

---

*CHAPTER - VI*

*EXPERIMENTAL*

---

## 6.1 INTRODUCTION

For the determination of stability constants, experimental techniques have been developed by a number of authors. The classical Calvin-Bjerrum technique as modified by Irving and Rossotti<sup>1</sup> was used for determination of stability constants. In the present work, the potentiometric method for determination of stability constants is used. The ligands used for the study are.

- i) 2-Acetyl thiophene guanylhydrazone (ATG)
- ii) 5-Bromo-2-acetyl thiophene guanylhydrazone (Br-ATG)

The metal ions  $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Cd}^{++}$  and  $\text{Mn}^{++}$  were used to study the equilibria in complexation reactions.

## 6.2 MATERIALS AND THEIR PURIFICATION

### Water:

Conductivity water obtained from all glass distillation unit was obtained. The water used for distillation was obtained from column of Amberlite mono-bed MB 8 mixed ion exchange resin column. The pure water obtained thus was stored in a polythene container.

### Ethyl alcohol:

Ethyl alcohol was dried over freshly calcined quicklime for overnight and distilled twice. The pure ethanol was stored out of contact with air.

### 6.3 PREPARATION OF SOLUTIONS

#### Sodium hydroxide:

Standard, carbonate free sodium hydroxide solution was prepared by the method of Vogel<sup>2</sup>. A.R. sodium hydroxide pellets (BDH) 50.0 gms were dissolved in 50.0 ml pure water in a corning flask. The solution was transferred to a 75 ml test tube of corning glass provided with well fitting stopper covered with tin foil. The solution was allowed to stand in a vertical position till the supernatant liquid is clear. To prepare approximately 1.0 N sodium hydroxide solution, 32.5 ml of clear supernatant and concentrated solution was withdrawn by pipette into 500.0 ml volumetric flask. Then it was diluted to mark with pure previously boiled carbon dioxide free water. It was then preserved out of contact with carbon dioxide by connecting a soda-lime guard tube. The standard succinic acid was used to determine the exact strength of the diluted solution of sodium hydroxide.

#### Perchloric acid:

The 70% A.R. perchloric acid (E-Merck) was diluted with pure water to obtain 2.0 M stock solution. This solution was further diluted to 0.2 M perchloric acid with pure water.

**Sodium perchlorate:**

The 4.0 M stock solution of G.R. sodium perchlorate (E.Merck) was prepared by dissolving the requisite quantity of compound in distilled water.

**Solutions of ligands:**

Solutions of the ligands of guanylhydrazones, 0.01 M were prepared by dissolving the appropriate quantity of the compounds in 50% ethanol.

**Metal-perchlorate solutions:**

Metal-perchlorate solutions were prepared by treating 20.0 ml of 2.0 M perchloric acid with excess of oxides or carbonates. The resulting neutral solutions were diluted to 100 ml to get approximately 0.2 M metal perchlorate solutions. The metal contents were determined by standard procedure<sup>2</sup>. Then requisite quantity of 0.2 M metal-perchlorate and 10.0 ml of 2.0 M perchloric acid were taken in 100.0 ml volumetric flask. This was diluted to the mark by distilled water, so that the final strength of the acid became 0.2 M and that of metal in perchlorate medium, 0.02 M

#### 6.4 SYNTHESIS

##### Synthesis of 2-acetyl thiophene guanylhydrazone (AIG):

As described in chapter-I.

##### Characterisation of AIG:

As described in chapter-I.

