CHAPTER 3 EXPERIMENTAL TECHNIQUE

3.1 Preparation of Copper(II) Cinnamate and Iodine-Doped Copper(II) Cinnamate

Copper(II) cinnamate was prepared from copper(II) acetate and cinnamic acid according to the following chemical equation.

\[ \text{Cu(CH}_3\text{COO)}_2 + 2\text{C}_6\text{H}_5\text{CH=CHCOOH} \rightarrow \text{Cu(C}_6\text{H}_5\text{CH=CHCOO)}_2 + 2\text{CH}_3\text{COOH} \]

Copper(II) acetate  cinnamic acid  copper(II) cinnamate  acetic acid

45.0029 g copper(II) acetate monohydrate [Cu(CH₃COO)₂.H₂O; MW 199.65; 0.225 mole] was mixed with 66.7859 g of cinnamic acid [C₆H₅CH=CHCOOH; MW 148.16; 0.450 mole] in a 250 cm³ round-bottomed flask containing 148 cm³ acetonitrile. The flask was fitted with a reflux condenser, stirred magnetically and heated under reflux in an oil-bath overnight. The reaction mixture was left to cool. The light-blue solid residue was filtered, washed with ethanol and dried in the oven at 50°C for 30 minutes. The yield is 83.4 g.

Copper(II) cinnamate doped with different amounts of iodine was prepared by mixing a known weight of iodine with a known weight of copper(II) cinnamate (see Table 3.1) in 20 cm³ of acetonitrile in a 100 cm³ volumetric flask. The mixture was
stirred magnetically at room temperature for 24 hours. The solid obtained was filtered, washed with acetonitrile, dried in the oven at 50°C for 30 minutes and the yield recorded.

Table 3.1 Percentage of Iodine in Copper(II) Cinnamate

<table>
<thead>
<tr>
<th>Weight of Copper(II) Cinnamate (± 0.0001g)</th>
<th>Weight of Iodine (± 0.0001g)</th>
<th>*</th>
<th>Weight of Doped Copper(II) Cinnamate (±0.0001g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0002</td>
<td>0.0841</td>
<td>4.0</td>
<td>1.9412</td>
</tr>
<tr>
<td>2.0005</td>
<td>0.1752</td>
<td>8.1</td>
<td>2.0195</td>
</tr>
<tr>
<td>2.0031</td>
<td>0.2727</td>
<td>12.0</td>
<td>2.1302</td>
</tr>
<tr>
<td>2.0009</td>
<td>0.3256</td>
<td>14.0</td>
<td>2.1476</td>
</tr>
<tr>
<td>2.0035</td>
<td>0.3809</td>
<td>16.0</td>
<td>2.2609</td>
</tr>
<tr>
<td>2.0033</td>
<td>0.4390</td>
<td>18.0</td>
<td>2.2634</td>
</tr>
<tr>
<td>2.0042</td>
<td>0.5067</td>
<td>20.2</td>
<td>2.3547</td>
</tr>
</tbody>
</table>

* % Iodine = \( \frac{\text{weight of iodine} \times 100}{\text{weight of copper(II) cinnamate} + \text{weight of iodine}} \)

3.2 Preparation of Sample for Electrical Measurement

The samples for electrical measurement were in the form of discs with silver electrodes on both sides (Fig 3.1). The equipment used for the preparation of disc consists of a die and a hydraulic pump system. The equipment was first cleaned with acetone. About 5 spatula (approximately 0.05g) scoops of finely powdered sample was placed in the die and pressed for 5 minutes by applying 5 tonnes of pressure using a hydraulic pump. The time and pressure must be kept constant for all samples as these parameters may affect the experimental results.
Figure 3.1 The sample for electrical measurement
(a) Side view
(b) Top and Bottom view

Two circular aluminium mask of different sizes were prepared. The first mask has a diameter of about 8 mm and the second mask has two circular holes whose
diameter of about 2 mm. The masks were placed on both sides of the disc as shown in Figure 3.1 and silver paste was painted over the mask to prepare the electrodes. Silver paste was also used to connect the copper wire from the measuring equipment to the electrodes.

