

Characterization and Thermodynamics of a Natural Mineral Dye-Based Chromium Complex Dye on Cotton Fabric

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Abstract

Transition metal complex of a bisazo dye derived from p-phenylenediamine extracted from a natural mineral dye and p-nitroaniline was synthesized with the azo dye acting as ligand for the metal complex dye. The ligand, azo dye and the metal complex were characterized using UV-visible spectroscopy, IR spectroscopy and GC-MS. The IR spectroscopy of both the ligand and the complex reveal the presence of azo group (N=N) at 1597 cm⁻¹, N-O at 1384 cm⁻¹ and other Metal-Ligand (M-L) bonds at 418 cm⁻¹. The results were used to establish the type of metal complex formed to be 1:1 (metal: ligand) and possible structure of the complex was proposed. The metal complex dye was applied on cotton fabric and the thermodynamics parameters of the dyeing process were determined. These parameters included the enthalpy change which was -58.94 KJmol⁻¹ and the entropy which was 0.159 KJmol⁻¹. The thermodynamics studies of the dye showed that the dye has high substantivity and fastness that can be useful in dyeing fabric.

Keywords: Mineral dye, p-phenylenediamine, bisazo dye, metal complex dye, cotton fabric

1.0 Introduction

Colourants, which include chromophores of dyes usually consisting of C=C, N=N and C=N as well as aromatic and heterocyclic rings containing oxygen, nitrogen or sulphur have been widely used as dyes owing to their versatility in various fields [1] and high technologies [2], including textiles, paper, leather and plastics industries [3]. Metal-complex dyes are otherwise known as pre-metallized dyes, in which one or two dye molecules are co-ordinated with a metal ion. The dye molecule is typically a monoazo structure containing additional groups such as hydroxyl, carboxyl or amino, which are capable of forming strong co-ordination complexes with transition metal ions such as chromium, cobalt, nickel and copper [4].

Most of the synthesized metal complex dyes involve the use of dyes containing azo groups as ligands. Azo compounds with two phenyl rings separated by an azo (-N=N-) bond are versatile molecules and have received much attention in research areas for both fundamental and application studies. Azo groups do not occur naturally. Most azo dyes contain only one azo group, but some contain two (*disazo*), three (*trisazo*) or more [5]. Azo dyes are the largest and most versatile group of synthetic organic dyes with a tremendous number of industrial applications including textile industries [6]. The general formula for making azo dyes requires two organic compounds namely a coupling component and a diazo component. The two steps involved in the synthesis are diazotization of aromatic primary amines and the coupling reaction between diazonium salts and activated aromatic compounds (phenols or aromatic amines). The formation of diazonium salts starts with the protonation of nitrous acid under strongly acidic conditions and the azo coupling is carried out at low temperature (0–5°C) in the presence of nucleophilic coupling components [7,8].

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Previous studies have reported the synthesis, characterization, application and antimicrobial activity of metal complex dyes [9,10]. In this study, the synthesis of bisazo dye derived from *p*-phenylenediamine extracted from a mineral dye and *p*-nitroaniline as coupling component was investigated. The dye obtained was used to prepare its metal (II) complex dye. The structural elucidation and dyeing rate of the metal-complex dye obtained were investigated; and the thermodynamics parameters of dyeing process were determined and discussed.

2.0 Material and Methods

2.1 Chemicals, Solvents and Equipment

All chemicals and solvents used in this study were of analytical grade. UV-VIS spectra were measured on Aquamate V4.60 spectrophotometer in 200-800 nm range in methanol. IR spectra were recorded using SHIMADZU FT-IR spectrometer in the range of 400-4000 cm^{-1} range.

