CHAPTER 2
EXPERIMENTAL METHODS

2.1 INTRODUCTION

In this chapter we discuss in details the various synthetic procedures of ligands and complex preparation and different experimental techniques used for their characterization.

The ligands used here are Schiff base which are quadridentate in nature and have been derived from condensation of ethylenedimine with salicyldehyde having an active carbonyl group\(^1\). The Schiff bases containing O\(_2\)N\(_2\) chromophores are very effective as coordinating ligands, because they bear a functional group –OH at sufficiently near the site of condensation. Because of the great synthetic flexibility in Schiff base formation, many ligands of diverse structural type have been synthesized\(^2,3\). Considerable attention has been drawn for the chemistry of metal complexes with multidentate ligands because these ligands have delocalized \(\pi\)-orbitals with several binding as well as vacant sites occupied by metals and for potential catalytic or enzymatic activity. Furthermore, substitution at the aromatic ring can modify the electronic and steric properties of the resulting complexes, which can enable fine-tuning of properties. The structure of Schiff base ligand is shown in Fig.2.1. The tetra- and penta- coordinated complexes of copper as the metal centre have been synthesized and characterized.
From various studies on copper proteins it has been known to us that Galactose oxidase a copper containing protein has $d^9$ Cu(II) centre coordinated to two tyrosines and two histidines at its active site$^4,5,6$ as shown in Fig.1.1. The phenolate coordination of tyrosine gives rise to a ligand-to-metal charge transfer interaction which is characteristics of this protein. Tyrosine-Cu(II) charge transfer is well known and may be compared with a wide range of Cu(II) complexes containing $O_2N_2$ type chromophore. The phenolate moieties of the Schiff bases mimic the two tyrosines (Tyr) coordination, while the imine functionalities and coordinated imidazoles provide some correspondence to the histidine (His) coordination in a protein. Since this copper protein is mainly associated with electron transfer processes, so studies on the redox behaviour of their Cu(II) Schiff base model complexes are studied in various solvent systems.

Similarly, Cyanocobalamin (Vitamin B$_{12}$) and Methylcobalamin are the two biologically important distinctive class of Co-enzyme$^8-12$ and the structure of Co-enzymeB$_{12}$ (Fig.1.5) is based on a corrin ring similar to the porphyrin ring found in heme, chlorophyll and cytochrome. The central metal ion is cobalt. Four of the six coordination sites are provided by four nitrogens of the corrin ring and fifth by a dimethylbenzimidazole group. The sixth coordination site, the center of reactivity, is variable, being a cyano group (-CN), a hydroxyl group (-OH), a methyl group (-CH$_3$) or a 5'-deoxyadenosyl group. Dimethylglyoxime, Pyridine, Imidazole and Methyliodide are the ligands used for the synthesis of models of
Cyanocobalamin (Vitamin B\textsubscript{12}) and Methylcobalamin. The model complexes have octahedral structure with the cobalt atom centrally located coordinated to the four N-atom of the dimethylglyoxime ligand at the four corners of the octahedron mimicking the four nitrogen atoms of a corrin ring in Vitamin B\textsubscript{12}. Its fifth position is occupied by N-atom of heterogenous base like pyridine; imidazole and 1-methyl imidazole representing the N-atom of a benzimidazole ligand and the sixth position is varying.

Various spectroscopic techniques like UV-Visible spectroscopy, Infrared spectroscopy, Electron Spin Resonance spectroscopy and Electrochemical techniques like Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV) are carried out for the complexes encapsulated in aqueous solution of various surfactant. The theoretical backgrounds of the various experimental techniques are also discussed. The preparation of the various micellar solution, degassing techniques and cleaning of electrodes are mentioned here.

