Studies on Cu(II)-p-hydroxy acetophenone thiosemicarbazone system

Present investigations

Experimental procedure

10 ml of buffer solution of required pH, 1 ml of 1 x 10^{-2}M p-HAPTSC solution, 1 ml of 1 x 10^{-3}M cupric sulphate solution are taken in a 25 ml standard flask. The contents of the flask are made up to the mark with distilled water. The contents of the flask are shaken well to maintain uniform concentration. The spectrum of the above experimental solution is recorded in the wavelength range 350 – 500 nm against corresponding blank solution.

Effect of pH

The author has studied the effect of pH in the range 4 to 9 on the colour reaction of Cu(II) with p-HAPTSC. The studies on the effect of pH have revealed that copper forms green coloured solution in the entire pH range of study. There is not much change in $\lambda_{\text{max}}$ values in the pH range studied. This indicates that same species is formed in all the pH solutions. The absorbance values increase from pH 4 to 7 and there after there is a decrease. The author has chosen a solution of pH 7 and wavelength ($\lambda_{\text{max}}$) of 356nm for further studies. The data relating to pH, wavelength, absorbance is presented in table 3.10.1. Graphs are plotted between pH and absorbance as well as pH and wavelength are shown in fig 3.10.1a and 3.10.1b. Absorption spectrum of complex in a solution of pH 7 is shown in fig 3.10.1c.
### Table 3.10.1
Effect of pH on the absorbance of Cu(II) – p-HAPTSC complex

\[
\begin{align*}
[Cu(II)] &= 4 \times 10^{-5} \text{M} \\
[p\text{-HAPTSC}] &= 4 \times 10^{-4} \text{M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>pH</th>
<th>Colour of the Complex</th>
<th>(\lambda_{\text{max}})</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0</td>
<td>Very light green</td>
<td>355</td>
<td>0.100</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>Light green</td>
<td>352</td>
<td>0.165</td>
</tr>
<tr>
<td>3</td>
<td>6.0</td>
<td>green</td>
<td>353</td>
<td>0.298</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>green</td>
<td>356</td>
<td>0.442</td>
</tr>
<tr>
<td>5</td>
<td>8.0</td>
<td>green</td>
<td>357</td>
<td>0.252</td>
</tr>
<tr>
<td>6</td>
<td>9.0</td>
<td>green</td>
<td>360</td>
<td>0.240</td>
</tr>
</tbody>
</table>

**Fig: 3.10.1a:** Effect of pH on the absorbance of Cu(II)-p-HAPTSC system

\([Cu(II)] = 4 \times 10^{-5} \text{M}, \ [p\text{-HAPTSC}] = 4 \times 10^{-4} \text{M}\)
Fig: 3.10.1b: Effect of pH on the wavelength (nm) of Cu(II)-p-HAPTSC system

\[ [\text{Cu(II)}] = 4 \times 10^{-5} \text{ M}, \quad [\text{p-HAPTSC}] = 4 \times 10^{-4} \text{ M} \]

Fig: 3.10.1c: Absorption spectrum of Cu(II)-p-HAPTSC Complex

\[ \text{pH}=7.0, \quad [\text{Cu(II)}] = 4 \times 10^{-5} \text{ M}, \quad [\text{p-HAPTSC}] = 4 \times 10^{-4} \text{ M} \]
Effect of metal ion on absorbance

The author has studied the effect of concentration of Cu(II) on the absorbance by keeping the reagent concentration constant. The amount of metal ion is varied from 0.508 to 5.084 µg/ml. The absorbance values are measured in each case at 356 nm against respective reagent blank solution. The data is shown in table 3.10.2. A graph is plotted between amount of Cu(II) and absorbance. It is shown in figure 3.10.2. A straight line plot is obtained and fitted into formula $A_{356} = 0.17041 C - 0.00697$.

Effect of reagent concentration

To study the effect of p-HAPTSC concentration on the absorbance, experiments were carried out. In these studies, the metal ion concentration is kept constant. The absorbance values are measured at 356 nm. The results are presented in table 3.10.3. When a graph is drawn between the concentration of reagent and absorbance, a linear plot is obtained up to 5 fold concentration of reagent. It is shown in figure 3.10.3. Beyond this concentration of the reagent, absorbance remains constant. Hence a 5 fold concentration of the reagent is required for complete colour development.

