Study on Complex Formation of Cu(II) with Water Insoluble PAN in Acidic Water, Using UV-Vis Spectrophotometer

Khokan Chandra Sarker 1*, Md. Rafique Ullaha 2

1. Post graduate student, Department of Chemistry, Faculty of Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh.
2. Professor, Department of Chemistry, Faculty of Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh.

1-(2-pyridylazo)-2-naphththal (PAN) is insoluble in water but soluble in organic solvent such as ether, alcholoh, chloroform, and surfactant solution etc. but we have used acid and water to soluble PAN. The absorption spectrum of the PAN solution system in 1M HCl medium was recorded using the UV-Vis. spectrophotometer. The absorption spectrum of the PAN are a symmetric curve with the maximum absorbance at $\lambda_{max}=440\text{nm}$ which is different from organic media that is at $\lambda_{max}=427\text{nm}$. Cu(II) at trace level form pink color complex with PAN in acidic media at pH 2.00 to 2.50. The amount of Cu(II)-PAN complex has measured by UV-Vis. spectrophotometer, PAN reacts in highly acidic solution with Cu(II) to give a pink chelate which has an absorption maximum ($\lambda_{max}$) that is 550nm. The reaction is instantaneous and absorbance remains stable for over 48 hrs. The average molar absorption coefficient ($\varepsilon$) was found to be $2.05 \times 10^4 \text{L mol}^{-1}\text{cm}^{-1}$, Sandell sensitivity is $3.23 \times 10^{-4} \mu\text{g cm}^{-2}$.

Keyword: Solubilization, Complexation, 1-(2-pyridylazo)-2-naphththal (PAN), UV-Vis. Spectrophotometer.

1. Introduction
PAN is insoluble in water, but soluble in organic solvent. We have used acidic water to soluble PAN. Different types of metal ions were used with acidic PAN solution to obtain colour complex through the novel reaction techniques. Finally Trace amount of toxic element copper was used by spectrophotometric method using PAN as a new spectrophotometric reagent. PAN has been reported as a spectrophotometric reagent for Co, Ni, Zn, Mn, Ca [1] but has not previously been used for spectrophotometric measurement of Cu(II) in acidic aqueous medium below pH 2.50. Reaction of non-absorbent PAN in highly acidic solution with copper to produce a highly absorbent deep pink chelate product, followed by direct measurement of the absorbance in aqueous solution.

2. Experimental:
2.1 Apparatus:
A shimadzu (Kyoto, Japan) (Model-1601PC) double beam UV/Vis. recording spectrophotometer and Jenway (England, U.K.) (Model-3010) pH meter were used for the measurement of absorbance and pH, respectively.

2.2 PAN Solution (4.01x 10^{-4} \text{M/L}):
PAN solution was prepared by dissolving the requisite amount of 1-(2-pyridylazo)-2-naphththal (PAN) (BDH chemicals) in a known volume of highly acidified (HCl) de-ionized water.
2.3 Cu(II) Standard Solutions:
A 100mL of stock solution of divalent copper was prepared by dissolving 0.03929mg of AR crystallize copper sulfate (CuSO_4\cdot5H_2O) (Merck) in doubly distilled de-ionized water. Aliquots of this solution were standardized by EDTA titration using Sulfon black-T as indicator.

3. Results and discussion:
3.1 Spectrum of PAN:
The spectrum of the PAN solution system in acidic (HCl) medium was recorded using the UV-Vis spectrophotometer. The absorption spectrum of the PAN at different pH and concentration are a symmetric curve with the maximum absorbance co-efficient is shown in Fig-1.a, Fig-1.c and graph of absorbance-concentration of PAN at pH 2.00 is given in figure-1.b, and figure-1.d describe absorbance-pH of PAN solution. In all instances measurements were made at λ_{max}=440nm against a reagent blank.

![1-(2-pyridylazo)-2-naphthal (PAN)](image)

Fig 1(a): Absorption spectrum at different concentration of PAN (4.0×10^{-6}M/L to 8.0×10^{-5}M/L) at pH=2.5, λ_{max}=440 nm in aqueous solution.

Fig 1(b): Absorption of different concentration of PAN (4.0×10^{-6}M/L to 8.0×10^{-5}M/L) at pH=2.5, λ_{max}=440 nm in aqueous solution.

Fig 1(c): Absorption spectrum at different pH (1.00 - 3.00) of PAN (6.0×10^{-6}M/L) at λ_{max}=440nm in aqueous solution.