The oxidation reduction potential of the copper complex is also calculated theoretically using different ab initio and DFT methods. In this case we have considered only the monomolecular copper complexes where the geometry of the complex having Cu\textsuperscript{2+} oxidation state has been optimised with STO-3G basis set and then the one electron oxidation-reduction energies of this complex are calculated with different basis set and DFT methods.
2.2(a) CHEMICALS

The chemicals used in this work are Cupric chloride dihydrate, Cobalt chloride hexahydrate, sodiumborohydride (from MERCK), dimethylglyoxime, pyridine, sodiumdodecysulphate (from QUALIGEN); potassium dihydrogenphosphate (SRL Laboratories Pvt. Ltd, Mumbai); imidazole (Merck); 1-methylimidazole; trishydroxyaminomethane (puriss AR Spectrochem Pvt. Ltd. Bombay, India); trishydrochloride (Loba chemie); tetrabutyl ammoniumperchlorate; ammoniumperchlorate; cetyltrimethylammoniumbromide (Sigma, USA).

2.2(b) SOLVENTS

Methanol, dichloromethane, acetonitrile (Sisco Research Laboratory Pvt. Ltd. Mumbai)

2.3 PREPARATION OF LIGANDS

2.3(a) SYNTHESES OF SCHIFF BASE LIGANDS

The quadridentate Schiff base ligands were prepared according to the literature method\textsuperscript{13-16}.  

2.3(a)(i) Salen or N,N'-bis(Salicylidene)ethylenediamine

0.01g (0.01 mole) of ethylenediamine in 10ml of methanol was mixed with 0.02g (0.01 mole) of salicyldehyde in 15ml of methanol as shown below (Reaction Scheme 1). The reaction is exothermic and a large amount of heat is evolved. On standing the yellow colored compound separates. This
was filtered and recrystallised from methanol. Yield: 0.25 g
Solubility: Soluble in methanol and ethanol.

Reaction Scheme 1

\[
\text{Salicyldehyde} + \text{Ethylenediamine} + \text{Salicyldehyde} \rightarrow \text{Salen}
\]

\[ R_1 = \text{H} \quad R_2 = \text{-CH}_2\text{CH}_2\text{-} \]

2.3(a)(ii) SalenS or N,N'-ethylenbis(Salicylalimine-5-sulphonate)

An equimolar amount of salicyldehyde and aniline was mixed in methanol and the reaction mixture was warmed until the deep yellow color solution is obtained. On keeping for sometime without any disturbance a yellow colored compound was separated. The compound N-phenyl salicyldiamine was cooled and recrystallised from methanol.

About 35 g of the yellow colored compound N-phenyl salicyldiamine was added to 96 ml of concentrated H\textsubscript{2}SO\textsubscript{4} and the mixture was warmed for 2 hours with occasional stirring at 100°C. The mixture was cooled and ice water was slowly added to it with vigorous stirring to precipitate a yellow product. The solution mixture was heated further to dissolve the yellow product and cooled. Yellow crystalline product, N-phenyl salicyldiamine sulphonic acid, was filtered off and washed with water. 25 g of N-phenyl salicyldiamine sulphonic acid was dissolved in
Na₂CO₃ solution and boiled vigorously in an open flask for 2 hours and glacial acetic acid was slowly added to the cooled solution to pH ≈ 5.0, followed by addition of equal volume of ethanol. The mixture was cooled to 0°C, filtered, washed with ethanol and dried to get white crystals of Sodium Salicyldeyde-5-Sulphonate or [Na (Sal S)].

**Reaction Scheme 2**

```
\[
\begin{align*}
\text{Salicyldehyde} & \quad + \quad H_2N-Pk \quad \rightarrow \quad \text{N-phenylsalicyldiamine} \\
\text{N-phenylsalicyldiaminesulphonic acid} & \quad \xrightarrow{H_2SO_4} \quad \text{Na}_2\text{H}_2\text{(Salen S)} \\
\text{Na}_2\text{CO}_3 & \\
\end{align*}
\]
```

\[R_1 = H \quad R_2 = -\text{CH}_2\text{CH}_2-\]

