

CHAPTER - II

EXPERIMENTAL

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Our intention in the present work was mainly to study the electroluminescent properties of some salts of 8- hydroxyquinoline such as magnesium, calcium, zinc, cadmium, aluminium, iron, cobalt, nickel, copper, manganese, chromium, tin and mercury.

The experimental work done for this study can be divided into three stages, namely,

1. Purification of 8- hydroxyquinoline,
2. Preparation of various metallic salts of 8 - hydroxyquinoline,
3. Studies on electro - optical properties of electroluminescent metal - oxinates.

### 2. 1 PURIFICATION OF 8- HYDROXYQUINOLINE (OXINE)

Solid organic compounds isolated from organic reaction were seldom pure. They were usually contaminated with small amounts of other compounds, i.e. impurities. Even a trace amount of impurity in the compound markedly changes its electro- optical properties and therefore, the purification of the organic compounds often must be performed prior to EL. study.

The purification of impure crystalline compounds is usually effected by crystallisation from a suitable solvent or mixture of solvents. The 8 - hydroxyquinoline

obtained from BDH company ( Glaxo laboratories, India)  
was recrystallised using 75% absolute alcohol as<sup>127,128</sup>  
described below.

The solid oxine was placed in a conical flask and slightly less than the required quantity of solvent mixture was added together with a few fragments of porous porcelain. Reflux condenser was then fitted to the flask. The mixture was heated in a water bath and more solvent was added down the condenser until a clear solution was produced. The boiling or hot solution was rapidly filtered before undue cooling has occurred. The filtered solution was covered with a watch glass and then set aside to cool undisturbed. The obtained crystals were separated from solution (or from mother liquor). The recrystallisation process was repeated several times and purity of 8 - hydroxyquinoline was confirmed by following recommended thin layer<sup>129</sup> chromatography technique. The obtained compound was found to be almost colourless, crystalline solid having a melting point of 75° C.

## 2.2 PREPARATION OF METAL - OXINATES.

8 - Hydroxyquinoline ( Oxine ) forms sparingly soluble derivatives with metallic ions, which have the composition  $M ( C_9 H_6 ON )_2$  if the co-ordination number of the metal is four ( e.g. Magnesium, calcium, Zinc,

Cadmium, Cobalt, Nickel, Copper, Manganese, Chromium, etc.),  $M(C_9H_6ON)_3$  if the co-ordination number is six (e.g. Aluminium, Iron), and  $M(C_9H_6ON)_4$  if the co-ordination number is eight, The solid metal complexes of 8 - hydroxyquinoline were prepared by the methods of Kolthoff and <sup>130</sup> Sandell.

Preparation of 8- hydroxyquinoline solution:

3 gm of purified 8 - hydroxyquinoline was dissolved in a small quantity of acetic acid and diluted to 100 ml with distilled water.

The pH of the solution was measured with digital pH meter ( Electronic Corporation of India Ltd. PH 5651 Serial No.372).

2.2- a ) MAGNESIUM OXINATE ( $Mg(C_9H_6ON)_2$ ):

To the magnesium salt solution [( 1 gm  $MgCl_2 \cdot 6H_2O$  ( Emerck)], molecular weight 203.30, dissolved in a small quantity of very dilute hydrochloric acid (A.R. Grade) and diluted to 100 ml), sufficient amount of ammonium acetate buffer was added, so as to maintain the pH of the solution 11.0. The solution was heated on a water bath. The solution of 8- hydroxyquinoline was added dropwise until a precipitate forms, excess solution was added till yellow colour of supernatant liquid appears

which insure the complete precipitation. The solution was heated for several minutes and then allowed to stand at room temperature for 2 to 3 hours. The precipitate was filtered through a sintered glass crucible. The solid was collected, well washed with hot and cold water, and dried for 6 hours at 135<sup>o</sup> C.

