FORMATION AND STABILITY OF NICKEL (II), IRON (II) AND COPPER (II) CHELATES OF INDIGOID

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ABSTRACT

The interactions of Fe(II), Ni(II) and Cu(II) with indigo carmine (IC) were studied by UV–Vis. absorption spectrophotometer. The effect of time on the stoichiometry and stability of the metal chelate formed, revealed a ratio of (1:2) for all chelates, except for Cu(II) which form two chelates with a ratio of (1:1) and (1:2) depending on the concentration of the metal ion and the ligand. The mean values of log $k_2$ for the chelates of Fe and Ni were found to be 7.2 and 8.05 respectively. For Cu chelate(1:1) the mean value of log $k$ was found to be 5.98. The value of log $k_2$ of Cu chelate (1:2) for the first day was found to be 9.2. The stability of these complexes was found to be in the order: Cu(1:2) > Ni > Fe > Cu(1:1). The effect of time on the stability of these complexes showed that, Cu(1:1) and Fe chelates were not affected by time, while there was a decrease in the absorbance of Ni and Cu(1:2) chelates. pH of these complexes were measured without adjustable and plotted against the absorbance. All the complexes were found to be stable in neutral and alkaline media. The study of the effect of direct sun light ensured that the complexes in acidic media were more stable toward sun light, except for Ni which was more stable at the neutral to alkaline media.

Keywords: Metal Chelates, Dye, Stability

INTRODUCTION

Natural dyes extracted from natural living sources such as plants and animals. These dyes, which include mainly carotenoids, hydroxyketones, anthraquinones, naphthoquinones, flavones, flavonols, flavonones, indigoids and related compounds, are obtained either as coloured compounds or as colorless extracts turn into colored compounds by certain reactions such as hydrolysis, oxidation, condensation, and complexation with transition metal ions (Bener et al., 2010).

Many metal chelates of indigo have been prepared (Larkworthy and Nyholm, 1959; Larkworthy, 1961; Ovarlez et al., 2011; Angewandte, 1989; Nawn et al., 2011; Oakley et al., 2010; Domenech et al., 2009; Raya et al., 2010), one of these chelates is the iron bis-indigo whose magnetic measurements suggests a tetrahedral configuration for the apparently 4-coordinate metal atom, but octahedral coordination to neighboring molecule is also possible. The study of catalytic activity of Rhodium-indigo complexes showed that they are effective catalysts for isotope exchange reaction between hydrogen and water (Sakharovskii et al., 1978). Indigo is considered as a new source of valuable antioxidants (Kim et al., 2012), its contents of bioactive compounds such as antioxidants and antiproliferative and their activities compare to that of another medicinal plant Prolipid has been studied (Xia et al., 2011). Most studies on indigo have focused on their properties as dyes (Littmann, 1982; Domenech and Domenech, 2009; Papanastasiou et al., 2012; Giustetto et al., 2011; Balfour, 1998). Indigo carmine have been used in the test for nitrate found as impurity in Bismuth salts (Ashutosh, 2005). Indigo carmine is not found to have any toxicity to human luteal cells (Mahadevan et al., 1993) when used as an alternative contrast-enhancing agent to methylene blue in carcinoma of the esophagus (Lamsabhi et al., 2005)

The disposal of industrial waste containing dyes is considered as one of serious pollutants to aquatic environment. Several methods are adopted for removing dyes from waste water (Olak et al., 2009;
Bayramoglu et al., 2009; Merzouk et al., 2009; Eyvaz et al., 2009; Ahmad and Puasa, 2007), among which the photodecomposition method is the most popular and widely studied (Saien et al., 2009; Mao and Weng, 2009). Several approaches are employed for the degradation of indigo carmine (Lichtfouse and Schwarzbauer, 2005; Guaraldo et al., 2011; Gemeay et al., 2003; Barka et al., 2008).

MATERIALS AND METHODS
Ammonium Ferrous Sulfate (Hopkins and Williams grade), Copper Chloride, Nickel Chloride and Indigo Carmine, (BDH grade) were weighted and dissolved in a double distilled water.