0.51g of Na (Sal S) was added to 75ml of ethanol and the mixture was heated to 60°C. Water was added dropwise to dissolve the solid, followed by 74μL of ethylenediamine in 2ml of ethanol. The mixture was stirred at 60°C for 1 hour, cooled to 0°C and filtered to get Na₂[H₂(Salen S)]. The product was washed with ethanol, then with ether and air dried. The reaction scheme for the preparation of SalenS is shown above (Reaction Scheme 2).
2.3(a)(iii) Sal(1,3-pn) or N,N'-bis(Salicylidene)1,3 propane diamine

0.01g (0.01mole) of 1,3 propane diamine in 10ml of methanol was mixed with 0.02g (0.01 mole) of salicyldehyde in 15ml of methanol as shown below (Reaction Scheme 3). The reaction is exothermic and a large amount of heat is evolved. On standing the yellow colored compound separates. This was filtered and recrystallised from methanol.

Yield = 0.73; Yield: 80-85%; Solubility: Soluble in methanol and ethanol.

Reaction Scheme 3

\[
\begin{align*}
\text{Salicyldehyde} & \quad 1,3 \text{ propane diamine} \\
& \quad \text{Salicyldehyde} \\
& \quad \text{Sal(1,3-pn)}
\end{align*}
\]

\[
R_1 = \text{H} \quad R_2 = -\text{CH}_2\text{CH}_2\text{CH}_2-
\]

2.4 PREPARATION OF COMPLEXES

2.4 (a) COPPER COMPLEXES

These complexes were prepared according to the literature method.\textsuperscript{2, 3, 13, 14, 17}
2.4 (a)(i) Cu(Salen)

To a hot solution of 1.0g (0.1 mole) of recrystallized copper acetate in methanol, 1.3g (0.1 moles) of hot solution of Schiff base in methanol were mixed followed by vigorous stirring. After cooling the mixture the product obtained was filtered, washed and dried in a vacuum desiccators. The compound was recrystallised from chloroform. The compound obtained as green flakes. Solubility: Sparingly soluble in water but highly soluble in chloroform and acetonitrile.

\[
[Cu(\text{acetate})_2]^2+ + 2\text{Salen} \rightarrow 2\text{Cu(Salen)}
\]

2.4(a)(ii) Cu(SalenS)

To 1.0g (0.1 mole) of copper acetate solution, 0.1N sodium hydroxide was added dropwise in order to precipitate copper hydroxide. When the precipitation was over the solution was filtered and the precipitate was mixed with 5.3g (0.1 mole) of ligand \(\text{Na}_2[\text{H}_2(\text{SalenS})]\) in water and refluxed till the precipitate dissolved completely. The resulting solution was allowed to stand for several hours at room temperature. The violet crystals were filtered, washed with acetone and dried in vacuum. Solubility: Soluble in water.

\[
[Cu(\text{acetate})_2]^2+ + \text{NaOH} \rightarrow \text{Cu(OH)}_2
\]

\(\text{Cu(SalenS)} \xrightarrow{\text{Refluxed}} \text{Na}_2[\text{H}_2(\text{SalenS})] + \text{Cu(OH)}_2\) ppt
2.4(a)(iii) Cu(Salicyldehyde)$_2$

To a hot solution of 1.0g (0.1mole) of recrystallized copper acetate in 100ml of hot methanol, 1.0g (0.1 mole) of salicyldehyde was mixed followed by vigorous stirring. After cooling the mixture the product obtained was filtered, washed and dried in a vacuum dessicator. The compound was recrystallised from acetonitrile. The compound obtained as green powder. Solubility: Sparingly soluble in water, soluble in organic solvents.

\[
[Cu(acetate)_2]^2 + \text{Salicyldehyde} \rightarrow Cu(\text{Salicyldehyde})_2
\]

2.4(a)(iv) Cu(Sal$_{1,3}$-pn):