The sample thickness, \( T \), was measured with a digital vernier before silver electrodes was painted on it and the diameter, \( D \), of the smaller electrode was measured with a travelling microscope. Five readings were taken for each sample.

3.3 Electrical Measurement at Room and Low Temperature

The conductivity of the samples was determined at room temperature (297K) and at low temperatures ranging from 80K to 300K. The experimental set up, shown in Figure 3.2, involve a Janis VPF–100 dewar cryostat, vacuum pump, temperature controller, Source Measure Unit (SMU) and Metrics Software Program. Figure 3.3 shows the circuit diagram for current – voltage measurement.

![Diagram](image)

**Figure 3.2 Experimental set-up**

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The sample was mounted in the cryostat (Figure 3.4). A thin aluminium sheet was placed on top of the sample mount of the dewar before the sample was placed on it. This is to ensure good thermal contact between the sample mount and the sample. The other end of the two copper wires that is connected to the electrodes was connected to the electrical pin connectors which is to be connected to the SMU.

For the forward process, the voltage across the sample was increased from 0 V to 100 V at 0.5 V interval and the current flow was recorded. For the reverse process, the current flow was recorded when the voltage was decreased from 100V to 0V for the same sample. The measurement was repeated for the forward and reverse process after applying a constant-voltage of 60 V for half an hour to empty the trap levels of the sample. A graph of log I versus log V was plotted to determine the ohmic region. A graph of I versus V was plotted in the ohmic region to determine the conductivity of the sample. The above procedures were repeated for copper(II) cinnamate doped with
Figure 3.4 Sample mounted in the cryostat
different amounts of iodine. The parameter used in the SMU set-up for current voltage measurement is as follows.

- **Mode**: Sweep
- **Type**: Linear
- **Measure**: Voltage and Current
- **No. of Points**: 200
- **Interval**: 0.5 Volts
- **Time delay**: 1 second
- **Integration**: 60 Hz
- **Filter**: 4 readings

For the low temperature measurement the pressure in the cryostat was pumped down to about $10^{-4}$ torr using the rotary and diffusion pump. The liquid nitrogen reservoir was filled with liquid nitrogen. The automatic temperature controller was connected to the relevant electrical pin on the cryostat. It is essential to wait for a few minutes before taking any readings to ensure that the sample has reached the required temperature. The temperature of the sample was set up at roughly 80K and current-voltage measurement was taken. A graph of log I versus log V was plotted to determine the ohmic region. The graph obtained is compared with the graph of log I versus log V at room temperature. A constant voltage was chosen for the measurement of variation of current with temperature. This voltage must be within the ohmic region for 80K and
room temperature. The voltage chosen is 80V and was applied for two hours to empty the
trap levels of sample, before the variation of current with temperatures was done.

3.4 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared (FTIR) spectra of copper(II) cinnamate and
copper(II) cinnamate doped with different amounts of iodine were recorded as potassium
bromide (KBr) discs. KBr was finely grounded, sieved and heated in an oven at 120°C
for 24 hours. A few spatulas of KBr powder was thoroughly mixed with a small amount
of the sample. The mixture was pressed using a die and hydraulic pump at a pressure of
8 tonnes for 15 minutes.

3.5 Annealing Process

Annealing is a process in which a substance is heated in a furnace for a specific
time and under a specific environment. Copper(II) cinnamate and copper(II) cinnamate
doped with different amounts of iodine were annealed at 50°C, 100°C, 150°C and 200°C.
The furnace used is the Carbolite furnace model CFN-1271. The furnace was first heated
to the required temperature. A steady flow of nitrogen gas was passed through during the
annealing process. When the temperature is stable, the sample (powder form) was placed
on a sample holder and inserted into the centre of the furnace together with the
thermocouple to measure the temperature. After every annealing process the sample was
allowed to cool down to room temperature in the furnace with a continuous flow of
nitrogen gas. Then the conductivity and the FTIR spectrum of the sample was determined
at room temperature (297K) as before.