Summary of the thesis

In the present thesis, some redox reactions have been studied using spectral and analytical methods. Comparative kinetic and mechanistic investigations of various reactions in alkaline medium were followed conveniently by UV-visible spectrophotometer in the absence and presence of suitable catalysts. Also some voltammetric oxidation and determinations of a few drugs were carried out with different voltammetric techniques in order to investigate the number of electrons involved, to deduce a suitable mechanism, to determine some important drugs with their detection limit and subsequently apply to drug determination in pharmaceutical samples, in urine as a real sample and so on.

The work carried out in this thesis is divided into seven chapters including the general introduction. Chapter two to seven have been divided into two parts as; Part A: Kinetic studies and Part B: Voltammetric studies. The details of such studies are given below.

Chapter - I: General introduction

This chapter introduces about the literature survey on theoretical concepts of kinetic studies, various principles and applications of kinetics and catalysis. Also this chapter includes about voltammetric studies, various techniques, charge transfer process, different electrodes and applications of voltammetry in general.
Chapter - II: Mechanistic aspects of uncatalyzed and ruthenium(III) catalyzed oxidation of DL-ornithine monohydrochloride by silver(III) periodate complex in aqueous alkaline medium

This chapter describes about the oxidation of an amino acid, DL-ornithine monohydrochloride (OMH) by diperiodatoargentate(III) (DPA) both in the absence and presence of ruthenium(III) (Ru(III)) catalyst in alkaline medium at 25 °C and at constant ionic strength of 0.10 mol dm\(^{-3}\) spectrophotometrically. The reaction between DPA and OMH in alkaline medium has the stoichiometry 1:2 (OMH:DPA) with a first order dependence on [DPA] and an apparent order of less than unit in [OMH], a negative fractional order dependence on [OH\(^{-}\)]. The order with respect to Ru(III) concentration was unity. Suitable mechanisms were proposed. The reaction constants involved in the different steps of the mechanisms were calculated for both the reactions. The catalytic constant (K\(_{C}\)) was also calculated at different temperatures. The activation parameters with respect to slow step of the mechanisms and also the thermodynamic quantities were determined.

\[
\text{NH}_2\text{NH}_2\text{COO}^- [\text{Ag(H}_3\text{IO}_6]_2^- 2^+ + \text{Ru(III)} + 3[\text{OH}^-] + 2\text{Ag(I)} + 4\text{H}_3\text{IO}_6^{2-} + \text{CO}_2 + \text{H}_2\text{O} \]
\[
\text{NH}_2\text{COOH} + \text{NH}_3
\]
Chapter - III: Os(VIII)/Ru(III) catalyzed oxidation of L-valine by Ag(III) periodate complex in aqueous alkaline medium: A comparative kinetic study

In this chapter, the kinetics of osmium(VIII) and ruthenium(III) catalyzed oxidation of L-valine (L-val) by diperiodatoargentate(III) (DPA) in aqueous alkaline medium at 25 °C and at constant ionic strength of 0.006 mol dm$^{-3}$ was studied spectrophotometrically. The stoichiometry is same in both the catalyzed reactions i.e., [L-val]:[DPA] = 1:1. The catalytic constant ($K_C$) was calculated for both catalysts at different temperatures. The effect of ionic strength, dielectric constant of reaction medium and added products on the rate has been investigated. Suitable mechanisms were proposed. The activation parameters with respect to slow step of the mechanisms were computed and discussed and thermodynamic quantities were also determined. It has been observed that the catalytic efficiency for the present reaction is in the order of Os(VIII) > Ru(III). The probable active species of catalysts and oxidant have been identified.