2.2 Extraction of *p*-phenylenediamine

The rock-like mineral dye (5 g) was ground to fine powder. The extraction of the organic component, *p*-phenylenediamine, was done using diethyl ether (100 ml). The powdered mineral dye was dissolved in the diethyl ether and the mixture was warmed gently until the colour of the mixture changed from colourless to a faintly brown colour. The resulting solution was decanted and the solvent (diethyl ether) was slowly evaporated by heating on a hot plate at 50°C and the *p*-phenylenediamine was collected [11]

2.3 Synthesis of the Ligand (Azo Compound)

p-phenylenediamine (0.4 g) was dissolved in a mixture of 5 ml of water and 10 ml of concentrated hydrochloric acid in an ice bath. Solution of sodium nitrite (2.5 g/10 ml water) was added and stirred for about 1 h till a dark yellow coloured solution was obtained. The coupling agent *p*-nitroaniline (0.12 g) dissolved in ethanol (20 ml) was cooled in ice bath and added to the azo solution slowly with continuous stirring while maintaining the temperature 0-5°C followed by addition of sodium acetate solution till neutralization. The dye was washed with cold water and collected by filtration [12]

2.4 Synthesis of the Complex

Potassium dichromate (1 mmol; 0.294.18 g) and 2 mmol of the ligand prepared separately in methanol (50 mL) were mixed together in a reflux for 2 h. The mixture was left at room temperature for 24 h and the precipitated complex was then filtered and dried [12]. The resulting metal complex was characterized using solubility and spectroscopic analysis (UV Visible Spectrophotometer Aquamate v4.6). The metal complex dye was then applied on cotton fabric and the thermodynamics of dyeing was determined

3.0 Results and Discussion

3.1 Characterization of the Compound

All the synthesized compounds (ligand and complex) were intensely coloured and amorphous powdered solids. The ligand was very soluble in polar organic solvents like methanol, ethanol, acetone, ethyl acetate; and insoluble in non-polar solvents like *n*-hexane (Table 1). The metal complex was soluble in only methanol and ethanol as well as in acidic medium (Table 2). According to the universal rule that "like dissolves like", it can be said that both the ligand and the metal complex dye prepared are polar in nature since they were generally soluble in polar solvents.

3.2 UV-Visible Spectroscopy Analysis

The UV-visible spectroscopy analysis results obtained showed that the ligand and the complex have wavelengths of maximum absorbance at 368 nm and 298.5 nm respectively. This shows the presence of chromophores and other unsaturations in the ligand and complex. The bands were attributed to π - π^* transition of the aromatic rings and n - π^* transition of the N=N group [13]

Table 1: Solubility Test and colour characteristics of the Azo compound (ligand)

Solvent	Solubility	Colour
Methanol	++	Yellow
Ethanol	++	Yellow
Ethyl acetate	++	Yellow
Diethyl ether	+	Pale yellow
n-hexane	--	No colour
Water	+	Pale yellow
Acetone	++	Yellow
Acidic medium	++	Reddish brown
Alkali medium	+	Pale yellow

Note: ++ means very soluble, + means partially soluble, -- means insoluble

Table 2: Solubility Test and Colour Characteristics of the Metal Complex Dye

Solvent	Solubility	Colour
Methanol	++	Brownish yellow
Ethanol	++	Brownish yellow
Ethyl acetate	--	Colourless
Diethyl ether	--	Colourless
n-hexane	--	Colourless
Water	--	Colourless
Acetone	--	Colourless
Acidic medium	++	Brown
Alkali medium	--	Colourless

Note: ++ means very soluble, + means partially soluble, -- means insoluble

3.3. ¹H NMR spectra

The ¹H NMR spectral data of azo dye was recorded in the dye solution. A multiplet at δ 6.17-8.42, obtained was attributed to aromatic protons and δ 1.26-1.94 was attributed to N-H protons [14]. The peak at δ 2.08-2.35 was due to DMSO protons. The ¹H NMR signals were in accordance with the expected structure of azo ligand.