The dried oxinate was shown to be stable and anhydrous from 200<sup>o</sup> to 375<sup>o</sup> C by Dupuis and Borrel and Paris.<sup>131</sup><sup>132</sup>

The preparative methods for all other metallic salts are the same except, pH of the precipitating solutions and drying temperatures. These different pH and temperature values are as below:

Name of the oxinate	pH	Buffer used	Drying Temperature.
2:2 b) Calcium oxinate (Ca (C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> )	10.0	Ammonium Acetate	125 <sup>o</sup> C
2:2 c) Zinc oxinate (Zn (C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> )	9.5	Ammonium Acetate	140 <sup>o</sup> C
2:2 d) Cadmium oxinate (Cd (C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> )	10.5	Ammonium Acetate	130 <sup>o</sup> C
2:2 e) Aluminium oxinate (Al (C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub> )	9.0	Sodium bicarbonate.	140 <sup>o</sup> C

All these compounds are found to be highly photoluminescent when excited with short wavelength U.V. light.  
(ULTRA-VIOLET PRODUCTS, INC. SAN GABRIEL, CALIF.).

In addition to above, other metallic salts of oxine such as Cobalt, Nickel, Copper, Manganese, Chromium and Iron were prepared in the laboratory, but as they were found to be non photoluminescent as well as non electroluminescent their preparative conditions are not described.

### 2.3 STUDY OF ELECTRO - OPTICAL PROPERTIES OF SALTS OF 8 - HYDROXYQUINOLINE ;

The prepared salts of 8- hydroxyquinoline, as mentioned above were subjected to the study of spectral intensity distribution ( S.I.D.) of their EL. emission at constant voltage and frequency. Then the voltage and frequency dependence of the EL. emission of the salts were also studied. The instruments used for these studies can be broadly divided into four units, namely,

- a) Electroluminescent cell,
- b) Excitation unit,
- c) Dispersion unit,
- d) Detection and measurement unit for measuring

the intensity of the emitted light.

#### 2.3 a) ELECTROLUMINESCENT CELL

Various types of electroluminescent cells ( EL. cells) have been described earlier ( Chapter I, 1.2. 1-b). We found the following arrangement more convenient and satisfactory for the measurement of spectral intensity distribution and relative intensity of EL. emission (cf. Fig.No.1 ).

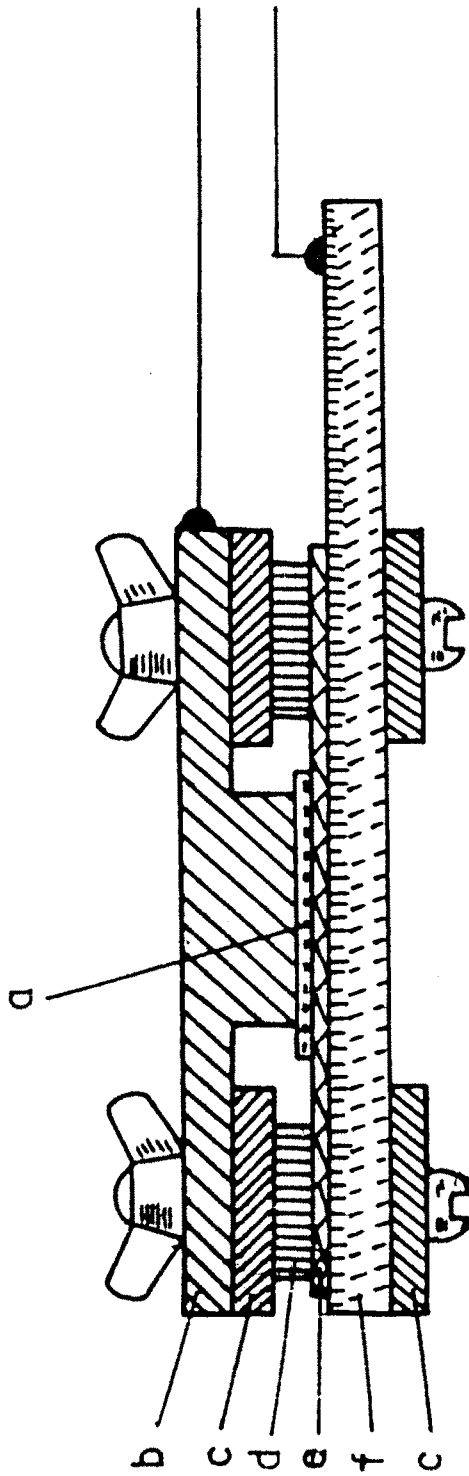


Fig. 1 - Cross section of Electroluminescent Cell .

a = El. material deposited on  
cellophane tape .

b = Aluminium electrode .

c = Lucite .

d = Spacer .

e = Insulating mica Sheet .

f = Conducting glass electrode .

