

## CHAPTER-2

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CHAPTER - I I

EXPERIMENTAL

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## CHAPTER - II

### EXPERIMENTAL

The experimental techniques of determination of stability constants have been developed by a number of authors. In the present work the author used potentiometric method for determination of stability constant/s.

The classical Calvin-Bjerrum technique as modified by Irving and Rossotti<sup>1</sup> was used for determination of stability constants. The following ligands were used for the study.

1. 3-Nitro salicylaldehyde
2. 5-Nitro salicylaldehyde
3. Salicylaldehyde thiosemicarbazone
4. 5-Nitro salicylaldehydethiosemicarbazone
5. 4-Methyl salicylaldehyde thiosemicarbazone
6. Resorcyaldehyde thiosemicarbazone
7. 3-Resorcyaldehyde oxime.

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

#### Materials and their Purification

##### Water

The double distilled 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.

### Ethanol

Ethanol was dried over freshly calcined quicklime for overnight. Then it was distilled twice and pure ethanol was stored out of contact with air.

### Preparation of Solutions

#### Solutions of the Ligands

Aldehydes and oximes : Solutions of these ligands, 0.04 M, were prepared by dissolving the required quantity of the compound in ethyl alcohol.

Thiosemicarbazones : 0.004 M solutions of the thiosemicarbazones were prepared by dissolving the requisite quantity of the compounds in ethanol.

#### Perchloric acid

The 70 % perchloric acid (E.Merck.A.R.) was diluted with pure water to obtain 2 M stock solution. This solution was further diluted to 0.2 M perchloric acid with pure water.

#### Sodium Perchlorate

The 4 M stock solution of sodium perchlorate (E.Merck.,G.R.) was prepared by dissolving the requisite quantity of compound in distilled water.

### Metal Perchlorate Solutions

Metal perchlorate solutions were prepared by treating 20 ml of 2 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 ml of 2 M perchloric acid were taken in 100 ml 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 with respect to the  $M^{2+}$  ion.

### Sodium hydroxide

Standard, carbonate free sodium hydroxide solution was prepared by the method of Vogel<sup>2</sup>. 50 g of sodium hydroxide (B.D.H., A.R.) pellets were dissolved in 50 ml of 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. For preparation of approximately 1 N solution of sodium hydroxide, 32.5 ml of clear supernatant and concentrated solution was withdrawn by pipette into 500 ml volumetric flask. Then it was diluted to mark with pure previously boiled carbon-di-oxide free water. The solution was preserved out of contact with carbondioxide 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.

### Apparatus

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

### Instrumentation

#### 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. The titration solution acts as an electrolyte.

#### Calibration of the pH Meter

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

1. 0.05 M potassium hydrogen phthalate which has pH 4.005 at 25°C
2. 0.05 M borax with 9.18 pH at 25°C pH meter was calibrated before each set of readings.

#### Correction of pH meter readings

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>

Values of the constant  $\delta = (\bar{E}_j = \log mH)$  in ethanol-water solvents at 25°C in pH units.

Wt. percent Alcohol	Ethanol-Water Solvent		
	Ref <sup>5</sup>	Ref <sup>6</sup>	Ref <sup>7</sup>
20	- 0.03	0.02	-
30			0.07
35	+ 0.08	0.1	-
50	0.17	0.21	0.23
65	0.19	0.24	-
71.89	-	-	0.29
80	0.11	0.11	-
90	- 0.40	- 0.40	-
100	- 2.36	- 2.91	- 2.77

#### 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 solution. The nitrogen gas was firstly washed by passing it through washing towers containing caustic ~~and~~ soda pellets, followed by alkaline pyrogellol and finally it was passed through reaction solution.

### Titration procedure

The method given by Irving and Rossotti<sup>1</sup> was used for determination of stability constant/s. In present work series of titrations were carried out with standard NaOH solution at three different temperatures 25°, 35° and 45°C. In all these titrations solvent compositions and final volumes were kept constant. The temperatures were controlled within  $\pm 0.1^\circ\text{C}$ . 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 the 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 ml of 0.2 M  $\text{HClO}_4$ , 0.78 ml of 4 M  $\text{NaClO}_4$ , 20 ml of ethanol and 15.22 ml of distilled water was taken in a clean and dry beaker. The resulting solution was titrated with standard alkali.

### Reagent titrations

A mixture of 4 ml of 0.2 M  $\text{HClO}_4$ , 0.78 ml of 4 M  $\text{NaClO}_4$ , 10 ml of ethanol (in case of thiosemicarbazone 20 ml of 0.004 M reagent without adding 10 ml of ethanol) and 15.22 ml of

distilled water was taken in a clean dry beaker and titrated with standard alkali.

#### Metal titrations

For the metal titration 2 ml 0.2 M  $\text{HClO}_4$ , 2 ml of 0.02 M metal perchlorate solution containing 0.2 M  $\text{HClO}_4$ , 0.77 ml of 4 M  $\text{NaClO}_4$ , 10 ml of 0.4 M reagent, 10 ml of ethanol and 15.23 ml of distilled water (in case of thiosemicarbazone 20 ml of 0.004 M reagent was taken in place of 10 ml of reagent and 10 ml ethanol) were taken in a beaker and titrated with standard alkali.

The solution taken in a beaker acts as an electrolyte. The potentiometric titrations were carried out by using Elico Digital pH Meter Model LI-120 and Philips glass calomel electrode assembly. These observed values were used to draw formation curves. The first titration curve is characteristic of the strong acid-strong base titration; which is a sigmoid curve. In the second curve there is 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  $\bar{n}_A$  and the proton ligand stability constant/s. 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 constant/s were determined.

Symbols used for the different quantities measured  
in titrations :

- pH : The pH meter reading
- N' : Concentration of NaOH in moles per litre.
- V<sup>0</sup> : Total volume of the solution taken in the beaker before titration.
- t : temperature in °C at which titrations were carried out.
- μ : ionic strength of the solution expressed in moles per litre.
- E<sup>0</sup> : Initial concentration of free HClO<sub>4</sub> in the titration solution expressed in moles per litre.
- T<sub>L</sub><sup>0</sup> : Initial concentration of ligand in the titrating solution expressed in moles per litre.

## REFERENCES

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