3.4 IR Spectroscopic Analysis

Tables 3 summarizes the IR spectroscopy analysis for the azo compound (ligand) and the complex prepared. The IR spectra of the complexes were compared with that of the free ligand in order to determine the co-ordination sites involved in chelation. From the IR spectroscopic analysis, it was discovered that both the ligand and the complex contain the azo group (-N=N-) as revealed from the peaks between 1515 cm⁻¹ and 1630 cm⁻¹. The peak 1519.96 cm⁻¹ is assigned to the -C=C- aromatic nucleus of both the ligand and the complex. The IR band at 3093.92 cm⁻¹ and 3095.65 cm⁻¹ in the spectrum of the ligand and complex respectively can be attributed to -C-H stretching of the aromatic ring [15]. The peak at 418.57 cm⁻¹ can be attributed to M-N bond (that is Cr-N bond) which was completely absent in spectrum of the ligand indicating the possible coordination between the metal and ligand. Likewise O-H stretching vibration 3394.83 cm⁻¹ was discovered in the spectrum of the complex. This has been attributed to possible coordination of water molecules in the complex dye as reported in a previous study [16].

Table 3: Interpretation of IR spectrum of the Ligand and Complex

Peak (cm ⁻¹)	Assignment	
	Ligand	Complex
1519.96	-C=C- (aromatic)	-C=C- (aromatic)
1344.43	-C-N-	-
3093.92	-C-H- (aromatic)	-
1597.11	-N=N-	-N=N-
1384.94	-N-O-	-N-O-
1111.03	-	-C-N-
3095.65	-	-C-H- (aromatic)
418.57	-	-Cr-N-
3394.83	-	-O-H-

3.5 Kinetics and Thermodynamics Studies of the Dyeing Process

3.5.1 Percentage Exhaustion (%E)

Figures 1, 2 and 3 show the percentage exhaustion of the dye by the fabric at different temperatures of 40°C, 60°C and 80°C respectively at different time interval of 10, 20, 30, 40, 50 and 60 minutes. It was discovered that %E attained its maximum value of 74% at 40°C after 50 minutes. Percentage exhaustion of any dye depends on two major factors namely the concentration of the dye bath and temperature. At higher concentration, the percentage exhaustion is always lower compared to lower concentration when the dye molecules will be able to diffuse well into the fabric due to high volume of the dye in the dye bath. At very high temperatures, the percentage exhaustion attains maximum value at a very short time, after which the phenomenon of bleeding occurs [17].

