidation of L-arginine by diperiodatonickelate (IV) (DPM) in aqueous alkaline medium is first order in [DPN], but fractional order each in [L-Arg] and [OH⁻] [229].

**Oxidation by Phenylisodoacetate:**

Kinetics and mechanism of oxidation of glycine, phenyl alanine, leucine, valine and alanine [230] by phenylisodoacetate was investigated in aqueous acetic acid medium in presence of perchloric acid. Lily and Bhavani [231] used phenylisodoacetate for the oxidation of some amino acids.

**Micellar Catalysed Oxidations**

Micellar catalysis of a large number of reactions has been the area of current research [232-250]. The oxidation of L-amino acids in presence of micelles by CAT have been studied by Shastry et al. The oxidation of acetone by Ce (IV) is subjected to micellar catalysis by Meenakshi [251]. SN₂ reactions between organic halides and the sulphite ion have been studied by Sinha et al. [252-253] in mixed solvents with micellar environment. They reported that the combined effect of NaLS and salts.
NaLS and solvent composition containing less water have caused retardation of the rate.

Cationic surfactants first became important when the commercial potential of their bacteriostatic properties was recognized by Domagk in 1953. From this came a proliferation of hundreds of commercial products. Today cationic surface active agents with antibacterial properties continue to play an important role as sanitizing and antiseptic agents, as components in cosmetic formulations, and as germicides and fungicides.

Perez-Benito and Rodenas [254] reported the kinetics of oxidation of alcohols by chromic acid in the presence of SDS micelles. Panigrahi and Mishra conducted the micellar catalysed oxidation of cyclohexanol [255] and benzyl alcohols [256]. Oxidation of malonic acid by chromic acid [257] in the presence of NaLS exhibits first order each in [Cr (VI)] and [H+] but second order in malonic acid. Ahmad and Hussain [258] have undertaken the systematic study of the oxidation of different α-amino acids to explore the effect of surfactant on the kinetic parameters and mechanistic changes. The presence of surfactant SDS enhanced the rate of oxidation of serine [259] by permanganate. Panichevo et al. reported the effect of sodium and copper laurate and palmitate on the kinetics of oxidation of amines with oxygen in aqueous phase. Recently, Gour [260] has studied the micellar catalysed oxidation of alanine in sulphuric acid media. Herriott and Picker [261] reported the oxidation of several organic substrate by potassium permanganate under phase transfer catalytic conditions using tri-capryl ammonium chloride with very good yield. Menger [262] obtained high yield of piperonylic acid by the oxidation of piperonal using NaLS. Weber
and Shephered [263] conducted controlled oxidation of olefins to the corresponding cis-glycols in moderate yield by potassium permanganate in dichloroethane using benzyl trimethyl ammonium chloride as catalyst. Rao et al. [264], the acid permanganate oxidation of dl-isoleosine [265] in the presence of SDS has been studied spectrophotometrically. Colloidal MnO₂ was reported to be the end product of this oxidation not intermediate as reported in earlier studies. Shastry et al. explored the kinetic oxidation of glycine and alanine by chloramine-T in the presence of cationic surfactant CTA₈ in the acidic medium in the absence of surfactant and the rate law is:

\[
\frac{d [\text{CAT}]}{dt} = \frac{k_w [\text{CAT}][\text{S}]}{1+k [\text{S}]}
\]

where in presence of surfactant the rate expression is –

\[
k_w = \frac{K_w K_S K_D [Dn]}{1+K_D [Dn]}
\]

Pandey et al. made a detailed kinetic oxidation of some amino acids by Vanadium (V) in micellar media [266-268].

In a report of micellar catalysis in the oxidation of hydrocarbons by Ce (IV), the mechanism of catalysis was discussed basing on the product distribution. Panigrahi et al. have oxidized many ketones in the presence of micelles. Ahmad oxidized serine by acid permanganate and reported that the reaction is restarted by the H⁺ in absence of SDS but catalysed in the presence of SDS. The oxidation of orange (II) has been studied in the presence and in the absence of micelle by Cr (VI) [269]. Micelles of
sodium dodecyl sulphate (SDS) have little effect on the rate. The kinetics of oxidation of dl-leucine and dl-serine by chloramines-T in the presence of detergents, SDS and CTAB have been studied [270-271]. The effect of cationic and anionic surfactants on the reaction of basic blue-3 with hydroxide ion has been studied [272]. Recently Panigrahi has oxidized mandelic acid by Cr(VI) in presence of sodium lauryl sulphate.

Reddy [273] et al. investigated the effect of surfactants of different charge type on the rate of oxalic acid catalysed oxidation of p-SO₂H. o-COOH, p-COOH and p-Cl benzene azodimethyl anilines by Cr(VI) in 10% acetic acid medium. SDS and CTAB inhibited while polyoxy ethylene (23) dodecanol (briz-35) catalysed the reaction. According to Bunton and Crichelli in the oxidation of ferrocene by ferric salts in presence of CTAB the rate decreases with increase in micellar concentration. The effect of nonionic micelles on the above system was also reported. In the study of electron transfer reactions involving dithionite ion and vilogens-3 Cludemontigny and Tondry made comparision between micelles and someother heterogenous systems. Micellar effect was also investigated on the oxidation of anthraquino-sulphonate radicals [274].

Molecular interaction between cetyltrimethyl ammonium bromide (CTAB) and Sodium salicylate (NASal) has been investigated. A 1:1 complex is formed in solution. The mixed solution at this composition micellizes at 0.12 mol dm⁻³ at 30⁰C, and the mixed micelle binds nearly 55% counter-ions [275]. The kinetics of the reaction of ninhydrin with six amino acids in the presence of cationic micelles of CTAB and anionic micelles of SDS have been studied spectrophotometrically at pH 5.0. at
575 nm. Both the micelles strongly inhibit the reaction due to the association of the substrate with the micelles. The results are best accounted for by the distribution of substrate into micellar and aqueous pseudo-phase as well as the combination of substrate molecules with surfactant molecules [276].

Scope of the Present investigation

The author for the first time has undertaken the systematic study of oxidation of different amino acids to explore the effect of surfactant on the kinetic parameter and mechanistic changes, if any.

The overall aim of the present proposed investigation is to determine the chemical studies and testing, products formed by oxidation of amino acids.

The oxidation in presence of micelles has prompted us to further investigate and develop earlier studies of certain reactions by attempting to illuminate the scope of catalysis in terms of variation in substrate and detergent structure.

Redox reactions are fundamentally important reactions of metabolism in living systems, catalysed by oxidase and reductase.

Considering all these facts the present investigation was undertaken in which some amino acids are chosen as substrate. The substrates which were chosen for micellar-catalysed reaction contains amino and carboxyl groups, both are responsible for completion of the reaction.

Sodium lauryl sulphate (NaLS) representing anionic surfactant was chosen for catalyzing the oxidation of amino acid with Vanadium (V). The
amino acids selected for present investigation are - glycine, valine, proline and phenylalanine.

There is great diversity in the chemical structure of these compounds. Rate and equilibria are often markedly effected by changes in the structure of oxidant and substrate.

The study has carried out to arrive at a probable mechanism for the oxidation of amino acids in presence of micelle. The study includes:

(1) Determination of CMC.
(2) Variation of substrate and oxidant concentration in absence and in presence of SLS.
(3) Effect of sulphuric acid concentration in absence and in presence of SLS.
(4) To determine various energy parameters, the reaction shall be carried out at different temperatures.
(5) Variation of concentration of SLS (micelle) on the rate of reaction.

Based on the result of kinetic and volumetric measurements, stoichiometry and nature of the products, mechanistic pathway have been proposed.