CHAPTER III

CHEMICALS AND INSTRUMENTAL TECHNIQUES
SYNTHESIS OF LICANDS OR AZO DYES:

All the ligands used are azo dyes, which are prepared by coupling diazotized aniline and its substituents with salicylic acid. The chemicals e.g. aniline and its derivatives used were all of B.D.H. AnalaR grade and salicylic acid used was of Rhodia (France). Although a few of these dyes are reported in literature, none is available commercially.

(i) Diazoization: 18.6g or 18.3ml (0.2 mol.) of aniline was dissolved in 57ml of hydrochloric acid (10N) and 57ml of water in a conical flask of 500ml capacity. The flask was immersed in a bath of ice and allowed to remain at a temperature below 5°C. 14.3g of sodium nitrite (0.2 mol.) was dissolved in 67ml of water and was added in small amounts (nearly 1ml at a time) to the cold solution of aniline hydrochloride, the temperature of which was always kept well below 5°C. Simultaneously, the solution was stirred well. Ice prepared from distilled water was added at intervals to keep the temperature below 5°C. The last installment of sodium nitrite solution (nearly 5%) was added quite slowly. The solution was kept for nearly 5 minutes in ice with occasional stirring and the excess of nitrous acid was tested with KI-starch paper which turned blue immediately, indicating the completion of the
reaction. The excess of nitrous acid formed was destroyed by
the addition of urea to it.

(ii) Coupling of the reactants: A solution of salicylic
acid was prepared in NaOH (total volume nearly 120ml). Well
crushed ice prepared from distilled water was added to it
and the pH was kept at about 11. Now this solution was added
to the salicylic acid solution with stirring keeping in view
that the pH of the solution remained nearly 11 (maintained
by addition of 3N NaOH), and the temperature well below 5°C.
When the whole of the diazotized solution was added and the
stirring was continued for about 5 - 10 minutes. At this
stage it was placed in a refrigerator for about 6 - 8 hours,
where its temperature remained quite below 5°C. It was then
placed in the working table in the laboratory (temperature
about 27°C.) for about 12 hours (over night).

The whole process can be shown as follows:

\[
\begin{align*}
\text{Aniline} + \text{NaNO}_2 + 2\text{HCl} & \rightarrow \text{Aniline diazonium chloride} \\
\text{Salicylic acid} + \text{NaOH} & \rightarrow \text{Sodium salicylate}
\end{align*}
\]

Sodium salt of unsubstituted dye
For the synthesis of other dyes of the series, the procedure followed and the ingredients used were exactly the same as described above. Instead of aniline, equivalent quantities of substituted anilines as shown below were taken and the pH conditions of the optimum yield were maintained.

<table>
<thead>
<tr>
<th>Name of the substituted aniline</th>
<th>Quantity taken in gms.</th>
<th>pH maintained during coupling</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-toluidine</td>
<td>21.4</td>
<td>11</td>
</tr>
<tr>
<td>m-toluidine</td>
<td>21.4</td>
<td>11</td>
</tr>
<tr>
<td>p-toluidine</td>
<td>21.4</td>
<td>11</td>
</tr>
<tr>
<td>o-anisidine</td>
<td>24.6</td>
<td>13</td>
</tr>
<tr>
<td>p-anisidine</td>
<td>24.6</td>
<td>13</td>
</tr>
<tr>
<td>m-chloroaniline</td>
<td>25.5</td>
<td>8</td>
</tr>
<tr>
<td>p-chloroaniline</td>
<td>25.5</td>
<td>8</td>
</tr>
</tbody>
</table>

**ISOLATION AND PURIFICATION OF THE DYES**

The dyes were obtained in the form of their sodium salts. They were then dissolved in water and filtered. Sodium chloride was added to the solution to precipitate them. The other impurities remained in the solution e.g. (the unreacted sodium salicylate). The impurity in the dyes would now be only of sodium chloride. The precipitated dyes were filtered and pressed between filter papers to remove as much mother liquor as possible. The sodium salts of the dyes were repeatedly crystallized from hot water, thus removing the sodium chloride,
if any, due to its relatively more solubility in water.

Crystallization of the sodium salts of the dyes involved the well known steps of preparation of the saturated solution in the solvent near its boiling point, filtration through a hot funnel to remove any insoluble impurities and cooling for deposition of crystals. The crystals deposited were again dissolved by heating and allowed to cool slowly by placing the same in vessels having large amounts of hot water while the solution was stirred with a glass rod. If any crystal adhered to the wall, it was pushed down into the solution so as to act as nucleus of further growth of the crystals of the dyes. Thus well formed crystals of the sodium salts of dyes free from absorbed impurities were obtained. The crystals were separated from the mother liquor and washed with a small quantity of water. To avoid the filter paper contamination, a sintered glass funnel was used for filtration in the last crystallization. Though the yield was almost quantitative, yet good losses occurred due to repeated crystallization.