**Apparatus:**
Measurements of absorption spectra were carried out using UV/Vis. Spectrophotometer (PerkinElmer, model Lambda 2, Germany), the solvent was used as a reference solution, Colorimeter Lab system (5826). pH measurements were carried out using WPA pH Meter Bench CD510C which calibrated against standard buffer solutions.

**Procedure:**
Solutions were made by dissolving an appropriate amount of the compounds in a double distilled water. The stoichiometry of the prepared complexes was determined by Continuous Variation Method (Werner, 1971). The Mole ratio method (Meyer, 1957) was used to confirm the empirical formula of 1:2 Copper complex.

RESULTS AND DISCUSSION
Absorption Spectra:- Figure 2. shows typical absorption curves for equi- molar solutions of Cu(II), Ni(II), and Fe(II) with Indigo Carmine. The molarities of all solutions were kept at 0.001M, and 0.0002 M for 1:2 Copper complex.

The peaks at ratios of 0.34 and 0.45 for copper (II) complex indicate that, under these conditions, two complexes containing Cu(II) and indigo carmine(Figure.1) in the ratios of 1:2 and 1:1 (respectively) are formed, which means that Cu(II) at low concentration combines with indigo carmine at the ratio of 1:2, while at higher concentration the complex formed was in the ratio of 1:1. Molar ratio method was employed to confirm these stoichiometries (Figure 3.)

The resulting curves for Ni(II) and Fe(II) (Figure 2.), showed sharp absorption maxima at 0.39 and 0.36 respectively. This indicate that the only Ni(II) and Fe(II) complexes formed with Indigo carmine in these solutions are in the ratio of 1:2. All these solutions which were prepared according to continuous variations were kept for six days and the stability constants were then determined. It was very interesting to show that the stability constant of Cu(1:2) Chelate is greater than those of the corresponding Fe(II) (1:2), Ni(II) (1:2) and Cu (1:1) chelates. The mean value of log k for Fe(II) (1:2), Ni(II) (1:2) and Cu(II) (1:1) was 7.9, 8.05 and 5.98 respectively, while log k for Cu(II) (1:2) for the first day was 9.7. (Figure4.) showed the plot of stability constant (log k) of Fe(II), Ni(II) and Cu(II) (1:1) versus time (in days).

![Figure 1: Indigo Carmine](image_url)
Figure 2: Continuous variation method. Volume of solutions, 20 cc; curve 1, CuCl₂H₂O (0.0002M), curve 2, NiCl₂.6H₂O, curve 3, FeSO₄(NH₄)₂SO₄.6H₂O, curve 4, CuCl₂.2H₂O

Figure 3: Molar ratio method of Cu-Indigo carmine (1:2); Cu and indigo = 0.002 M

Figure 4: Stability constant (log k) of solutions containing 0.001M metal ions (Fe, Ni and Cu) with 0.001M indigo carmine

All the stability constants were calculated using the following equation:

\[ K_n = \left[ \left( \frac{A}{A_{ex}} \right) C_M \right] \left[ C_M \left( 1 - \frac{A}{A_{ex}} \right) \left( \frac{A}{A_{ex}} \cdot 1/n \right)^n \right] \]

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Where:

- \( n \) = number of moles of ligand per mole of metal.
- \( A \) = maximum absorbance on the curve.
- \( A_{ex} \) = extrapolated absorbance
- \( C_M \) = Total concentration of metal.
- \( C_L \) = Total concentration of ligand.

The results, in general, showed that there is a convergence in the stability constant throughout the week. It is noted that the stability constant of indigo carmine with the metal ions Fe\(^{II}\), Ni\(^{II}\) and Cu\(^{II}\) increases steadily to reach maximum with copper 1:2. The copper 1:1 Chelate is less stable than all complexes in this study.

