CHAPTER II

EXPERIMENTAL
Section (i) - Preparation of the compounds investigated and solutions employed in the studies

(a) Preparation of Resacetophenone (2,4-dihydroxy acetophenone)

15 ml of glacial acetic acid are taken in a 250 ml beaker and heated to boiling. 15 g of anhydrous zinc chloride are dissolved in it. 10 g of resorcinol are added to the mixture with constant stirring and the temperature of the contents raised to 142°C. The reaction mixture is kept at this temperature for an hour a drop of the reaction mixture when treated with 1:1 hydrochloric acid forms a crystalline solid indicating the completion of condensation. The entire reaction mixture is then poured into 1:1 hydrochloric acid taken in a beaker. The solid separated is filtered, washed and recrystallised from hot water containing little alcohol. Colourless needles of resacetophenone (m.p. 142°C) are obtained. Yield (9.0 g).

$$\text{Resorcinol} \xrightarrow{\text{Glacial acetic acid, Anhydrous ZnCl}_2} \text{Resacetophenone}$$
(b) **Preparation of Benzoic acid hydrazide**

4.5 ml of methyl benzoate (4 g dissolved in 90 ml of methanol) are mixed with 10 ml of 60% hydrazine hydrate (60 g in 100 ml of methanol) in warm condition and the mixture is refluxed for 20 minutes on steam bath. It is then cooled, diluted largely with double its amount of water and 2-3 drops of acetic acid are added. The white solid separated is filtered, washed with aqueous methanol and dried. Yield 3.0 g (crude). The solid on crystallisation from aqueous methanol gives colourless micro-needles m.p. 148°C.

\[ \text{Methyl benzoate} \rightarrow \text{Hydrazine hydrate} \rightarrow \text{Benzoic acid hydrazide} \]

(c) **Preparation of Salicylic acid hydrazide**

4.5 ml of methyl salicylate (4 g dissolved in 90 ml of methanol) are mixed with 10 ml of 60% hydrazine hydrate (60 g in 100 ml methanol) in warm condition and the mixture is refluxed for 20 minutes on steam bath. It is then cooled, diluted largely with double its amount of water and 2-3 drops of acetic acid are added. The white solid separated is filtered, washed with aqueous methanol
and dried. Yield 3.5 g (crude). The solid on crystallisation from aqueous methanol gives colourless microneedles m.p. 147°C.

Methyl salicylate

Salicylic acid hydrazide

(d) Preparation of Resacetophenone benzoic acid hydrazone (RBH)

Benzoic acid hydrazide (0.57 g) dissolved in ethanol (10 ml) and resacetophenone (0.21 g) are mixed and refluxed for 0.5 hrs on water bath, white crystalline solid obtained on cooling is recrystallised from ethanol (m.p. 242°C), yield 0.75 g.
(e) Resacetophenone salicylic acid hydrazone (RSH)

Salicylic acid hydrazide (0.57 g) dissolved in ethanol (10 ml) and resacetophenone (0.21 g) are mixed and refluxed for 0.5 hrs on water bath, white crystalline solid obtained on cooling is recrystallised from ethanol (m.p. 295°C). Yield 0.75 g.
B Preparation of Experimental solutions

(a) RBH solution

The reagent solution is prepared by dissolving 0.2693 gm of the compound in dimethylsulphoxide in 100 ml standard flask and making up the solution to the mark with dimethylsulphoxide. The solution stored in an amber coloured bottle.

(b) RSH solution

The reagent solution is prepared by dissolving 0.2863 gm of compound in dimethylsulphoxide in 100 ml standard flask and making up the solution to the mark with dimethylsulphoxide. The solution is stored in an amber coloured bottle.

(c) Other solutions

The chemicals employed in the studies are generally of analytical grade. But wherever it is necessary, the solvents and other chemicals are purified by the standard procedures reported in literature. In the case of solid substances, known amounts are weighed into standard flask and dissolved in distilled water or in suitable solvent. The solutions thus obtained are made upto the mark with distilled water or with solvent. In the case of liquids requisite volume of the liquid is placed with the help of a burette into the standard flask, dissolved in distilled
water or in any other solvent and is made up to the mark. The solutions thus prepared are standardised by standard procedures wherever necessary. The purity grade and the quantity of the chemicals used are shown in Table II.i.1.

**TABLE II.i.1**

Purity grade and the quantity of chemicals used

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity grade and make</th>
<th>Sp. Gr. (g/ml) or Mol. wt.</th>
<th>Volume/weight of sample taken in 100 ml Standard flask</th>
<th>Molarity of the stock solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid AR, BDH, India</td>
<td>1.05</td>
<td>6 ml</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Acid hydrochloride AR, BDH, India</td>
<td>1.18</td>
<td>18 ml</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Acid nitric AR, BDH, India</td>
<td></td>
<td>-</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Acid perchloric Pro analysis E.Merck, Darmstadt</td>
<td>1.53</td>
<td>22.4 ml</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Acid sulphuric AR, BDH, India</td>
<td>1.84</td>
<td>5.6 ml</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ammonia solution AR, BDH, India</td>
<td>0.90</td>
<td>14.2 ml</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide E.Merck</td>
<td>40.0</td>
<td>4 g</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Sodium acetate AR, BDH</td>
<td>136.1</td>
<td>13.61 g</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