To a hot solution of 1.0g (0.1mole) of recrystallized copper acetate in 200ml methanol, 1.3g (0.1 mole) of Schiff base (Sal$_{1,3}$-pn) in 200ml was mixed followed by vigorous stirring. After cooling the mixture the product obtained was filtered, washed and dried in a vacuum dessicator. The compound was recrystallised from acetonitrile. The compound obtained as green crystals. Solubility: Soluble in water and organic solvents.

\[
[Cu(acetate)_2]^2 + \text{Sal}(1,3\text{-pn}) \rightarrow Cu(\text{Sal}_{1,3}\text{-pn})
\]

The structure of the complexes were shown in Fig.1.4 (Chapter 1)

2.4(b) COBALT COMPLEXES

The experimental procedures for the preparation of cobaloximes and alkylcobaloximes are as follows$^{18, 19, 20, 21}$. 
2.4(b)(i) Bisdimethylglyoximato-cobalt(III)pyridinato complex

A suspension of 5.5g of dimethylglyoxime and 5g of cobalt chloride hexahydrate in 200ml of 95% ethanol was stirred continuously on a water bath under warm condition until the cobalt chloride has dissolved completely. To the above solution mixture 4ml of pyridine was added and the mixture was continuously stirred and the whole mixture was allowed to cool to room temperature. Air was passed through the whole solution for 24 hours and the whole solution was allowed to stand for 30 minutes and then filtered to get a brown solid. The solid product was washed with 5ml of water, then ethanol and ether and then dried in air. The compound was recrystallized from dichloromethane. The compound was obtained as brown colored crystals. Solubility: Soluble in water and organic solvents.

\[
\text{dmg} + \text{CoCl}_2\text{.6H}_2\text{O} + \text{Pyridine} \xrightarrow{\text{Stirring at room temp.}} \text{CoCl(dmg)}_2\text{Py}
\]

2.4(b)(ii) Bisdimethylglyoximato-cobalt(III)bisimidazol/ BisdiniethyIglyoximato-cobalt(in)bisl-methylimidazoie complex

Bisdimethylglyoximato-cobalt(III)bis1-methylimidazole complex

A suspension of 5.5g of dimethylglyoxime and 5g of cobalt chloride hexahydrate in 200ml of 95% ethanol was stirred continuously on a water bath under warm condition until the cobalt chloride has dissolved completely. To the above solution mixture 4ml of L (imidazole/1-methylimidazole) were added and the mixture was continuously stirred and the whole mixture was allowed to cool to room temperature. Air was passed
through the whole solution for 24 hours and the whole solution was allowed to stand for 30 minutes and then filtered to get a reddish brown solid. The solid product was washed with 5 ml of water, then ethanol and ether and then dried in air. The compounds were recrystallized from dichloromethane. The compounds were obtained as reddish brown colored crystals. Solubility: Soluble in water and organic solvents.

\[
\text{dmg} + \text{CoCl}_2 \cdot 6\text{H}_2\text{O} + \text{L} \xrightarrow{\text{Stirring at room temp}} \text{Co(dmg)}_2(\text{L})_2
\]

\[
\text{L} = \text{Imidazole, 1-methylimidazole}
\]

2.4(b)(iii) Methylpyridinatocobaloxime

To a suspension of bisdimethylglyoximatocobalt(III)pyridinato complex (ca.0.6 g) in methanol (ca.5 ml), sodium borohydride (ca.0.1 g) was added until a blue solution was obtained. To the above solution excess of methyliodide (ca.0.3 ml) was then added followed by more sodium borohydride until the solution became orange in color. The volume of the solution was then reduced to 50% by heating or warming; orange crystals were then precipitated by the addition of water (yield: 0.5 g, 90%). The crystals were recrystallized from aqueous methanol, washed with water and light petroleum and dried in a vacuum desiccator. Solubility: Soluble in water and organic solvents.

\[
\text{CoCl(DMG)}_2\text{Py} + \text{NaBH}_4 + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{Co(DMG)}_2\text{Py}
\]

The structures of the complexes were shown in Fig.1.8 (Chapter1).
2.5 CHARACTERISATION OF THE COMPOUNDS

The compounds were characterized by Elemental and Spectral (UV-Visible, IR) analysis and X-ray crystallographic data. The results were compared with those of similar compounds reported in the literature.