The powdered salt of 8-hydroxyquinoline was sieved and its pasty suspension in alcohol was applied to an aluminium plate of the desired size in the form of thin film. It is then dried. In order to study the behaviour of EL-emittance in presence of various dielectrics, the pasty suspension of these metal oxinates were prepared in various dielectric materials, such as castor oil, silicon oil, high vacuum grease and transformer oil, and applied to an aluminium plate by taking the care to exclude the air completely. The film was covered with a sheet of transparent mica of uniform thickness having high dielectric constant and sufficient breakdown strength. The sheet of mica was covered with conducting glass, having a resistance of 400-500  $\Omega$  /cm<sup>2</sup> and optical transmission of the order of 80% or more, served as second electrode. Such conducting glasses were prepared by spraying a solution of tin salt in alcohol, on to a glass plate heated to just below the melting point. Thus, the cell works as a luminous condenser, the phosphor being sandwiched between two parallel electrodes. This condenser was enclosed in an ebonite frame, provided with a small window in the middle of the top of the surface, and a screw arrangement to adjust the interelectrode distance and the pressure. From the two electrodes, leads were taken out and high electric field was applied to the EL-material. The emitted light was observed through the transparent conducting glass. This assembly was found to have the following advantages, namely, a uniform pressure



can be applied to the phosphor layer with the help of the screwing arrangement, inter-electrode distance can be kept constant, the emission can be observed at low voltages and the extraneous light is completely avoided by fixing the photomultiplier tube to the dispersion unit.

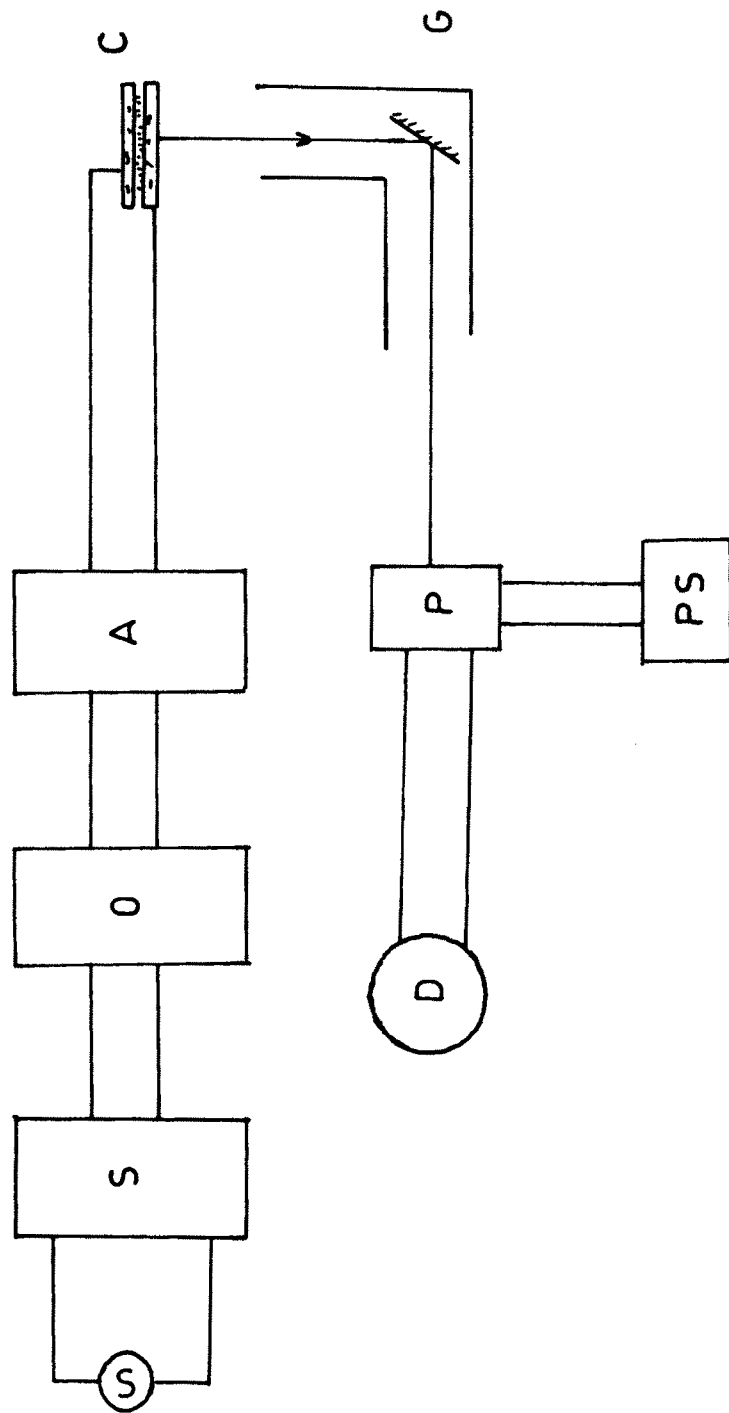
### 2.3 b) EXCITATION UNIT.