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH} - \text{CH} - \text{CO}^- + [\text{Ag(H}_3\text{IO}_6]^2- + 2\text{OH}^- & \xrightarrow{\text{Ru(III)/Os(VIII)}} \text{CH}_3\text{CH} = \text{CHO} + \text{Ag(I)} + 2\text{H}_3\text{IO}_6^{2-} \\
& + \text{HCO}_3^- + \text{NH}_3
\end{align*}
\]
Chapter - IV: Thermodynamic quantities for the different steps involved in the oxidation of furosemide drug by alkaline Ag(III) periodate complex in absence and presence of osmium(VIII) as a homogeneous catalyst

In this chapter, the kinetics of oxidation of a loop diuretic drug furosemide (Fur) by diperiodatoargentate(III) (DPA) has been investigated both in the absence and presence of osmium(VIII) used as homogeneous catalyst in alkaline medium at a constant ionic strength of 0.20 mol dm\(^{-3}\) spectrophotometrically attached with HI-TECH SFA-12 stopped flow accessory. The stoichiometry was same in both the cases, i.e., [Fur]:[DPA] = 1:2. Suitable mechanisms were proposed. The reaction constants involved in the different steps of the reaction mechanisms were calculated for both reactions. Kinetic experiments suggest that [Ag(H\(_2\)IO\(_6\))(H\(_2\)O)\(_2\)] is the reactive silver(III) species and [OsO\(_4\)(OH)\(_2\)]\(^{2-}\) is the reactive Os(VIII) species.

\[
\text{Cl} \quad \text{H}_2\text{NO}_2\text{S} \quad \text{COO}^- \quad + \quad 2 \quad \text{[Ag(H}_2\text{IO}_6\text{(H}_2\text{O)}_2\text{)]} \quad + \quad 5\text{OH}^- \\
\quad \text{H}_2\text{NO}_2\text{S} \quad \text{COO}^- \quad + \quad 2\text{Ag}^0 \quad + \quad 2\text{H}_2\text{IO}_6\text{O}^- \quad + \quad 7\text{H}_2\text{O} \\
+ \quad \text{Os}^{\text{VIII}}
\]
Part B: Voltammetric Studies

Chapter V: Voltammetric oxidation and determination of loop diuretic furosemide at a multi-walled carbon nanotubes paste electrode

This chapter deals with the electrochemical oxidation of loop diuretic drug furosemide in 5.0 pH with 0.04 M Britton-Robinson buffer as supporting electrolyte at 25 ± 0.1 °C at a multi-walled carbon nanotubes-paraffin oil paste electrode using cyclic and differential pulse voltammetric techniques. The electrochemical process was observed to be adsorption controlled, irreversible and involving two-electron oxidation. Effects of anodic peak potential, anodic peak current and heterogeneous rate constant have been discussed. A differential pulse voltammetric method with good precision and accuracy was developed for the determination of furosemide in pharmaceutical formulations and urine as a real sample.

Chapter VI: Voltammetric behavior of theophylline and its determination at multi-walled carbon nanotubes paste electrode

In this chapter, the voltammetric behavior of theophylline was investigated using cyclic and differential pulse voltammetric techniques. The cyclic voltammetric results indicate that multi-walled carbon nanotubes paste electrode can remarkably enhance electrocatalytic activity towards the oxidation of theophylline in pH 3.0 phosphate buffer solution than the carbon
paste electrode. The oxidation of theophylline was observed to be a two-electron process, irreversible with diffusion character. Effects of anodic peak potential, anodic peak current and heterogeneous rate constant have been discussed. Under optimal conditions, the anodic peak current was proportional to theophylline concentration in the range of $2.0 \times 10^{-6}$ to $1.5 \times 10^{-4}$ M with a detection limit of $1.97 \times 10^{-8}$ M using differential pulse voltammetry. The proposed method was employed to determine theophylline in pharmaceutical formulations and urine as a real sample.

Chapter - VII: Electro-oxidation of nimesulide at gold electrode and its determination in pharmaceuticals and human biological fluids

This chapter describes an electro-oxidation of nimesulide by cyclic and differential pulse voltammetry at different pH at gold electrode. The oxidation process was irreversible and exhibited a diffusion-controlled behavior. According to the linear relation between the peak current and the nimesulide concentration, differential pulse voltammetric method for the quantitative determination in pharmaceuticals was developed. The linear response was obtained in the range of $2.0 \times 10^{-7}$ to $1.2 \times 10^{-6}$ M with a detection limit of $1.11 \times 10^{-9}$ M with good selectivity and sensitivity. The electrochemical behaviors of nimesulide were studied and electron-transfer coefficient ($\alpha = 0.5$), proton number ($X = 1$) and electron transfer number ($n = 2$) have been determined. The proposed method was also applied for the detection of nimesulide in urine as a real sample.