Effect of time

The author has studied the effect of time on complexation reaction between Cu(II)-p-HAPTSC. The data is presented in the table 3.10.4. From the data it is observed that the difference in absorbance values is minimum. The complex remains stable and clear for a reasonable time period.
### Table 3.10.2

Applicability of Beer's law on Cu(II)-p-HAPTSC complex

<table>
<thead>
<tr>
<th>[p-HAPTSC]</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 x 10&lt;sup&gt;-4&lt;/sup&gt;M</td>
<td>356 nm</td>
<td>7.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Amount of metal ion (µg/ml)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.508</td>
<td>0.082</td>
</tr>
<tr>
<td>2</td>
<td>1.017</td>
<td>0.169</td>
</tr>
<tr>
<td>3</td>
<td>1.525</td>
<td>0.252</td>
</tr>
<tr>
<td>4</td>
<td>2.033</td>
<td>0.321</td>
</tr>
<tr>
<td>5</td>
<td>2.542</td>
<td>0.438</td>
</tr>
<tr>
<td>6</td>
<td>3.050</td>
<td>0.518</td>
</tr>
<tr>
<td>7</td>
<td>3.559</td>
<td>0.597</td>
</tr>
<tr>
<td>8</td>
<td>4.067</td>
<td>0.688</td>
</tr>
<tr>
<td>9</td>
<td>4.575</td>
<td>0.771</td>
</tr>
<tr>
<td>10</td>
<td>5.084</td>
<td>0.859</td>
</tr>
</tbody>
</table>

**Fig: 3.10.2:** Effect of metal ion concentration on absorbance

\[
A_{356} = 0.17041 C - 0.00697
\]
Table 3.10.3

Effect of reagent concentration on the absorbance of complex

\[ [\text{Cu(II)}] = 4 \times 10^{-5} \text{M} \]
\[ \lambda_{\text{max}} = 356 \text{ nm} \]
\[ \text{pH} = 7.0 \]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>p-HAPTSC x 10^4M</th>
<th>[M] : [L]</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>1 : 1</td>
<td>0.092</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1 : 2</td>
<td>0.174</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>1 : 3</td>
<td>0.265</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>1 : 4</td>
<td>0.359</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1 : 5</td>
<td>0.450</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>1 : 6</td>
<td>0.453</td>
</tr>
<tr>
<td>7</td>
<td>0.7</td>
<td>1 : 7</td>
<td>0.454</td>
</tr>
</tbody>
</table>

Fig: 3.10.3: Effect of Reagent concentration on Cu(II)-p-HAPTSC complex

\[ [\text{Cu(II)}] = 4 \times 10^{-5} \text{M} ; \text{pH} 7.0 ; \]
\[ \lambda_{\text{max}} = 356 \text{ nm} \]
Table 3.10.4
Effect of time

<table>
<thead>
<tr>
<th>Cu(II)</th>
<th>(3 \times 10^{-5})M</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-HAPTSC</td>
<td>(3 \times 10^{-4})M</td>
</tr>
<tr>
<td>(\lambda_{\text{max}})</td>
<td>356 nm</td>
</tr>
<tr>
<td>pH</td>
<td>7.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>02</td>
<td>0.338</td>
</tr>
<tr>
<td>10</td>
<td>0.339</td>
</tr>
<tr>
<td>20</td>
<td>0.339</td>
</tr>
<tr>
<td>30</td>
<td>0.339</td>
</tr>
<tr>
<td>40</td>
<td>0.341</td>
</tr>
<tr>
<td>50</td>
<td>0.341</td>
</tr>
<tr>
<td>60</td>
<td>0.341</td>
</tr>
<tr>
<td>70</td>
<td>0.343</td>
</tr>
<tr>
<td>80</td>
<td>0.343</td>
</tr>
<tr>
<td>90</td>
<td>0.345</td>
</tr>
</tbody>
</table>

Effect of organic solvents

It is well known that presence of an organic solvent influences a complexation reaction. The author has studied the effect of organic solvents keeping them 50 percent by volume in each case. The absorbance values are measured in each case and data is presented in table 3.10.5. An analysis of the data reveals that the absorbance values decrease in presence of the solvents employed. The results may be attributed to the changes in the composition of the medium as well as unfavorable conditions for complex formation.
Composition of the complex

The author has determined the stability constant and composition of the complex employing 1. Job's method and 2. mole ratio method.