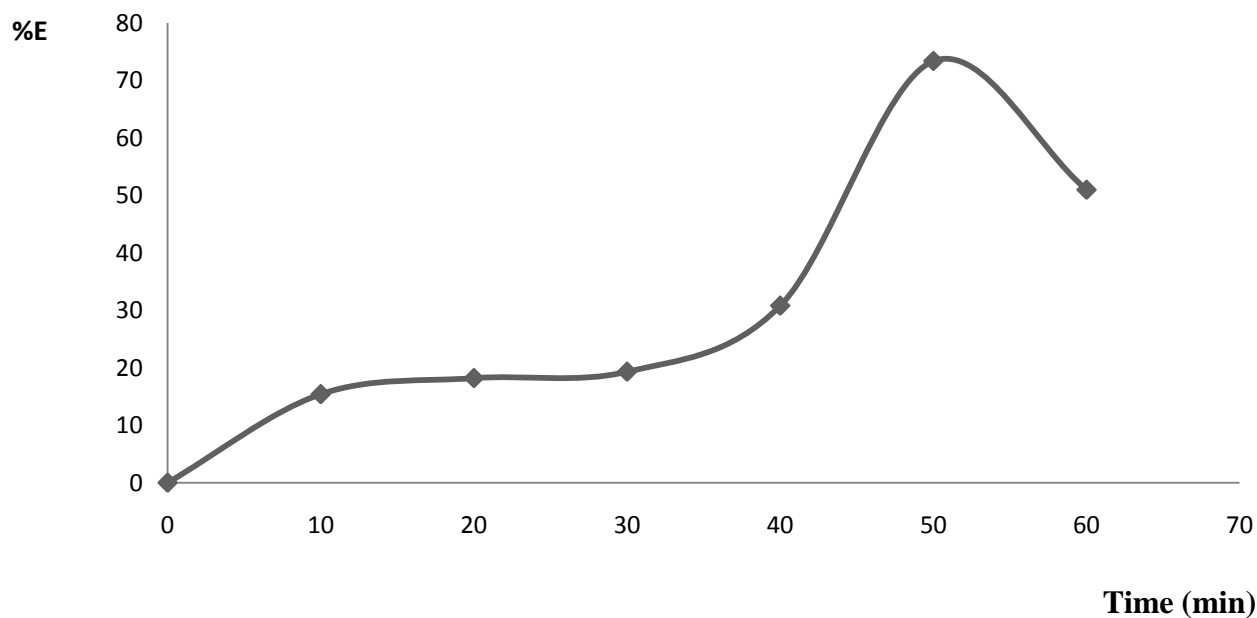


Figure 1: Graph of %E against time at 40°C

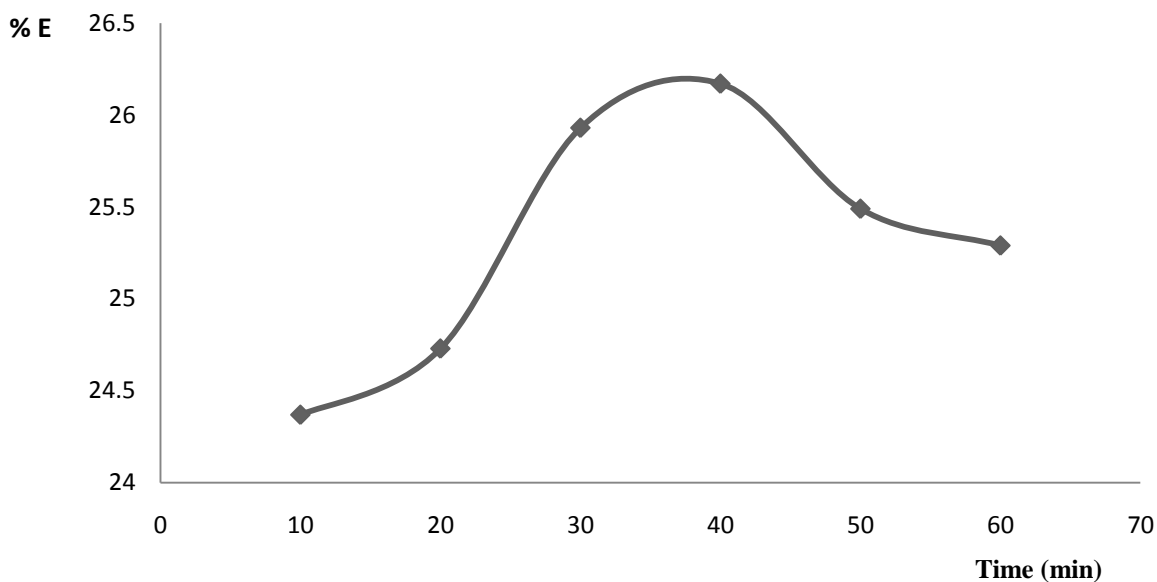


Figure 2: Graph of %E against time at 60°C

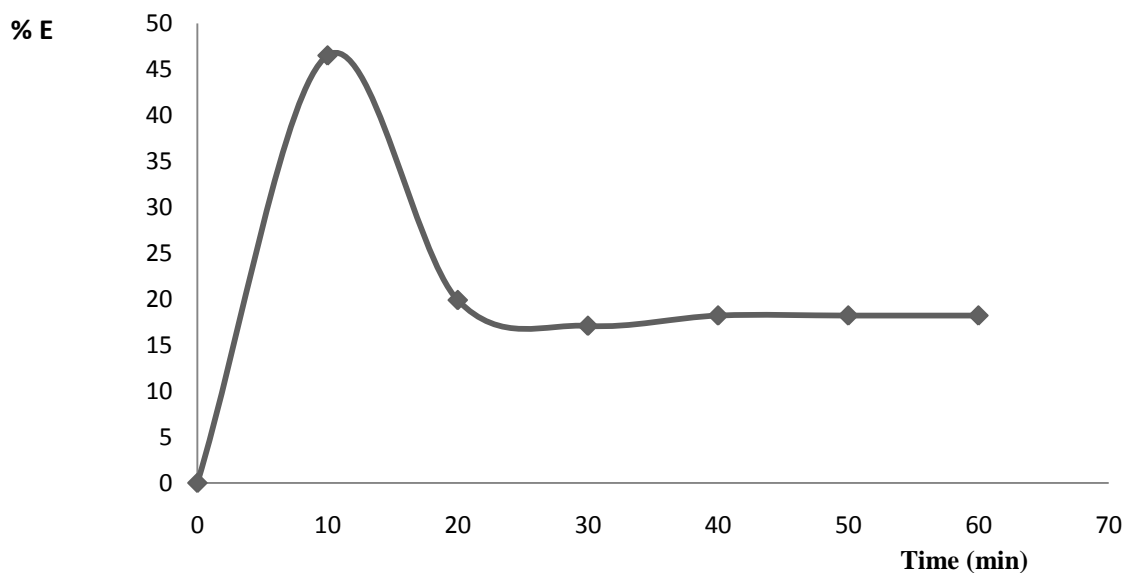


Figure 3: Graph of %E against time at 80°C

3.5.2 Rate of Dyeing

From Figures 1, 2 and 3, the dyeing rates were found to be high at 40°C and observed to increase greatly within the first 10 minutes after which the rate of dyeing drops. This observation revealed the tendency of dye to bleed into hot water as the temperature increases and reduce its dye ability when compared to cooled water. Hence, the dye will ultimately be absorbed by the fabric at lower to moderate temperature than at higher temperatures when equilibrium is established. Greater degree of exhaustion at high is an indication of greater affinity of the dye. Therefore, high %E at 40°C could mean that the dye is of high affinity and substantivity.

3.5.3 Partition Coefficient and Dye Affinity

The partition coefficient of the dye was observed to be high at 40°C and very low at higher temperatures with the lowest value obtained at 80°C. The highest value of partition coefficient at 40°C is an indication of faster rate of migration of dye molecules to the fabric and hence high sorption of the dye molecules to the fabric. High value of partition coefficient has been observed to be an indication of high fastness and substantivity of dye [16, 17].

3.5.4 Enthalpy and Entropy of Dyeing

Figure 4 shows the linear relationship between $\Delta\mu/T$ and $1/T$ on enthalpy change (ΔH) for the dye. The enthalpy change for the dye was determined from the slope of the graph while the entropy change was obtained from the intercept at the $\Delta\mu/T$ axis. The values of the enthalpy and entropy change obtained from the graph are $-58.94 \text{ KJmol}^{-1}$ and 0.159 KJmol^{-1} respectively. Since enthalpy change is related to the measure of absorption strength of the dyes, moderately large negative value of ΔH corresponds to the idea of high potential affinity and a more thermodynamically favourable condition as observed elsewhere [11, 15].

