CHAPTER II

EXPERIMENTAL
CHAPTER II
EXPERIMENTAL

2. INTRODUCTION

The principles and the experimental procedures for the analytical methods and the physico-chemical techniques employed in the present investigation are described in this chapter. These include the pH metric titration[1] to determine the stability constants of various metal nitrilotriacetate and hydrazido carboxylate[2] complexes, preparation of various electroless bath solutions for the deposition processes, pretreatment of plastic and copper metal plates for electroless plating, monitoring and control of different bath parameters during deposition, characterization of plated materials using different techniques and study of structural properties.

2.1 CHEMICALS USED

Commercially available chemicals, analar or equivalent grades, were used in the investigation. All the solutions were prepared from these reagents or compounds prepared in situ. Chemicals used include, perchloric acid, sodium perchlorate monohydrate, nickel sulphate, ferrous sulphate, cobaltous chloride, zinc chloride, nickel chloride, manganese(II) chloride, magnesium chloride, nitrilotriacetic acid, ascorbic acid, sodium
hypophosphite hydrated, palladium chloride, hydrazine hydrate, Eriochrome black −T indicator, Xylenol orange indicator, Murexide indicator, stannous chloride.

2.1.1 PREPARATION OF HYDRAZIDO CARBOXYLIC ACID

Carbon dioxide gas was slowly and continuously bubbled through 50 mL of hydrazine hydrate taken in a narrow mouthed small reagent bottle (Fig. 2.1) for 48 hours. A syrupy liquid initially formed changes to thick white. It was then diluted with 25 mL of 50% ethanol solution and CO₂ gas again bubbled for another 90 minutes for the remaining hydrazine to react. White crystalline hydrazido carboxylic acid[3] so formed was filtered through Whatman filter paper No 1 in buchner funnel. The residue was first washed with 50% ethanol and subsequently with pure ethanol. Filtrate, which was tested[4] for hydrazine, showed negligible hydrazine content.

\[ \text{N}_2\text{H}_4 + \text{CO}_2 \rightarrow \text{N}_2 \text{H}_3\text{COOH} \]

The white residue in the buchner funnel was transferred into a petridish and kept for 48 hours in a vacuum dessicator over P₂O₅ and used as and when required. This compound was characterized chemically and also by IR spectroscopy.
Fig 2.1 Experimental set up for the preparation of hydrazidocarboxylic acid
2.1.2 PREPARATION OF SOLUTIONS

Of the several solutions prepared in the course of the study the following are of particular importance:

1. \(2 \times 10^{-2}\) M Perchloric acid,
2. 2M Sodium perchlorate,
3. 0.003 M Nitrilotriacetic acid (NTA),
4. 0.003 M Hydrazido carboxylic acid (\(N_2H_3COOH\)),
5. \(5 \times 10^{-4}\) M Metal salt solutions.
2.2 CHEMICAL ANALYSIS

Estimation of metal ions in solution was carried out by complexometric titrations using standard EDTA (Na-salt) solution. These solutions of metal salts were used in pH-metric titrations in the stability studies. The thin film deposit, obtained in the electroless plating experiments, was leached out with 0.2 M HNO₃ and further was subjected to volumetric analysis for the nickel metal.

2.2.1 ESTIMATION OF Mg, Zn and Mn

Metal(II) ions like magnesium, manganese and zinc were volumetrically estimated against standard EDTA (0.001) solution using Eriochrome Black-T indicator. The solution was maintained at pH=10 using appropriate buffer solution containing ammonium chloride and ammonia. The end point was the color change from red to blue.

2.2.2 ESTIMATION OF NICKEL

In a typical experiment, a pinch of freshly prepared Murexide indicator was added to nickel solution, followed by the addition half test tube of 1M NH₄Cl and liquor NH₃ till solution turns yellow, and then 10 mL of liquor ammonia. The mixture was titrated against standard EDTA. At the end point the color of the solution changes from yellow to bluish violet.
2.2.3 ESTIMATION OF COBALT

A known volume of the solution containing Co$^{+2}$ was pipetted out in a titration flask. The pH of the solution was increased by adding hexamethyl tetramine, which acts as a buffer of pH=6. A few drops of Xylenol orange were added as an indicator. The resultant solution was titrated with EDTA solution[4] until the colour changed from red to yellow.