Job's method

Equimolar concentrations of Cu(II) and p-HAPTSC are taken and their volumes are varied. The absorbance values are measured and a graph is plotted between mole fraction of the metal ion and absorbance. The data is shown in table 3.10.6. From figure 3.10.4. It is observed that composition of complex is 1:1 between Cu(II) and p-HAPTSC. The stability constant of the complex is found to be $2.412 \times 10^7$.

Molar ratio method

The author has kept the concentration of metal ion constant and reagent concentration is continuously varied. The data is shown in table 3.10.7. A graph is drawn between the volume of the reagent and absorbance. It is shown in figure 3.10.5. The composition of the complex is 1:1.
Table 3.10.5

Effect of Organic solvents

\[
\begin{align*}
[Cu(II)] &= 3 \times 10^{-5} M \\
[p\text{-HAPTSC}] &= 3 \times 10^{-4} M \\
\lambda_{\text{max}} &= 356 \text{ nm} \\
pH &= 7.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>Solvent (50% V/V)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.345</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.328</td>
</tr>
<tr>
<td>DMF</td>
<td>0.238</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.206</td>
</tr>
<tr>
<td>Dioxane</td>
<td>0.003</td>
</tr>
</tbody>
</table>
Table 3.10.6
Job’s method of continuous variation of Cu(II)-p-HAPTSC complex

\[ [\text{Cu(II)}] = [\text{p-HAPTSC}] = 4 \times 10^{-5}\text{M} \]
\[ \lambda_{\text{max}} = 356 \text{ nm} \]
\[ \text{pH} = 7.0 \]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Mole fraction of Metal ion</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.020</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.034</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.049</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.064</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.075</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>0.061</td>
</tr>
<tr>
<td>7</td>
<td>0.7</td>
<td>0.045</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>0.030</td>
</tr>
<tr>
<td>9</td>
<td>0.9</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Fig: 3.10.4  Job’s method of continuous variation of Cu(II)-p-HAPTSC complex
**Table 3.10.7**

Molar ratio method of Cu(II)-p-HAPTSC complex

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Mole of Reagent per 0.5ml of Metal ion</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.020</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.035</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>0.051</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>0.065</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.080</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>0.083</td>
</tr>
<tr>
<td>7</td>
<td>0.7</td>
<td>0.087</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>0.090</td>
</tr>
<tr>
<td>9</td>
<td>0.9</td>
<td>0.093</td>
</tr>
</tbody>
</table>

**Fig: 3.10.5** Molar ratio method of Cu(II)-p-HAPTSC complex
Effect of foreign ions

The effect of foreign ions on determination of Cu(II) is studied. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ±2% in the absorbance. The tolerance limit values of various foreign ions in the determination of 2.542 µg/ml copper are presented in the table 3.10.8

Statistical analysis of the data

Statistical analysis of the data obtained in the experiment on copper with p-HAPTSC system is carried out. The standard deviation and relative standard deviation are calculated and the data is presented in the table 3.10.9
Table 3.10.8

Tolerance limit of foreign ions

Tolerance limit of foreign ions in the determination of 2.542 µg/ml of Cu(II)
\( \text{pH} = 7.0; \lambda_{\text{max}} = 356 \text{ nm} \)