The composition of the Schiff base ligands and complexes are confirmed by Infra-Red spectroscopy. The \( \nu_{\text{C-N}} \) band of schiff base ligand and \( \nu_{\text{C=C}} \) of the phenyl ring appears at 1635 cm\(^{-1} \) and 1600 cm\(^{-1} \) and \( \nu_{\text{O-H}} \) stretching and bending vibrations of the same appears at 3600 cm\(^{-1} \), 1285 cm\(^{-1} \) and 855 cm\(^{-1} \). In complexes \( \nu_{\text{C=N}} \) band splits due to the lowering of symmetry and \( \nu_{\text{O-H}} \) stretching and bending vibrations bands are absent. The 1580 cm\(^{-1} \) band in the ligand due to the vibration of the phenyl ring C=C conjugated to the C=N bond shifted to 1560 cm\(^{-1} \) due to coordination of N-atom to the metal ion. The 1500 cm\(^{-1} \) band due to phenyl ring vibration disappears on complex formation because of the restricted vibration of the phenyl ring in the complex. The C-O stretching at 1310 cm\(^{-1} \) is relatively unaltered when a complex is formed. The metal-chelate ring vibrations occur at 640 cm\(^{-1} \), 630 cm\(^{-1} \) and 620 cm\(^{-1} \). Several bands in the region between 2860-3060 cm\(^{-1} \), 1450-1330 cm\(^{-1} \) and 740-780 cm\(^{-1} \) remain unchanged on complex formation and they are assigned to C-H stretching, in plane bending and out-of-plane deformation respectively, of the CH, CH\(_2\) and aromatic CH-groups in the molecule. The structures of some of the compounds were confirmed by X-ray crystallographic data.
From the electronic spectrum it is found that the Copper Schiff base complexes show a weak band at around 570nm which is due to d-d transition and a high intensity band at around 320nm to 385nm which is attributed to charge-transfer transition from the filled d-orbitals ($d_{x^2}$, $d_{yz}$) of copper(II) to antibonding orbitals of the phenolate residues $[d(Cu)...\pi^*(Phenolate)]$. The electronic spectrum of cobalt complexes shows a low energy broad shoulder at around 675nm due to $^1A \rightarrow ^1T_1$ transition and two slightly high intensity band at around 296.0 and 249.2nm due to $^1A \rightarrow ^1B_2$ and $^1A \rightarrow E$ transitions. Its methyl derivative gives band at around 442 and 382nm due to $^1A_1 \rightarrow ^1E$ and $^1A_1 \rightarrow ^1A_2$ transitions. The electronic spectra of VitaminB$_{12}$ shows two low energy band at around 549 and 531nm due to two $^1A_1 \rightarrow ^1E$ and $^1A_1 \rightarrow ^1A_2$ transitions.

2.6 INSTRUMENTATION AND EXPERIMENTAL TECHNIQUES

2.6(a) UV-VISIBLE SPECTROSCOPY

Spectroscopic measurements were carried out in a Hitachi Model U-3210 double beam grating monochromator spectrophotometer. The instrument is microprocessor based with display monitor and thermal head printing output accessories. Spectra were obtained in a matched pair of 1cm path length quartz cuvettes.
2.6(b) INFRARED SPECTROSCOPY

Infra red spectra were recorded on a Perkin Elmer 1600 series FTIR spectrophotometer.

2.6(c) X-RAY SINGLE CRYSTAL DIFFRACTION

The X-ray single crystal diffraction data were collected at 296K with MoKα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation against F2 of all reflections. The H-atoms, except those attached to nitrogen and oxygen atoms were placed at their calculated positions and refined in the isotropic approximation; those attached to nitrogen and oxygen were located in the difference Fourier maps and refined with isotropic displacement coefficients.