2.3 pH METRY TITRATIONS: APPARATUS

In this method a number of pH-metry titrations (Fig. 2.2) were carried out using a microburette. The titrations were carried out at 303K. However, in the case of hydrazido carboxylic acid, the titrations were carried out between 273-277K to prevent the decomposition of hydrazido carboxylic acid since this acid is unstable above 277K. Borosil microburette of 1 mL capacity with 0.01 mL accuracy was used for these titrations. A pH meter (ELICO Ioniser Li-126) with 0.0001 unit sensitivity was used for measurements. The pH meter was calibrated before every titration using standard buffer solution of pH 4.01. The temperature was recorded using temperature sensor supplied with the instrument.
Fig. 2.2 Instrumental setup for pH-metry titration
2.3.1 pH METRY TITRATIONS

In the Calvin –Bjerrum[1] pH titration method usually a set of three titration are carried out. Titration of the solution containing mineral acid, the ligand and the metal salt against the standard alkali.

- Titration of the same quantity of mineral acid and ligand solution without metal salt against the same standard alkali.
- Titration of the mineral acid alone against the same standard alkali.

The details of titrations carried out are as follows:

2.3.1.1 Metal titration:

In a typical experiment, 50mL solution containing, 5 mL of \((2\times10^{-2}\text{M})\) perchloric acid, 5mL of \((2\text{M})\) sodium perchlorate, 5 mL of \((5\times10^{-4}\text{M})\), metal ion solution, 30 mL of double distilled water and 5 mL of the \((0.003 \text{ M})\) complexing agent (reagent or ligand solution) were pipetted out in the same order into 100mL-beaker. The solution was titrated against a standard sodium hydroxide \((0.4\text{M})\) solution at constant temperature till the pH of the solution was around 12.

With hydrazido carboxylic acid as ligand / complexing agent, the temperature was maintained between 273-277K to prevent its decomposition in acid medium.
The ternary system, containing two ligands viz. NTA and hydrazido carboxylic acid, along with metal ions, the temperature of the solution was maintained between 273-277K and titrated against 0.4 M NaOH.

Thus the titrations carried out were as follows:

(a) 5 mL of perchloric acid+5mL NaClO₄ +5mL NTA +5mL solution containing metal ions + 30 mL double distilled water at 303 K. v / s 0.4 M NaOH.

(b) 5mL HClO₄ +5mL NaClO₄+5mL L₂ +5mL metal ions solution +30mL water at 273 K to 277 K v / s 0.4 M NaOH

(c) 5mL HClO₄+5mL NaClO₄+5mL NTA(L₁)+5mL hydrazido carboxylic acid (L₂) +5mL solution containing metal ions +25 mL double distilled water at 273 K to 277 K v/s 0.4 M NaOH

The metal ion solutions of NiCl₂, CoCl₂, ZnCl₂,MnCl₂ , MgCl₂ ,of concentration 5x10⁻⁴M each, were used in pH-metry titration.

2.3.1.2 Reagent titration (Complexing agent/ ligand)

The composition of the titrant was almost the same except that additional 5 mL double distilled water was taken instead of 5mL metal salt solution. The mixture used for titration was

(a) 5mL HClO₄+5mL NaClO₄+5mL NTA(L₁)+ 35 mL double distilled water at 303K v/s 0.4 M NaOH.
(b) 5mL HClO₄ + 5mL NaClO₄ + 5mL L₂* + 35 mL double distilled water at 273-277K vs 0.4M NaOH.

Where, L₂* represent hydrazido carboxylic acid (N₂H₃COOH).