Fig 1(d): Absorbance at different pH (1.00 -3.00) of PAN (6.0×10^{-6}M/L) at λ_{max}=440nm in aqueous solution.
3.2 Spectrum of PAN and Cu(II)-PAN Complex:
The spectrum of the PAN and Cu(II)-PAN solution system was recorded using the UV-Vis. spectrophotometer. Overlay of absorption spectrum of PAN and Cu(II)-PAN against the reagent blank at pH=2.50 in aqueous solution is shown in Fig.-2. At \( \lambda_{\text{Max}} = 550\text{nm} \) the absorbance values of PAN solution is about to zero. The reaction mechanism of the present method is as reported earlier \[2\].

![Fig 2: Absorption spectrum of PAN and Cu(II)-PAN against the reagent blank at pH=2.50 in aqueous solution.](image)

3.3 Acid and pH Effects:
Hydrochloric acid was found to be the best acid for the system. To see the effect of different pH we have taken 0.5ppm Cu(II) solution, the absorbance was measured at different pH from 1.00 to 3.00. The absorbance was maximum when the pH of the solution is 2.50 at room temperature (25±5) \(^\circ\)C. Outside this range of acidity, the absorbance decreased, Fig.-3 and overlay of absorption spectrum shown in Fig.-3.a, pH of the solution was controlled using hydrochloric acid and ammonium hydroxide. At higher concentration of PAN solution starts to form ppt even at pH 2.00. So we have used the lower concentrated solution \( (4.0 \times 10^{-4}\text{M/L}) \) of PAN.

![Fig 3: Effect of pH on the absorbance of Cu(II)-PAN 1:10) complex.](image)

3.4 Effect of Time:
The reaction is instantaneous and remained strictly unaltered for 48 hours at room temperature (25±5) \(^\circ\)C. The overlay of absorption spectrum of Cu(II)-PAN (1:10) at different time is shown in Fig.-3. At pH over 3.00 Cu(II)-PAN complexes and PAN itself start to form ppt in solution.

![Fig 3(a): The overlay of absorption spectrum of Cu(II)-PAN (1:10) at different pH (1.00-3.00).](image)
3.5 Effect of Reagent Concentration:
Different molar excesses of PAN were added to fixed metal ion concentration and absorbances were measured. It was observed that at the 1ppm Cu(II) metal the reagent molar ratios of 1:2–1:20 produce a constant absorbance of the Cu(II)-PAN complex (Fig. 5). For all subsequent measurements different amount (mL) of $4.01 \times 10^{-4}$ M/L, PAN reagent was added.

3.6 Test of Beer’s law:
The effect of metal concentration was studied over 0.01–5.0 µg L$^{-1}$. The absorbance was linear for 0.1–4.0 µg L$^{-1}$ of Cu(II)-PAN at $\lambda_{max}=550$ nm. The molar absorption coefficient, ($\varepsilon$) $^{[3]}$ was found to be $2.05 \times 10^{4}$ L mol$^{-1}$ cm$^{-1}$. Of the calibration graph which that showing the limit of linearity range is given in (Fig.-6).

3.7 Composition of the absorbent Complex:
Job’s method $^{[4]}$ of continuous variation and the molar-ratio method $^{[5]}$ were applied to ascertain the stoichiometric composition of the complex. A Cu(II)–PAN (1:2) complex was indicated by both methods.
Selected Analytical Parameters Obtained with the Optimization Experiments:

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<tr>
<th>Parameter</th>
<th>Studied Range</th>
<th>Selected Value</th>
</tr>
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<tbody>
<tr>
<td>Wavelength, $\lambda_{\text{max}}$(nm)</td>
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<tr>
<td>pH</td>
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<td>2.30 – 2.50</td>
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<tr>
<td>Time, hours</td>
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<td>24</td>
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<tr>
<td>Temperature, °C</td>
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<td>25 ±5</td>
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<tr>
<td>Reagent (fold molar excess, M: R)</td>
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<td>1 : 5 – 1: 10</td>
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<tr>
<td>Linear range, µgL-1</td>
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<td>0.1 – 5.0</td>
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<tr>
<td>Detection limit, µgL-1</td>
<td>0.1 – 20</td>
<td>0.1 – 4.0</td>
</tr>
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</table>

4. Conclusions:
In this Thesis a new simple, sensitive, and inexpensive technique to soluble PAN in water and Cu(II)-PAN complex formation and measurement of Cu(II)-PAN complex in acidic aqueous medium. Although many organic solvents are available for solubilization and complex formation with Cu(II), and measurement using UV-Vis Spectrophotometer, factors such as the low cost, easy handling, lack of requirement for consumables etc. have caused this to a popular, easy solubilization and complexation procedure in aqueous medium at room temperature (25±5) °C.

5. References