2.6(d) ELECTROCHEMISTRY

Electrochemical measurements were performed on a BAS 100B electrochemical Analyzer, Bio-analytical system, USA. The instrument was used for Cyclic Voltammetry, Osteryoung Square Wave Voltammetry.
(OSWV) and other electrochemistry experiments. A three electrode cell assembly with gas purging lines was used in combination with the analyzer. The instrument was supplied with a display monitor and HP DeskJet printer output devices. A glassy carbon disc or a platinum disc was used as working electrodes, which was polished by using 0.1µm alumina supplied by BAS100B, USA. Further cleaning of working electrode was done by sonicate in an ultrasonicating bath. The reference electrode used was an Ag-AgCl (3.0M NaCl aqueous) electrode supplied by BAS. The reference electrode was kept immersed in 3M aqueous NaCl solution to get a reproducible electrode potential and potential of the reference electrode was periodically checked. A platinum wire was used as the auxiliary electrode. The ionic strength of the solution was 0.1M. The supporting electrolyte was 0.1M NaN03 at about 100 times the concentration of the electroactive species. The reference electrode potential was calibrated by measuring the \( E_{1/2} \) of \([\text{Fe}^{III}(\text{CN})_6]^{3-}/[\text{Fe}^{II}(\text{CN})_6]^{4-}\) couple in water (Fig.2.2 for Cyclic voltammogram and Fig.2.3 for OSWV of \([\text{Fe}^{III}(\text{CN})_6]^{3-}/[\text{Fe}^{II}(\text{CN})_6]^{4-}\) couple in water using Pt as working electrode).

2.6(d)(i) REMOVAL OF DISSOLVED OXYGEN

Trace amount of oxygen present in the solution give rise to a low intensity broad signal at ca. -0.2 to -0.4 Volt (vs Ag-AgCl) in different system. Nitrogen available commercially was purified mainly to remove and
moisture and was purged through the solutions for 5-10 minutes and a blanket of it was maintained throughout the experiment.

Before purging nitrogen gas was bubbled through a chromous chloride solution and then through a column of NaOH pellets. Chromous chloride is prepared by reacting amalgamated zinc with potassium dichromate in concentrated hydrochloric acid medium. After mixing the reactants the solution is allowed to stand for 2-3 days when it develops green colour. Chromous chloride solutions deteriorate slowly, turning brownish and then depositing precipitates. It can be regenerated by solution of concentrated hydrochloric acid. NaOH column removes traces of acid vapour and moisture.

2.6(d)(ii) BACKGROUND VOLTAMMOGRAMS FOR SURFACTANT SOLUTIONS

Background voltammograms for surfactant solutions using glassy carbon electrode were obtained for all the surfactants used, namely CTAB, SDS and TritonX-100, with the supporting electrolyte NaNO₃. The background voltammograms for surfactants were recorded. The voltammograms were reproduced for CTAB, SDS and Triton X-100 (Fig.2.4) respectively.

The system is free of redox interferences in the potential range of interest which is indicated in the voltammograms. SDS and TX-100 solutions offer a convenient media for potential scanning in the range of ca.
1.0V in the anodic range to ca.-1.5V in the cathodic side. The cathodic limit in CTAB medium is also about ca.-1.5V vs Ag-AgCl. The anodic limit in CTAB medium is restricted to ca.0.6V vs Ag-AgCl for bromide oxidation beyond this limit. The buffers used in this study were acetate, phosphate and tris HCl and supporting electrolyte such as NaNO₃ or TBAP (Tetrabutylammoniumperchlorate). They did not give any signal in the potential range.

2.6(d)(iii) MEASUREMENT OF MID-POINT POTENTIAL

Cyclic voltammetry (CV) is perhaps the most versatile electrochemical technique for the study of electroactive species in solution. CV consists of cycling the potential of an electrode, which is immersed in an unstirred solution and measuring the resulting current. The potential of this working electrode is controlled versus a reference electrode such as a saturated calomel electrode (SCE) or a silver-silver chloride (Ag-AgCl) electrode.