2.3.1.3 Acid titration: Here, the composition of the titrant was almost the same, as in 2.3.1.2, except an additional amount of 5 mL of double distilled water was used instead of 5mL of the reagent (complexing reagent) solution.

The mixture used for a titration was:

(a) 5mL HClO₄ + 5mL NaClO₄ + 40 mL double distilled water at 303K vs. 0.4M NaOH.

After the completion of titration, the combined electrode was washed thoroughly with distilled water and kept in 0.1 M HCl solution for 15 minutes and again washed with double distilled water and made to stand in distilled water for at least 2 hours before further use.

The experimental data relating to all these measurements with different reagents, metal ions and at different temperatures is given in the next chapter.

2.4 ELECTROLESS PLATING

Electroless plating [5,6] involves the deposition of metal or alloy from the bath solution by using suitable reducing agent. The main features of the electroless plating process are (i) pretreatment of the base material (substrate), (ii) preparation of suitable bath solution, and (iii) electroless deposition.
2.4.1 PREPARATION OF PLATES

Two types of plates, of 5 x 1.5 cm$^2$ each, of pure copper metal and plastic were used for the electroless deposition experiments. However, for analysis by XRD and atomic absorption spectroscopy, plates of 2.5 X 6.0 cm$^2$ were used.

2.4.1.1 PREPARATION OF COPPER PLATES

Electroless plating experiments on copper substrate were carried out with novel bath. Thin copper plates, of desired shape and dimensions (1.5x 5 cm), were cut from copper metal foil (99.5% purity). The plates were etched or cleaned by rubbing with cotton dipped in 2N HNO$_3$. The plates were then washed with de-ionized water, dried at 313K and weighed.

These plates were then sensitized by dipping in 3% SnCl$_2$ solution (3 g SnCl$_2$ +40 mL conc. HCl, diluted to 100 mL) for 10 seconds and then activated by dipping in PdCl$_2$ solution (0.00625 g PdCl$_2$ dissolved in the dilute HCl by adding the acid dropwise till the solution is clear) for 5 seconds. The plates were then rinsed in deionized water and thereafter dipped in the bath solution for electroless plating.
Table 2.1 Pretreatment of copper plates used in the present investigation

Cutting and Sizing

Etching with dil. HNO₃

Rinsing with deionized water

Drying in oven at 313 K and then weighing

Sensitization by SnCl₂ solution

Rinsing with deionized water

Activation by PdCl₂

Rinsing with deionized water

Electroless Plating

Rinsing with deionized water
2.4.1.2 PRETREATMENT OF PLASTIC PLATES.

Electroless plating experiments on thin and thick plastic substrate were also carried out with a novel bath. Thin and thick plastic plates of desired dimensions (1.5 cm X 5 cm or 2 cm X 6 cm X 0.5 cm) were cut from OHP transparency or thick acrylic plastic. These plates were then washed with dilute NaOH to remove grease and then rinsed with de-ionized water followed by rinsing with dil. HCl and water again. Lastly the plates were cleaned with acetone. The plates were dried and then roughened and again rinsed with deionised water, dried in an oven at 313 K and weighed.

These plates were then sensitized by dipping in 3% SnCl₂ solution (3 g SnCl₂ + 40 mL conc. HCl, diluted to 100 mL) for 1 minutes, rinsed with water and then activated by dipping in PdCl₂ solution (0.00625 g PdCl₂ dissolved in dil. HCl by adding it dropwise) for 30 seconds. The plates were then quickly rinsed in deionised water and then dipped in the bath solution for electroless plating.
Table 2.2: Pretreatment of plastic plates used in the present investigation

Cutting and Sizing

Swabbing with acetone

Rinsing with deionised water

Degreasing with dil. NaOH

Rinsing with deionised water

Scratching the surface with sand paper

Rinsing with deionised water

Drying at 313 K and then weighing

Sensitization by SnCl₂ solution

Rinsing with deionised water

Activation by PdCl₂

Rinsing with deionised water

Electroless plating

Rinsing with deionised water
2.5 MONITORING THE QUALITY OF DEPOSITION

For technical applications it is necessary that the chemically (electroless) deposited metal or alloy should have a good adhesion on the substrate material. A metal-metal bonding between the deposit and the substrate [7] metal is envisaged in electroless plating.