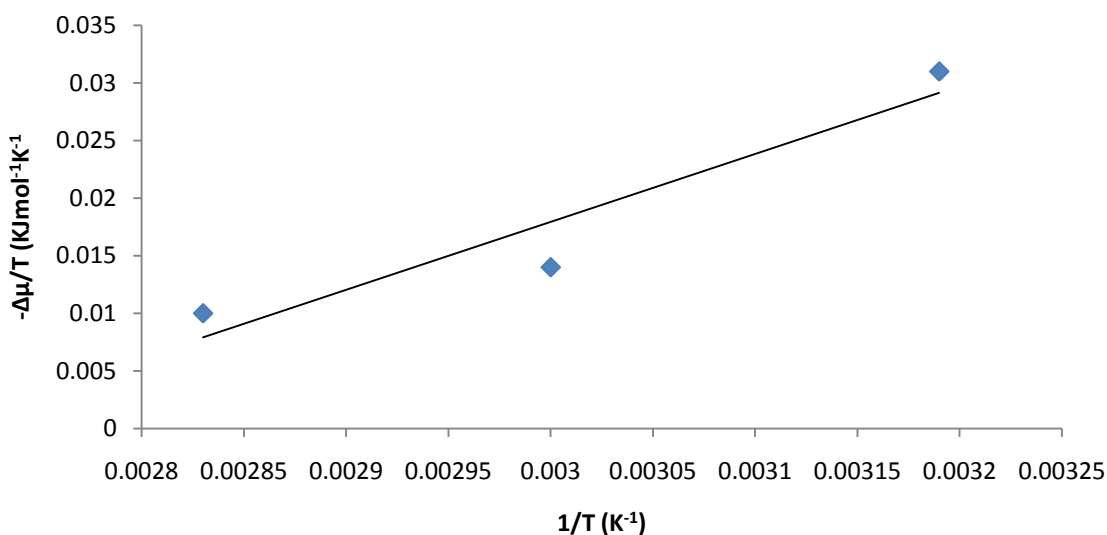


Figure 4: Plot of $-\Delta\mu/T$ against $1/T$

4.0 Proposed Structure of Metal-Complex Dye

The result of the IR spectroscopy analysis showed that a complex was formed, since new bands were observed in the spectrum of the complex which was attributed to metal-ligand bonding. Hence, a possible structure for the complex was proposed (Figure 5).

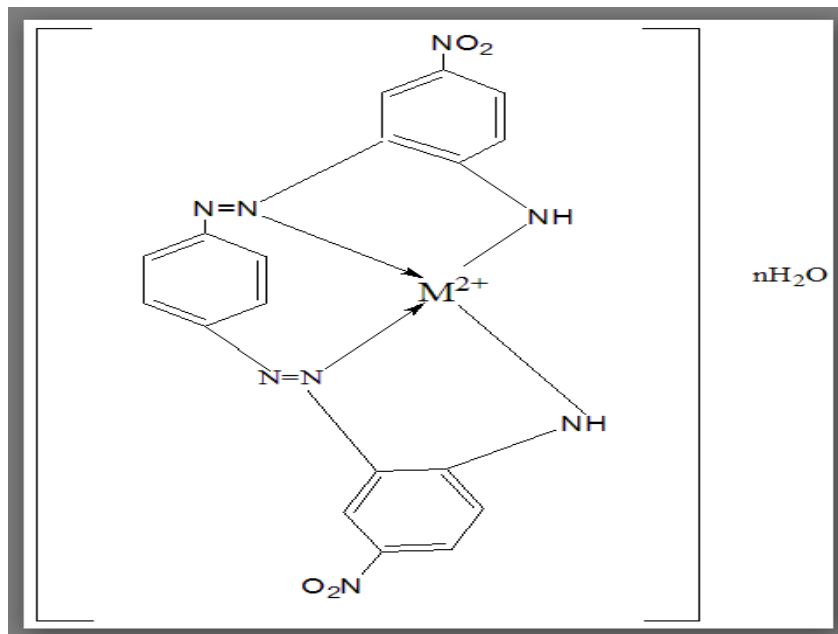


Figure 5: Proposed structure of the metal-complex dye (M is Cr)

5.0 Conclusion

Thermodynamic studies following the application of the metal complex dye on cotton fabric showed that the dye is of high substantivity and fastness at lower temperature.

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