CHAPTER - III

Materials & Methods
This chapter comprises the details regarding techniques employed, instrumentation, methodology, preparation of reagents, solutions and the experimental procedure adopted.

Techniques employed

D.C. polarography, cyclic voltammetry, atomic absorption spectrophotometry are employed in the present investigation. The details regarding principles and applications of these techniques are presented in Chapter I.

D.C. Polarograph

Instrumentation

The current-voltage curves are recorded using d.c. polarographic analyser model CL-358 coupled with optional printer manufactured by Elico Private Limited (Hyderabad, India).

The basic components of the apparatus used in the study of d.c. polarography are:

1. Electrolytic cell
2. DC polarographic analyser
3. Optional printer

The electrolytic cell used is mainly an assemblage of (i) the dropping mercury electrode as working electrode whose potentials are controlled at desired values, (ii) saturated calomel electrode connected to anode terminal acts as reference electrode with reference to which potential of the working
electrode is measured. A third auxiliary or counter electrode completes the electrolytic circuit. Mercury drop assembly consists of mercury reservoir, a glass bulb filled with double distilled mercury and the glass capillary of 0.05 mm bore diameter from which mercury flows, are connected through tygon tube in d.c. polarograph.

The cell is a specially made glass vessel with a provision to insert the working electrode (DME), reference electrode (SCE), auxiliary electrode, nitrogen gas inlet and outlet. A 50 ml of the electrolytic solutions is sufficient for the electrodes to dip in the solution.

Experimental Conditions

All the experiments are performed at 25 ± 0.1°C using freshly prepared solutions. Triple distilled mercury and double distilled water are used. The dissolved oxygen in the solutions is removed by passing pure nitrogen gas for 10-15 minutes.

Experimental Procedure

A measured volume of the supporting electrolyte is added to the electroactive species under the study and the pH is adjusted to the desired value. The solution is made upto 100 ml in a standard flask with double distilled water and transferred to a polarographic cell. The solution is degassified by purging oxygen free nitrogen gas for about fifteen minutes. The working, reference, auxiliary electrodes are inserted through the corresponding inlets without tilting and close enough for lowering any appreciable cell resistance after deaeration.
While recording the polarograms the passage of nitrogen gas is continued over the surface of the solution to prevent the atmospheric oxidation. Polarogram of the supporting electrolyte without adding electroactive species i.e., blank run is taken in order to record the residual currents. The maximum suppressors, gelatin and triton X-100 are used whenever necessary.

In case of Cobalt(II) an air free solution of the ligand is added to the previously deaerated buffer solution and with continued passage of nitrogen, air free solution of CoCl₂ is added. This order of mixing prevents precipitation of Co(II) with ligand in aqueous medium.

Methodology

The important factors involved to characterise the nature of the catalytic waves and analytical parameters studied to develop quantitative experimental conditions are:

Effect of pH

The metal ion, ligand and supporting electrolyte concentrations are fixed and the pH is changed. Variations in the peak potentials and the wave heights are measured to know the nature of the wave and involvement of any buffer constituent in the catalytic process. The optimum pH conditions for a well defined and well developed wave is also obtained by studying this effect.
Effect of supporting electrolyte Concentration

At a fixed pH, metal ion and ligand concentration, the effect of supporting electrolyte concentration on the nature of the polarogram is studied. This is used for identifying the catalytic character of the polarographic waves.

Effect of ligand concentration

At different ligand concentrations by fixing pH, supporting electrolyte and metal concentration at optimum values, polarograms are recorded to get the maximum quantity of ligand required for complete complexation to get maximum current.

The dependence of wave height as a function of ligand concentration is also useful for understanding the characteristic nature of the catalytic current and to study the adsorption phenomenon using Langmuir adsorption isotherm plot.

Effect of metal ion concentration

At a fixed pH, supporting electrolyte and ligand concentration the metal concentration is varied to know the sensitivity of the method.

Effect of mercury pressure

The height of the mercury reservoir is varied using a metal ion concentration within the proportionality limits of catalytic current ($i_c$) and quantitative experimental conditions and polarograms are recorded to interpret the nature of the electrode process.
Effect of maximum suppressor

Maximum suppressors such as Triton X-100 and gelatin have been used by varying their concentration and keeping all other factors constant to identify the catalytic nature of the waves.

Effect of temperature

Temperature effects from 15°C to 45°C on the catalytic waves are studied taking the solutions in a specially made cell. The temperature of the sample solution is maintained within a range of ±0.1°C by circulation of hot water through the outer jacket of the cell at a desired value and maintained constant while recording the polarogram.