In case of non-metallic substrate (plastic, ceramic) mechanical bonding forces do play an important role. The following simple tests are commonly used for qualitative determination of adhesion in electroless plating.

A strong adhesive tape is fixed on the plated surface and then removed. A good adhesion is indicated [8] by non-removal of plated matter.

In bending test, the coated plate is bent through 180°. A good adhesion will not [9] exhibit lifting of the coating on bending.

Quenching test is a simple, common and reliable method [5] of qualitative determination of adhesion of coated matter in electroless plating. Here, the coated plate is heated to about 473-500K, and then, quenched by dipping it in water at room temperature. A weak adhesion is indicated, by lifting of the coating. It is very common to use peel-off method after quenching for better assessment. All the three tests mentioned above were used in this study.
2.6 MONITORING RATE AND THICKNESS OF THE COATING.

The rate of deposition of metal on substrate material was evaluated periodically by using weight gain method. In this method the weight of dry plate was found out (i) before plating process and (ii) after electroless plating process i.e. at the end of the experiment. The difference in weight or gain in weight or plating, the area of the plated surface and approximate density of metal (s) deposited was then used to calculate [6] the rate of deposition by using the following equation.

\[
\text{Rate of deposition} = \frac{(W \times 10^4)}{A \times d \times t} \, \mu\text{m} / \text{hr}
\]

Where,

\begin{align*}
W &= \text{weight of the alloy deposited in g.} \\
A &= \text{area of the coated surface in cm}^2 \\
t &= \text{plating time in hours} \\
d &= \text{average density of alloy (---- g / cm}^3) \\
\end{align*}

[density of Ni =8.9 g / c.c., density of Fe=7.87 g / c.c.

Average density was calculated on the basis of percentage composition of the metals and substituted in the above formula.

Thickness of plating = Rate of deposition \times time
2.7 TESTING THE POROSITY OF DEPOSIT

The porosity can be tested by (i) the feroxyl test and (ii) the hot water bath. In the feroxyl test, a solution of feroxyl is used [25g / L of $K_3Fe(CN)_6$ and 15 g / L of NaCl] in which the plate with deposit is dipped. By the short circuit element of corrosion which is present in the area of the pores, the ion dissolves inside the pores and lead inside the pores and leads to turn bull–blue coloration.

In the hot water test the plates with the deposit are kept in water with pH of about 7 at a temperature of 363 K–368 K, the pores can be identified as red spots.

2.8 INSTRUMENTAL TECHNIQUES

Instrumental techniques play an important role in the characterization or revealing the structural features of the compounds, metals, alloys, etc.

In the present investigation the instrumental techniques used were infrared spectroscopy, X-ray diffraction, atomic absorption spectroscopy and scanning electron microscopy (SEM)

2.8.1 X- RAY POWDER DIFFRACTION

Philips X-ray diffractometer model 1840 with Cu Kα radiation with nickel filter was used to obtain the X-ray diffraction patterns [10] of the plates which were subjected to electroless plating.
2.8.2 ATOMIC ABSORPTION SPECTROSCOPY

Atomic absorption spectroscopy (AAS) was employed for the estimation [11] of iron in the film obtained in plating since the chemical method was found to be unsuitable. Estimation showed that the quantity of iron in the alloy was too less. In the atomic absorption spectroscopy (AAS) the absorption is measured by the difference in the transmitted signal in the presence and absence of test element. The main component of the AAS is the lamp. It may be Hollow cathode lamp or the electrode discharge tube. The cathode construction differs for the various metals. These lamps with their narrow band emission provide virtually complete specificity for each element. The instrument GBC 932AA (Fig 2.3) atomic absorption spectroscope was used during the course of this investigation.