The important parameters of a cyclic voltammogram are the magnitudes of cathodic and anodic peak potentials (Epₑ and Epₐ) and the corresponding peak currents (ipₑ and ipₐ) are illustrated in Fig.2.2. The following are the criteria for a reaction to be reversible²⁴,²⁵:

(a) The separation in peak potentials, ΔEp = 59mV.

(b) The ratio of the peak currents ipₑ/ipₐ = 1.0.

(c) The current function ipₑ/ν¹/₂ independent of scan rate.
Redox couples whose peaks shift further apart with increasing scan rate are categorized as quasi-reversible systems. In these systems:

1. Peak separation increases with scan rate.
2. Current function is not independent of scan rate.

If reverse peak is obtained on reversing the potential scan, the electrode process is termed as irreversible.

The proper equilibrium ratio at a given potential is given by Nernst equation

\[ E = E^\circ + \frac{RT}{nF} \ln\left\{ \frac{[R]}{[O]} \right\}_{x=0} \] ........................ (1)

Where the constancy of \( E^\circ \) (formal redox potential) requires the reductions of \( "O" \), the oxidized species of oxidation of \( "R" \) at the electrode surface \( (x=0) \) as required by the applied potential, \( E \), at the working electrode.

In cyclic voltammetry, the peak current, \( i_p \), for a reversible system is given by the following equation\(^2\)

\[ i_p = 0.447F^{3/2}A\cdot n^{3/2}D_o^{1/2}C\cdot v^{1/2}/(RT)^{1/2} \] ........................(2)

where \( 'n' \) is the number of electrons involved in oxidation or reduction, \( 'A' \) is the area of the electrode \( (cm^2) \), \( 'D_o' \) is the diffusion coefficient of the system \( (cm^2s^{-1}) \), \( 'C' \) is the concentration of electroactive species in the solution \( (mol cm^{-3}) \), \( 'v' \) is the potential sweep rate \( (Vs^{-1}) \), \( 'F' \) is the Faraday constant, \( 'R' \) is the gas constant and \( 'T' \) is absolute temperature.
The current depends on two steps in the overall process, the movement of the electroactive material to the surface and the electrode potential transfer reaction. The electron transfer rate is an exponential function of the electrode potential which accounts for the steep rise in the current. However, the electrolysis of the reactant depletes its concentration near the surface.

Since the experiment is performed at a stationary electrode in an unstirred solution, diffusion is the principal means of moving the reactant to the surface. This relatively slow mode of mass transport cannot maintain a steady concentration profile in the region close to the electrode surface. Therefore the depletion zone grows (Fig. 2.2).

The value of $E_{1/2}$ as determined by cyclic voltammetry was confirmed by a relatively new technique in electrochemical analysis, namely Osteryoung Square Wave Voltammetry (OSWV). It is now-a-days used as an easy and quick means to locate the mid-point potential of electroactive species in solution. This method has an edge over conventional pulse voltammetric techniques because the time taken to complete the experiment is much smaller.

The Osteryoung Square wave form is a pulse train of square waves superimposed on a staircase wave form. At each staircase step, the forward pulse ascends in the same direction as the staircase, while the reverse pulse can take place at any point on the step. For OSWV there is one square wave cycle per staircase step (Manual of BAS 100A electrochemical analyzer,
supplied by BAS). The potential of the reference electrode was checked periodically with $K_3Fe(CN)_6$ (Fig.2.2) which illustrates the potential of $[Fe^{III}(CN)_6]^{3-}/[Fe^{II}(CN)_6]^{4+}$ couple in water with 0.1M sodium nitrate ($NaNO_3$) as supporting electrolyte.

Supporting electrolyte concentration is an important factor in determination of peak potentials. If the concentration of supporting electrolyte is too low (less than 100 times of the electroactive species) it will contribute to IR loss in solution. In all the experiments ca. 0.1M NaCl was used as supporting electrolyte. This instrument has in built IR compensation circuitry for IR compensation$^{26,27}$.