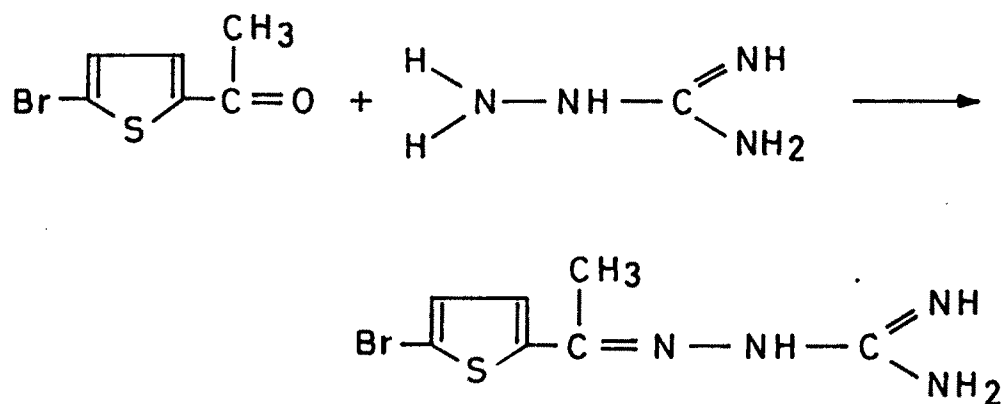
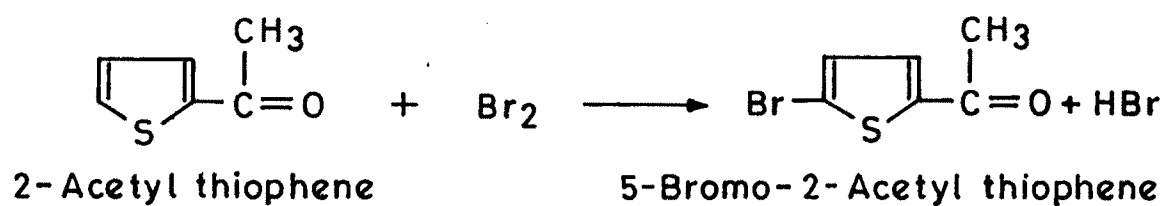
##### Synthesis of 5-bromo-2-acetyl thiophene guanylhydrazone

##### (Br-AIG):

In a 2.0 ml 2-acetyl thiophene, 2.0 ml bromine in acetic acid was added. The mixture was kept as such for overnight. Decoloration of bromine indicates the bromination reaction.

The above mixture is dissolved in 10.0 ml ethanol. Aminoguanidine bicarbonate, 2.0 g was dissolved in 60% nitric acid and was added to the solution of bromo derivative of 2-acetyl thiophene. The mixture was kept as such for four hours. The product was filtered, washed and recrystallised from ethyl alcohol to obtain brown, shining crystals of 5-bromo-2-acetyl thiophene guanylhydrazone (~ 2.0 g)  
M.P. = 197°C ± 1°C.

The reaction is



5-Bromo-2-acetyl thiophene guanylylhydrazone  
( Br-ATG )

**Characterisation of Br-ATG:**

The micro elemental analysis of the chromatographically purified reagent confirmed the formula to be  $C_7H_9N_4SBr$ . (Molecular weight = 260.9). The results are given below.

Br-ATG	Carbon	Hydrogen	Nitrogen	Sulphur
Calculated % of elements	32.20	3.45	21.46	12.27
Experimentally found % of elements	31.95	3.51	21.57	12.20

**6.5 APPARATUS**

All glassware apparatus used were of corning borosilicate glass. Graduated micro-burette was used. The burette was calibrated by the method given by Vogel<sup>3</sup>. Micropipettes were similarly calibrated. Other apparatus such as measuring flasks, pipettes etc. were standardised with the standard burette.

**pH - Meter:**

Potentiometric titrations were carried out by using Elico-Digital pH-meter (Model LI-120) and philips glass-calomel electrode assembly. Calomel half-cell acts as a response electrode.

Two standard buffers were used for calibration of pH-meter<sup>4</sup>.

- i) 0.05 M Potassium hydrogen phthalate (pH=4.05) and
- ii) 0.05 M Borax (pH=9.18).

The pH meter readings were taken in 50% ethanol-water V/V. These readings were corrected for solvent effect by applying previously reported correction<sup>4-6</sup>.