<table>
<thead>
<tr>
<th>Foreign ion</th>
<th>Tolerance limit (µg/ml)</th>
<th>Foreign ion</th>
<th>Tolerance limit (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride</td>
<td>35.35</td>
<td>Al (III)</td>
<td>12.01</td>
</tr>
<tr>
<td>Chloride</td>
<td>35.00</td>
<td>Pb (II)</td>
<td>19.27</td>
</tr>
<tr>
<td>iodide</td>
<td>203.05</td>
<td>W (VI)</td>
<td>21.67</td>
</tr>
<tr>
<td>nitrate</td>
<td>32.42</td>
<td>Co (II)</td>
<td>3.93</td>
</tr>
<tr>
<td>acetate</td>
<td>248.42</td>
<td>Se (IV)</td>
<td>10.19</td>
</tr>
<tr>
<td>oxalate</td>
<td>42.50</td>
<td>Mn (II)</td>
<td>8.89</td>
</tr>
<tr>
<td>EDTA</td>
<td>78.0</td>
<td>Cd (II)</td>
<td>8.56</td>
</tr>
<tr>
<td>thiosulphate</td>
<td>36.13</td>
<td>Zn (II)</td>
<td>10.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ru (III)</td>
<td>26.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ni (II)</td>
<td>10.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Th (IV)</td>
<td>16.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr (VI)</td>
<td>0.315</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U (VI)</td>
<td>15.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti (IV)</td>
<td>6.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zr (IV)</td>
<td>9.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V (IV)</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn (II)</td>
<td>4.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sr (II)</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ir (III)</td>
<td>32.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe (II)</td>
<td>8.87</td>
</tr>
</tbody>
</table>
Table 3.10.9

Statistical analysis of the data

\[
\begin{align*}
[Cu(II)] & = 4 \times 10^5 M \\
[p-HAPTSC] & = 4 \times 10^4 M \\
\lambda_{\text{max}} & = 356 \text{ nm} \\
pH & = 7.0
\end{align*}
\]

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Volume of metal ion (1 ml)</th>
<th>Volume of reagent (1 ml)</th>
<th>Absorbance (x)</th>
<th>d (X - M)</th>
<th>d^2 (X - M)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.452</td>
<td>-0.0037</td>
<td>0.00001369</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0.453</td>
<td>-0.0027</td>
<td>0.00000729</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
<td>0.453</td>
<td>-0.0027</td>
<td>0.00000729</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0.456</td>
<td>+0.0003</td>
<td>0.00000009</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0.456</td>
<td>+0.0003</td>
<td>0.00000009</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>1</td>
<td>0.455</td>
<td>-0.0007</td>
<td>0.00000049</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
<td>0.457</td>
<td>+0.0013</td>
<td>0.00000169</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1</td>
<td>0.455</td>
<td>-0.0007</td>
<td>0.00000049</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>1</td>
<td>0.459</td>
<td>+0.0033</td>
<td>0.00001089</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>0.461</td>
<td>+0.0053</td>
<td>0.00002809</td>
</tr>
</tbody>
</table>

Standard Deviation (S.D.) = 0.002648 for ten determinations
R.S.D. = 0.581 %
Applications

One liter of tap, distilled water sample was filtered, the pH adjusted to 1 with concentrated HCl to prevent losses by sorption or coprecipitation, and preserved in high quality clean plastic containers.

To investigate the applicability of the present method to natural water samples, the recoveries of known amounts of Cu(II) added to these samples were examined.

A known aliquot of the sample solution was taken in a 25 ml standard flask containing 10 ml of buffer solution, then $1 \times 10^{-3}$ M of the reagent solution was added. The contents were made up to the mark with distilled water. The absorption of the complex was measured at 356 nm against respective reagent blank solution. The absorbance values were referred to the predetermined calibration plot to compute the unknown amount of the metal ion.

Table 3.10.10

Determination of copper(II) in natural water samples

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Cu(II) added</th>
<th>Spectrophotometric method</th>
<th>AAS method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Found ($\mu$g/ml)</td>
<td>Recovery(%)</td>
</tr>
<tr>
<td>Distilled water</td>
<td>-</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.596</td>
<td>99.33</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.492</td>
<td>99.47</td>
</tr>
<tr>
<td>Our laboratory water</td>
<td>-</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.593</td>
<td>98.83</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.491</td>
<td>99.40</td>
</tr>
</tbody>
</table>

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