Effect of ionic strength or indifferent cations

By varying the concentrations of chlorides of K⁺, Na⁺, Li⁺ and Ca²⁺ and keeping all other factors constant polarograms are recorded to test the kinetic character of the currents.

Effect of foreign ions

The effect of various anions and commonly associated metal ions in 100 fold excess of the metal ion under study are recorded to secure better specificity for the developed method and to remove any interfering ions using suitable masking agents.
Electrocapillary curves

The potential vs SCE is plotted against the droptime of the mercury, ‘t’ for simple ligand and metal complex separately in buffer solution of respective pH to draw electrocapillary curves. This is useful to study the surface character of the system.

Cyclic Voltammetry

Voltammograms are recorded using voltammograph model CV-27 coupled with R-XY recorder manufactured by BAS, USA.

The CV-27 cyclic voltammograph comprises of mainly three parts (i) Potentiostat (ii) Wave form generator connected to (iii) R-XY recorder.

The desired potential range is selected on the potentiostat and is displayed by digital multimeter. The potentiostat is connected to the recorder unit through the wave form generator. The desired functions such as scan rate are selected by using the display knob. Provision is also made for adjusting the scan rate.

The current sensitivity is adjusted using the R-XY recorder. The recorder also has arrangements through the push buttons to start or to hold the sweep at a desired potential or to restart the recording.

The electrochemical cell is a specially made glass container closed with a lid which is provided with holes to insert HMDE, SCE, auxillary electrode, nitrogen gas inlet and outlet. The hanging mercury drop electrode is the working electrode in recording voltammograms, the potential of which is referred against saturated calomel electrode.
The cell is mounted on the magnetic stirrer fixing all the electrodes properly in the solution and nitrogen is passed for fifteen minutes while stirring. A fresh mercury drop is used discarding the old one for each scanning. Drop size is maintained constant by rotating the mercury head to a fixed marked line. The area of the working electrode is found to be 0.0232 cm². This is repeated several times and obtained constant value.

Experimental Procedure

The experimental procedure for recording cyclic voltammograms is the same as that of d.c. polarography. Experiments are performed with different concentration of metal ion and complexing agent at a fixed pH, supporting electrolyte concentration and at different sweep rates ranging from 0.04 to 0.32 vs¹.

Atomic Absorption Spectrometry

Atomic absorption spectrophotometer, perkin-Elmer Model 2380 with a sensitivity of 0.31 mg/L and slit width of 0.2 nm is used in the present work for the analysis of samples of Co, Ni, Mn and Cu. The metal solution in aqueous medium is aspirated directly into the flame (air-acetylene) and the absorbance values are noted.
AAS Characteristics for metal ions used in the present investigation

<table>
<thead>
<tr>
<th>Lamp</th>
<th>Wave-length (nm)</th>
<th>Slit (nm)</th>
<th>Sensitivity (mg/L)</th>
<th>Sensitivity Check (mg/L)</th>
<th>Flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>240.7</td>
<td>0.2</td>
<td>0.12</td>
<td>7.00</td>
<td>Acetylene-Air</td>
</tr>
<tr>
<td>Ni</td>
<td>232.0</td>
<td>0.2</td>
<td>0.14</td>
<td>7.00</td>
<td>Acetylene-Air</td>
</tr>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>0.7</td>
<td>0.077</td>
<td>4.00</td>
<td>Acetylene-Air</td>
</tr>
<tr>
<td>Mn</td>
<td>238.2</td>
<td>0.2</td>
<td>0.13</td>
<td>7.00</td>
<td>Acetylene-Air</td>
</tr>
</tbody>
</table>

pH meter

The pH measurements are made by using digital pH meter model LI-120 with combined glass electrode supplied by the Elico private limited, Hyderabad, India. The sensitivity of the instrument is ±0.001 pH units.

Preparation of reagents and solutions

Xanthates

All starting materials required for the preparation of the reagents are of analytical reagent grade or of a sufficient purity for the purpose intended. The xanthates used in the present investigation were prepared using the well established methods\(^1,2,3\).

a) **Potassium hexyl xanthate (Khxan)**

60 ml of hexyl alcohol and 9 g of potassium hydroxide solution are taken in a conical flask and the reaction temperature is maintained below 20°C. 14 ml of carbon disulphide is added gradually to the mixture and stirred continuously for 20 minutes. After complete addition of
carbodisulfide a thick reddish brown mass is formed which is separated by gentle suction. The solid mass is dissolved in a few ml of pure acetone. The impure polysulfides form two separate red and yellow layers. By the addition of petroleum ether to the yellow layer solution a fine faint yellow solid of potassium hexyl xanthate is obtained. It is filtered, washed with petroleum ether and dried in a vacuum desiccator. The process of recrystallization is repeated for high purity.