**2.6(e) ELECTRON SPIN RESONANCE**

The Electron Spin Resonance (ESR) spectrometer used in this work was a JEOL JES-FA200 spectrometer using X-band frequency of 9.2 GHz. The aqueous solution samples were first degassed by passing pure N$_2$ gas for about 30 min. The solutions were then quickly transferred to quartz capillary tubes, which were then placed in the sample tube in ESR cavity.

**2.6(f) PREPARATION OF MICELLAR SOLUTIONS**

Micellar solutions were prepared by dissolving different surfactants (SDS, CTAB or Triton X-100) in double distilled water. Tetramethylammoniumbromide (0.1M) was added in the micellar solutions to have a more rigid and compact structure with reduced critical micellar
concentration (CMC) and aggregation number\textsuperscript{28-31}. The resulting suspensions were warmed at 50°C to give clear micellar solutions. The pH of the micellar solution was adjusted with dilute acid (HNO\textsubscript{3}) or dilutes alkali (NaOH). The complexes were added to the micellar solution and the mixture was equilibrated at 40-50°C for one hour. Samples prepared in this way obeyed Beer’s Law over a concentration range of $10^{-8}$-$10^{-3}$M. The pH of the micellar solution was adjusted with dilute acid (HNO\textsubscript{3}) or dilutes alkali (NaOH). Solutions at adjusted pH were again allowed to stand at ca. 45°C in dark.

2.6(g) pH METER

pH measurement were made by Elico model No. 11-10 Digital pH meter. The pH electrode was SCE-glass combined electrode (Elico) which was standardized with known buffer solutions in the described pH range. The pH meter gives reproducible result up to ± 0.02 pH. Throughout this work we have used buffer solutions and adjusted the pH accordingly. Buffers used in this work are 0.1M acetate or phosphate or Tris HCl for different pH ranges. Ionic strength of solutions is 0.1M NaNO\textsubscript{3}.

2.7 CONCLUSION

In this chapter we discussed the various instrumental and experimental techniques employed in this work. To avoid the repetition of the various experiments and methods in the following chapters we described
here in details the various experimental procedures for the preparation of copper and cobalt complexes and the various techniques used for their characterization.
Fig. 2.1: Structure of Schiff Base Ligand

\begin{align*}
\text{(Salen)} & \quad: \quad R_1 = H; \quad R_2 = -\text{CH}_2\text{CH}_2- \\
\text{(SalenS)} & \quad: \quad R_1 = \text{SO}_3\text{Na}^+; \quad R_2 = -\text{CH}_2\text{CH}_2- \\
\text{(Sal 1,3-pn)} & \quad: \quad R_1 = H; \quad R_2 = -\text{CH}_2\text{-CH}_2\text{-CH}_2- 
\end{align*}
Fig.2.2: Cyclic Voltammogram of $\text{K}_3\text{Fe(CN)}_6$ in $\text{H}_2\text{O}, 10^{-3}\text{M}$ solution,

S.E. = $\text{NaNO}_3$, Working electrode = Platinum

$E_p^c = +268\text{mV}$ \hspace{1cm} $E_p^a = -209\text{mV}$

$i_p^c = +2.287 \times 10^{-6}\text{A}$ \hspace{1cm} $i_p^a = -2.297 \times 10^{-6}\text{A}$

$E_{1/2} = 238.5\text{ mV}$, $\Delta E_p = 59\text{mV}$, $i_p^c/i_p^a = 0.9$
Fig. 2.3: OSWV of K$_3$Fe(CN)$_6$ in H$_2$O, 10$^{-3}$M solution, S.E. = NaNO$_3$,

**Working electrode = Platinum**

$E_{p_c} = +236$ mV

$i_{p_c} = +1.287 \times 10^{-5}$ A
Fig. 2.4: Background voltammograms in different micellar solutions

(a) CTAB  (b) SDS and (c) TritonX-100
References