The relative stabilities of these chelates are in general, agreement with Irving – Williams, order (Catherine et al., 2008). The stability order increases in the order shown below.

\[ Cu(1:1) < Cu(1:2) > Ni > Fe \]

**Effect of experimental variables on the extent of formation and stability of transition metal ions chelates.**

**Effect of time:**
The effect of time on the absorption of chelates was measured at interval of 24 hours for 6 days. The result showed that no change in the absorption of Fe\(^{II}\) and Cu\(^{II}\) (1:1), while the absorbance was remain constant for the first three days for Ni\(^{II}\) Chelate, then decreased, steadily, for the rest of the days. For Cu\(^{II}\) (1:2) chelate the absorbance was decreased steadily (Figure 5).

**Effect of pH**
The effect of pH on the extent of formation and stability has been investigated. An appropriate amount of metal ion and ligand in the ratio required for complex formation were introduced into each of seven sample tubes. The pH of solutions was varied using 0.1 M Sodium hydroxide solution in the range of 3.5 – 10.2. The initial concentration of both metal ion and ligand was kept equal. The result showed that the absorbance of Fe\(^{II}\) and Cu\(^{II}\) (1:1) complexes decreases above pH 9.4, while for Cu\(^{II}\) (1:2) chelate the maximum absorbance occurred at pH 5.2. As the pH increases, the absorbance decreases steadily. The absorbance of Ni\(^{II}\) chelate slightly increases up to the maximum at pH 7.2, then starts to decrease at constant rate at pH range of 7.9 – 9.3, above this value the absorbance decreases again. For Cu\(^{II}\) (1:1) chelate the extent of complex formation increases with increasing in the pH up to 9.4 above which the absorbance starts to decrease. The absorbance reaches its maximum at pH between 6.8 and 8.8.
(1:2) chelate the maximum absorbance obtained at pH 5.2. It was shown that as the pH increases, the absorbance decreases steadily. The result shown in Figure 6.

**Figure 6:** The plot of absorbance versus pH for four metal chelates; Temp. =35 ± 2 °C

**Effect of direct sun light:**
The solutions of metal chelates at different pH were exposed to direct sun light for five hours a day and the absorbance was measured at interval of one hour. For Fe(II) complex, the result revealed that, at pH 3.7, 5.8, and 8.2 the absorbance were remained constant, which means that the chelate is stable in both acidic and basic media within the given pH range and time. Strong alkaline solution caused decrease in the absorbance after exposure for three hours. For Ni(II) complex, the absorbance at pH 3.6 was slightly decreased to a constant value at the end of the first hour exposure. At pH 7.2 the absorbance remains constant, and at pH 7.9 the absorbance decreases at the end of the fourth hour exposure. At pH 10.2 the absorbance decreases steadily and the color of the complex was changed from blue to green after the fifth hour. This result concluded that Nickel chelate was stable towards sun light at pH 7.2. For Cu(II) (1:1) the absorbance at pH 3.5 and 4.4 were not changed. At pH 8.8 the absorbance decreases after one hour and the color was changed from blue to green after four hours exposure. The absorbance at different pH were plotted against the time of exposure (Figure 7, 8, 9).

**Figure 7:** The plot of the absorbance versus exposure’s time (hours) of Fe(II)-indigo carmine chelate; Temp 35 °±2 °C.
Other solutions of Fe(II), Ni(II) and Cu(1:1) chelates with indigo carmine at different pH were exposed to direct sunlight for five hours a day for 6 days. The absorbance was measured at the end of every five hours exposure. The result showed that the stability of Fe(II) complex at pH 3.7 remain constant for the six days. For Cu(II) (1:1) complex, it is observed that there is a decrease in the stability on going from the first day to sixth day, where the stability at pH 3.5 remains constant throughout the six days. The study of Ni(II) complex (Figures 10,11,12) showed a maximum absorbance at pH 5.6 and 7.2 on the second day of exposure. Above pH 7.2 the absorbance decreases steadily. It is concluded that the metal chelates of indigo carmine, in general, are unstable upon exposure to direct sunlight.
Figure 11: The plot of absorbance versus exposure’s time (5 hours a day) for Cu (1:1) chelates; Temp. 35°± 2

Figure 11: The plot of absorbance versus exposure’s time (5 hours a day) for Ni chelates; Temp. 35°± 2

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