These crystallized dyes were first dried in an air oven at 100 - 110°C and afterwards in drying pits (Towers, electrically heated) at 110°C over P₂O₅ in vacuum (pressure 3-5 mm), thus ensuring complete removal of water of crystallization.
The purity was tested by analysing for carbon and hydrogen contents.

**RESULTS OF ANALYSIS:**

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1,5-phenyl azo sodio salicylate</td>
<td>59.09%</td>
<td>59.39%</td>
<td>3.05%</td>
<td>3.09%</td>
</tr>
<tr>
<td>2,2-methyl phenyl azo sodio salicylate</td>
<td>60.43%</td>
<td>60.80%</td>
<td>4.31%</td>
<td>4.39%</td>
</tr>
<tr>
<td>3,3-methyl phenyl azo sodio salicylate</td>
<td>60.43%</td>
<td>60.57%</td>
<td>4.31%</td>
<td>4.37%</td>
</tr>
<tr>
<td>4,4-methyl phenyl azo sodio salicylate</td>
<td>60.43%</td>
<td>60.60%</td>
<td>4.31%</td>
<td>4.35%</td>
</tr>
<tr>
<td>5,2-methoxy phenyl azo sodio salicylate</td>
<td>57.14%</td>
<td>57.28%</td>
<td>3.74%</td>
<td>3.82%</td>
</tr>
<tr>
<td>6,4-methoxy phenyl azo sodio salicylate</td>
<td>57.14%</td>
<td>57.39%</td>
<td>3.74%</td>
<td>3.77%</td>
</tr>
<tr>
<td>7,3-chloro phenyl azo sodio salicylate</td>
<td>56.88%</td>
<td>56.92%</td>
<td>3.70%</td>
<td>2.71%</td>
</tr>
<tr>
<td>8,4-chloro phenyl azo sodio salicylate</td>
<td>56.88%</td>
<td>56.87%</td>
<td>3.70%</td>
<td>2.73%</td>
</tr>
</tbody>
</table>
(II) ESTIMATION FOR ZINC AND VANADIUM:

(a) ZINC: Zinc was estimated gravimetrically by the pyridine method. This method is accurate and rapid one.

To the cold solution of zinc sulphate in distilled water, solid ammonium thiocyanate (A.T) was added, which was followed by pure pyridine. The solution was heated and allowed to cool and stirred frequently. The white, crystalline precipitate of dipyridine-zinc-dithiocyanate was separated. The precipitate was filtered through a weighed sintered glass crucible and transferred with the aid of solution (i). The precipitate was washed 3 - 4 times with solution (ii). The walls of the crucible were washed with solution (iii) and then the precipitate was finally washed 5 - 6 times with solution (iv). The crucible and the precipitate were dried in a vacuum dessicator for 15 minutes and weighed. The drying was repeated for a constant weight. The amount of zinc sulphate present in the complex was calculated.

Solution (i): 100ml of water containing 0.3g of NH₄SCN and 0.5ml of pyridine.

Solution (ii): 85.5ml of water, 15ml of 95% alcohol, 0.1g of NH₄SCN and 1.5ml of pyridine.

Solution (iii): 10ml of absolute alcohol and 1ml of pyridine.

Solution (iv): 15ml of absolute (sodium dried) ether and 2 drops of pyridine.

The estimation corresponds to the formula ZnSO₄·7H₂O for the compound.
(b) VANADIUM - Tetravalent vanadium was estimated as 10 $V_2O_5$. A known weight of the vanadyl sulphate was taken and dissolved in distilled water. A hot solution of ammonium benzoate (saturated when cold) was added to it in order to precipitate vanadium. The mixture was boiled for 3 - 3 minutes and then allowed to stand for 3 - 4 hours. The precipitate was filtered through Whatman filter paper No. 41 and was washed with a cold saturated solution of benzoic acid; the filtrate was tested for the complete removal of tetravalent vanadium. The precipitate was dried at 100 - 120°C, ignited for about 15 minutes and weighed as vanadium pentoxide ($V_2O_5$). Heating was repeated and the residue was reweighed after cooling. The sulphate content was estimated by precipitating it as barium sulphate by barium chloride.