Contd.
Table II.i.1 (continued)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity grade and make</th>
<th>Sp. Gr. (g/ml)</th>
<th>Volume/weight of sample taken in 100 ml Standard flask</th>
<th>Molarity of the stock solution (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium peroxydisulphate</td>
<td>E. Merck</td>
<td>270.3</td>
<td>0.2703 g</td>
<td>0.01</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>BDH, India</td>
<td>-</td>
<td>-</td>
<td>6%</td>
</tr>
<tr>
<td>Chromium(III) chloride</td>
<td>Baker, Analysed sample</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Cobalt(III) chloride</td>
<td>AR, BDH, India</td>
<td>237.9</td>
<td>2.379 g</td>
<td>0.1</td>
</tr>
<tr>
<td>Copper(II) sulphate</td>
<td>AR, BDH, India</td>
<td>249.68</td>
<td>2.4968 g</td>
<td>0.1</td>
</tr>
<tr>
<td>Ferric ammonium sulphate</td>
<td>AR, BDH, India</td>
<td>482.0</td>
<td>4.82 g</td>
<td>0.1</td>
</tr>
<tr>
<td>Ammonium meta vanadate</td>
<td>Reanal Budapest</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>GR, SM, India</td>
<td>192.4</td>
<td>-</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Section (ii) - Brief description of the instruments used in the studies.

1. **Spectrocol Model CL 23**

   The instrument manufactured by M/s. ELICO Private Limited, Hyderabad (India) is used for most of the photometric studies. A light source, which is transistor stabilised to ensure constant intensity even during mains fluctuations is employed as the source of radiation in the spectrocolorimeter. The instrument has a gradient density interference filter having a narrow bandwidth. The use of a narrow slit facilitates a better scanning width of the spectrum. The gradient intensity filter enables the wavelength to change continuously from 400-700 nm of the entire visible range. The detector is a photocell. The absorbance is read on a panel meter with antiparallel mirror scale calibrated in both optical density and percentage transmission. Matched cuvettes of 1 cm pathlength are used in the studies. Adjustment of the wavelength to the desired value is obtained by rotating the wavelength drum on a calibrated scale. An automatic shutter arrangement in the sample chamber protects the photocell from direct illumination from the lamp in the absence of the test solution. The instrument gives reproducible results within ± 0.01 unit in the absorbance value.
2. Polarograph

Current-voltage curves are recorded using a DC pen recording Polarograph Model CL-25 manufactured by M/s ELICO Private Limited, Hyderabad (India).

This consists of three units - (1) Dropping mercury electrode, (2) Mains operated DC Polarograph unit CL-25 and (3) Mains operated self-balancing strip chart recorder model LR 101P. The span EMF is applied between cathode and anode by the selection of an appropriate initial EMF and the position of EMF selector switch. The resultant electrolysis current is made to pass through a precision placed resistor \( R \) in series with the cell. The voltage drop across the precision resistor \( IR \) is fed to a self-balancing potentiometric strip chart recorder and is represented as X-axis. A suitable current sensitivity is obtained with the help of (a) the current sensitivity knob and (b) recorder sensitivity knob. The polarograph unit is capable of recording polarograms with either increasing or decreasing applied voltage continuously changing from -3 V to 0 V or 0 V to +3 V with an accuracy of ± 1 mV. The current sensitivities can be varied from 0.003 \( \mu \)A/mm to 1.4 \( \mu \)A/mm in 20 steps. The recorder has sensitivity ranges 1 mV and 2 mV and its linear accuracy is better than ± 0.25% full scale deflection. The movement of chart paper is synchronised with span drive motor,
the span scanning voltage is represented as Y-axis. The simultaneous shift of the pen on X-axis represent cell current charge movement, on Y-axis represent cell voltage.

**Polarographic cell**

The Lingane type of H-cell with a capacity of 25 ml is used in the studies. It consists of one narrow limb and wider limb joined by horizontal tube containing a porous plate at the centre of it. Solution to be polarographed is taken in the wider limb and calomel electrode (reference electrode) is set up in the narrow limb. The reference electrode compartment is separated from the solution to be polarographed by an agar-agar bridge set up in the horizontal tube. The wider limb is provided with a side tube to serve as the inlet for the inert gas and with a tap at the bottom to drain off the solution after the experiment.

3. **pH Meter (ELICO)**

ELICO pH meter, Model LI-10 (manufactured by M/s ELICO Private Limited, Hyderabad) is used for the measurement of pH. Provision is made for temperature control in the instrument. Beckmann type glass electrode EH-60 (range 0-13 pH) and a saturated calomel reference electrode are employed. Buffers of pH 4.0 for the acid range and pH 9.0 for alkaline range are used to calibrate the instrument. The pH is read directly on a panel meter. The instrument records the pH to the second decimal.