b) Potassium isobutyl xanthate (Kbxan)

25 ml of isobutyl alcohol and 14g of potassium hydroxide are taken in a conical flask and the reaction temperature is maintained below 20°C. 15 ml of carbodisulfide (E.Merck) is added gradually and the mixture is simultaneously stirred by a mechanical stirrer for about 20 minutes. The remaining procedure is same as in potassium hexyl xanthate.

c) Potassium cyclopentyl xanthate (Kcpxan)

25 ml of cyclopentyl alcohol and 14 g of potassium hydroxide are taken in a conical flask and the reaction temperature is maintained below 20°C. 15 ml of carbon disulfide added gradually and the mixture is simultaneously stirred by a mechanical stirrer for about 20 minutes. The remaining procedure is same as in potassium hexyl xanthate.
Solutions

Metal ions

All the metal salts used are of reagent grade. The stock solutions of the metal ions (0.01 M) in double distilled water are prepared from accurately weighed samples and diluted to required strength.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Metal ion</th>
<th>Salt taken</th>
<th>Formula of the salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ni(II)</td>
<td>Nickel chloride (E.Merck)</td>
<td>NiCl₂₆H₂O</td>
</tr>
<tr>
<td>2.</td>
<td>Co(II)</td>
<td>Cobalt sulphate (GR)</td>
<td>CoSO₄₇H₂O</td>
</tr>
<tr>
<td>3.</td>
<td>Cu(II)</td>
<td>Copper sulphate (E.Merck)</td>
<td>CuSO₄₅H₂O</td>
</tr>
<tr>
<td>4.</td>
<td>Mn(II)</td>
<td>Manganese sulphate (E.Merck)</td>
<td>MnSO₄₇H₂O</td>
</tr>
</tbody>
</table>

Supporting electrolyte

2 M ammonium chloride solution was prepared using double distilled water.

1% hydrochloric acid and 5% ammonium hydroxide solutions were prepared in double distilled water. Suitable portion of these solutions were mixed to get the desired pH. The pH meter was used to obtain the required pH of the solution, by adding either acid or base solutions.

Maximum suppressors, gelatin of SISCO make and triton X-100 supplied by Merck are used.
Preparation of various samples

Water Samples

One litre of the drinking water sample collected from Kalyani Dam, Tirupati town is pre-concentrated by evaporation and spiked with metal ion for analysis.

Industrial effluents

One litre of the industrial effluents collected are filtered and are pre-concentrated by evaporation and filtered upon cooling. Aliquots of this solution is taken for metal analysis.

Agricultural samples (leafy vegetables and food grains)

Freshly collected plant samples were cleaned and dried in open air, preventing them from mineral contamination. Each dried sample was pulverised in a mortar for the purpose of analysis, to a convenient size. The powdered material was then subjected to dry ashing to oxidise the organic matter.

Dry Ashings

A known quantity of the powdered sample was taken into a pre-cleaned crucible and heated gently on a hot-plate, to volatalize as much moisture and organic matter as possible. From time to time, the sample was stirred with a pre-cleaned silica rod, to accelerate drying. When the sample was fairly dried (30-60 minutes) the crucible was transferred to a
temperature-controlled muffle furnace, which was maintained at 450°C and retained in the furnace for about 8 hours, to complete the decomposition process. The crucible was then removed from the furnace, allowed to cool and 10 ml of 2.0 M hydrochloric acid was added to the ash. It was warmed gently on a hot-plate to dissolve the sample ash and the elements from the insoluble residue were extracted, filtered through an acid washed filter paper and finally the residue was washed with hot water. The filtrate and the washings were collected in a 100 ml volumetric flask, finally made upto the mark with de-ionised distilled water and mixed thoroughly to ensure homogeneity.

Alloy Sampling

An accurately weighed quantity of an alloy was taken in a beaker to which 10-15 ml of concentrated hydrochloric acid and a few drops of concentrated nitric acid were added. The beaker was gently warmed until the alloy sample was completely dissolved and was then heated till the solution reduced to a smaller volume. The solution was allowed to cool and then filtered. The filtrate was collected into a volumetric flask and the solution made upto the mark in a standard flask with double distilled water.

Soil samples

About 2 gm of soil, collected from agricultural farms is dried, and digested by wet digestion method and brought into solution.
REFERENCES

5. Gorsuch, T.T., Analyst, 1959, 84, 135.