The estimation corresponds to the formula $VC(SO_4)_2H_2O$ for the compound.

(III) CHEMICALS USED FOR THE INVESTIGATIONS:

Zinc sulphate $ZnSO_4 \cdot 7H_2O$ (E. Merck) and vanadyl sulphate $VOSO_4 \cdot 2H_2O$ (Piederel-De-Heen AG, Germany) were used for the present investigations.

The ligands, the azo dyes, were synthesized by the author and their purity was tested by the analysis of carbon and hydrogen contents (as described in the preceding pages).
IV) PREPARATION OF SOLUTIONS:

1. Zinc sulphate and vanadyl sulphate: The zinc sulphate and vanadyl sulphate solutions were prepared by dissolving the required quantities of the analysed samples in conductivity water. Freshly prepared solutions were used in all the experiments.

2. Ligands: Standard solutions of azo dyes were prepared by dissolving the weighed amounts in conductivity water. The solutions were diluted to different concentrations and used for the experiments.

3. Sodium hydroxide solution: A carbonate free sample of A.R. sodium hydroxide solution was standardized against oxalic acid solution. A suitable volume of it was diluted to obtain 1 molar solution which was preserved out of contact with carbon-di-oxide by connecting a sodalime guard-tube. Solutions of other molarities were prepared by suitable dilutions of the 1 molar solution.

4. Perchloric acid solution: The sample of A.R. perchloric acid was standardized against standard alkali and was diluted to prepare 0.1 molar solution.

5. Sodium perchlorate solution: 0.5 molar solution of the compound was prepared by dissolving the required weight of A.R. sodium perchlorate in conductivity water.
6. **Purification of nitrogen**: The nitrogen gas was purified first by bubbling through Fieser's solution which was made by dissolving sodium dithionate (16 g), sodium anthraquinone-2-sulphonate (0.8 g) and sodium hydroxide (15 g) in water (100 ml). Freed from oxygen and carbon dioxide in this way, the nitrogen was next freed from alkaline spray by bubbling through a little water.

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**DESCRIPTION OF THE INSTRUMENTS EMPLOYED DURING THE PRESENT INVESTIGATIONS**

**Spectrophotometer**:

Carl-Zeiss model PMQ II Spectrophotometer was used for the optical density measurements. This instrument incorporates a hydrogen tube source (for a range of 200 - 325 mp) or a Tungsten source (for a range of 325 - 2500 mp), a monochromator type M4211 equipped with a quartz prism, two photoelectric detectors (a multiplier type 1P28 for 200 - 600 mp and a photocell type MC100RV for 600 - 1000 mp), an indicating instrument consisting of an amplifier and a power supply unit consisting of a voltage stabilizer for the tungsten lamp. The measuring values are read on the light mark scale which appears on a ground glass. The whole unit is fed from a 220 V 50 c/s alternating circuit.
Four matched silica cells of 1.0cm light path were used for the specimen and the solvent. Care was taken in not interchanging the cells with each other. They were cleaned and dried everytime before introducing a new sample. These cells were mounted on a sliding platform and by manipulating the latter, the solvent and sample solutions could be brought successively to the path of light as desired. The instrument was brought to the position of maximum sensitivity by manipulating the slit width and the sensitivity knobs. The adjustments of the dark current knob and sensitivity knob were checked between readings and readjusted as necessary.

**pH-Meter:**

pH measurements were taken with the help of a Beckmann model H2 direct reading pH-Meter. The electrode system, glass-calomel, was supplied by the same firm. The instrument got a limit of error of 0.1 pH (readable upto 0.05 pH) and a reproducibility of 0.02pH. It was standarded with buffers of pH 4 and pH 9, supplied by Toshniwal Company before use. In order to avoid voltage fluctuations, a stabilizer was connected to the instrument.

**Conductivity Bridge:**

A Toshniwal model CM101, magic eye type conductivity bridge operated on 220 volts A.C. 50 cycles with an
accuracy of ± 2% was used for conductance measurements. The measurements were carried out on a test frequency set at 3 k.cycles per second. A compact and stout dip type conductivity cell was used.

**Potentiometer:**

The E.M.F. measurements were taken on a Toshniwal Titration Potentiometer model C106, having a magic eye and a reading range of 0 - 1600 mV. A calomel electrode was used as a reference electrode and a platinum electrode as indicator electrode.
REFERENCES


5. Fierz - David and Blangey Fundamental processes of Dye Chemistry, Interscience Publisher, Translated by Vittum, p. 239-48, 261.


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