The excitation unit consisted of an audio-frequency oscillator ( Philips India, make GM 2308, 0-16 KHz, 0-90 volts out put) whose output was fed in to a high frequency - high voltage transformer ( 0-5 KV, Telmex, India). The output of this transformer was given to the EL. cell, the voltage across the two electrodes was measured with Simpson Multimeter (Model 260, series = 5 M).

### 2.3 c) DISPERSION UNIT.

A Carl Zeiss Jena ( spekol ) grating monochromator ( high- intensity grating ) having a relative aperture of 1:3.4 and equipped with fixed slits for a spectral bandwidth of 11 nm. The wavelength drum revolves the grating by the required number of degrees, thus permitting the spectral range to drift from 360 to 750 nm over the exit slit. The exit slit permits a spectral range of the half-band width of 11 nm to emerge which is then passed on to the measurement phase. The monochromator functions similarly to a colour filter having a spectral half-band width of 11 nm. The preselected wavelength can be read from the

FIG. 2 BLOCK DIAGRAM OF EXPERIMENTAL SET UP.



- S = STABILIZER .
- O = A. F. OSCILLATOR .
- A = STEP UP TRANSFORMER .
- C = ELECTROLUMINESCENT CELL .
- G = GRATING MONOCHROMATOR .
- P = PHOTOMULTIPLIER TUBE .
- PS = POWER SUPPLY OF P.M. TUBE .
- D = SPOT REFLECTING GALVANOMETER .

wavelength drum ( 1 scale division = 1 nm).

The EL.cell was placed at a fixed distance from the entrance slit of the grating monochromator.

### 2.3 d) INTENSITY MEASURING UNIT ;

The intensity of EL. emission was measured with the help of an IP-21 photomultiplier tube coupled with a very sensitive spot reflecting galvanometer ( Polyflex type, Toshniwal, India, Sensitivity =  $1.2 \times 10^{-9}$  amp per mm deflection). The IP- 21 photomultiplier tube attachment (IP- 21 fitted in a rectangular box ) was fixed in front of the exit slit of the grating monochromator unit. This arrangement helped to avoid the stray light entering the phototube and hence to minimize the dark current. Complete assembly was covered with a black cloth to avoid the extraneous light. The P.M. tube was operated at a stabilized d.c. voltage ( anode to cathode voltage  $\approx$  1000 volts) and the dark current was reduced to zero by applying an opposing current.

The intensities of EL. emission were measured in arbitrary units ( in terms of galvanometric deflection).

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