#### Bubbling of Nitrogen:

The titrations were carried out in "oxygen-free" atmosphere. Hence nitrogen gas was bubbled through solutions. It offers oxygen-free atmosphere and is also useful for stirring the solution.

#### 6.6 TITRATION PROCEDURE

The method given by Irving and Rossotti<sup>1</sup> was used for determination of stability constants. In present work, a series of titrations were carried out with standard NaOH solution at temperature  $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ . In all these titrations, solvent compositions and final volumes were kept constant. Before any titration was performed, the solution was kept in thermostat for half an hour to attain the bath temperature. Nitrogen gas was then bubbled through it and the titration was carried out with standard NaOH solution, using calibrated microburette which was connected to the



soda lime guard tube. Before each reading of the pH-meter, the solution was stirred with a magnetic bar stirrer and readings were noted by stopping the brisk stirring of the solutions. After the completion of the titration, the electrodes were treated in usual manner and left in phthalate buffer.

**Acid titrations:**

A mixture containing 4.0 ml of 0.2 M  $\text{HClO}_4$ , 4.0 ml of 1.0 M  $\text{NaClO}_4$ , 20.0 ml pure ethanol and 12.0 ml distilled water was taken in a clean, dry beaker. The resulting solution was titrated with standard sodium hydroxide.

**Reagent titrations:**

A mixture of 4.0 ml 0.2 M  $\text{HClO}_4$ , 4.0 ml of 1.0 M  $\text{NaClO}_4$ , 10.0 ml of 0.01M reagent, 15.0 ml of pure ethanol and 7.0 ml of distilled water was taken in a clean, dry beaker and titrated with standard sodium hydroxide.

**Metal titrations:**

For the metal titration, 4.0 ml of 0.2 M  $\text{HClO}_4$ , 4.0 ml of 1.0 M  $\text{NaClO}_4$ , 10.0 ml of 0.01 M reagent, 15.0 ml of pure ethanol, 2.0 ml of 0.01 M metal ion solution and 5.0 ml of distilled water was taken in a clean, dry beaker and titrated with standard sodium hydroxide.

The solution taken in a beaker acts as an electrolyte. The potentiometric titrations were carried out by using pH-meter. The observed pH values were used to draw formation curves.

- 1) The first titration curve is characteristic of the strong acid-strong base titration, which is a sigmoid curve.
- 2) In the second curve, there is a slight drooping in the upper portion of the sigmoid curve. In this titration, ligand molecule gets deprotonated with the addition of a base.

The first and second curves were used to determine  $n_A$  and the proton-ligand stability constants.

- 3) The third curve is more drooping as metal abstracts the proton from the ligand. Drooping in the third titration curve indicates the formation of the complex or chelate.

By using first, second and third curves metal-ligand stability constants were determined.

#### 6.7 SYMBOLS

Symbols used for the different quantities measured in titrations are:

pH : The pH-meter reading

$N'$  : Concentration of NaOH in moles per litre

- $V^*$  : Total volume of the solution taken in the beaker before titration
- $t$  : Temperature in °C at which titrations were carried out (25°C)
- $\mu$  : Ionic strength of the solution expressed in moles per litre.
- $E^*$  : Initial concentration of free  $\text{HClO}_4$  in the titration solution expressed in moles per litre
- $T_L^*$  : Initial concentration of ligand in the titrating solution expressed in moles per litre.

#### 6.8 REFERENCES

1. Irving, H. and Rossotti, H.S.; J.Chem.Soc.; 2904(1954).
2. Vogel, A.I.; "Text Book of Quantitative Inorganic Analysis"; Longman, Green, London (1961).
3. Vogel, A.I.: "A Text Book of Practical Organic Chemistry", Longmans, Green, London, p.721 (1958).
4. Vogel, A.I.; "A Text Book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis;" Longman, Green, London; p.1161 (1961).
5. Gutbezahl, B.J.; Amer. Chem. Soc., 75, 565 (1953).
6. Bates, R.G. and Schwarzenbach, G.; Helv. Chim. Acta.; 38, 699 (1955).