In the present study, thin film deposit on plastic plate was leached out in 100mL of 0.2N HNO₃ prepared by using millicure water. The solution was quantitatively analysed for Fe content by using 0.2 N HNO₃ as blank with AAS. The standard solution of Fe was obtained from MERK for AAS. It provides the following standard data to help in finding out the amount of Fe in the unknown solution. This result was further confirmed by carrying out the gravimetric estimation of Fe. For preparation of 100 μg /mL Fe solution, 1.0 g of Fe was dissolved in 20mL of 5 N HCl, and 5 mL of 6N HNO₃ and further diluted to 1 liter to obtain 1000μg /mL Fe.
Fig. 2.3 Atomic Absorption Spectroscope GBC 932 AA
### Table 2.3 Standard calibration data for estimation of Fe by AAS

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Slit width (nm)</th>
<th>Working range (μg/ml)</th>
<th>μg /mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>248.3</td>
<td>0.2</td>
<td>2-9</td>
<td>0.05</td>
</tr>
<tr>
<td>372</td>
<td>0.2</td>
<td>20-80</td>
<td>0.45</td>
</tr>
<tr>
<td>386</td>
<td>0.2</td>
<td>36-145</td>
<td>0.80</td>
</tr>
<tr>
<td>392</td>
<td>0.2</td>
<td>680-2700</td>
<td>15</td>
</tr>
</tbody>
</table>

#### 2.8.3 SURFACE MORPHOLOGY.

Surface morphology of plated material was investigated by using high resolution photography with Leica–orthoplan Pole Microscope at the magnification of 250 times. This microscope was used to obtain the micrograph of the covered surface to understand the surface morphology of the coating as well as to assess changes occurring due to atmospheric exposure. Scanning electron microscope (SEM) was also used for this purpose to scan some coated surfaces. The SEM uses the secondary electrons produced by the scanning beam to give life like, almost three dimensional image of the surface of the specimen being scanned. The magnification range of the SEM is more than 10,000 times.

Enlarged photographs of the copper and plastic plates were also obtained after exposing these plates to atmosphere for a period of one year.
2.8.4 INFRARED SPECTROSCOPY

Every molecule has a number of fundamental vibration frequencies and each fundamental frequency may be associated with absorption of radiation of its own frequency. This absorption of frequencies obtained in the form of spectrum in the infrared spectroscopy [12-14]. Infrared spectrophotometer was used during the course of this investigation.

The spectra of the solid samples were obtained in the range of 4000 to 400 cm\(^{-1}\) using Fourier Transform Infrared Spectrophotometers (F.T.I.R.). The F.T.I.R. used in the present investigation is shown in Fig.2.4.

The spectrum of the solid sample of hydrazidocarboxylic acid was recorded by dispersing it in Nujol or fluorolobe (Mull technique), and pellet technique using KBr, wherever possible. The observed infrared bands were calibrated with the standard frequencies of polystyrene [15].
Fig. 2.4 Fourier Transform Infrared Spectrophotometer SHIMADZU
SUMMARY

In this chapter, the various chemicals used, the preparation of solution required for the experimental work, preparation of hydrazido carboxylic acid is described. Volumetric methods used for the estimation of Ni, Co, Zn, Mn, Mg during the present investigation are described. The experimental work involves two parts (i) pHmetry titrations to determine the stability constants of complexes and (ii) electroless plating from bath solution containing Fe^{2+} and Ni^{2+} ions.

In the electroless plating, the pretreatment of plates, preparation of bath solution and monitoring the quality of deposit is described citing the tests involved. The instrumental techniques used for characterization and quantitative estimation are described under IR spectroscopy, XRD and AAS. Lastly the method used to study the surface morphology is described in brief.
REFERENCES.


7. E. Raub and K. Muller, Handbuch der Galvanotechnik Bdl Teil 1, Hanser Verlag, Munchen [1963],110.


GBC Scientific Equipment PTY Ltd., Victoria, Australia. Analytical
data. 9-8.


15. C. N. R. Rao, “Chemical Applications of Infrared Spectroscopy”,