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Synthesis of an azo dye and its cobalt complex derived from 3-aminophenol

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Abstract. *An azo dye derived from 3-aminophenol and its cobalt complex have been synthesized and characterized using Fourier transformed and ultraviolet visible spectrophotometer. The ligand (dye) exhibited an absorption maximum at 470 nm but the absorbance maxima for the synthesized Schiff base complex deviated from 470 to 473 nm which indicated the existent of interaction between the cobalt and the ligand to form metal-dye complex. Moreover, the infrared absorbance band for -N=N- stretching vibration at 1513.3 cm^{-1} for azo dye nut in the complex the frequency shifted to 1457.4 cm^{-1}. The calculated percentage yield of the azo dye was found to be 84% while that of its cobalt complex was 59%.*

Key Words: *Azo dye, ligand, cobalt complex, 3-aminophenol*

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1.0 Introduction

Dye, is a substance used to impart color to textiles, paper, leather and other materials such that the coloring is not readily altered when washed or expose to heat, or other factors the product will be exposed when in use (Stothers, 2017). Dyes possess color because they absorb light in the visible spectrum (400–700 nm), they have at least one chromophore (color-bearing group), possesses a ~~have a~~ conjugated system (i.e. a structure with alternating double and single bonds) and exhibit resonance of electrons, which is a stabilizing force in organic compounds (Abrahart, 1977). Popular chemical groups for dye production include anthraquinone, phthalocyanine and azo groups. However, azo groups are the most important chemically important and most versatile class of synthetic dyes. Azo dyes are widely used in cosmetic, pharmaceuticals, textiles, leather and food industries (Nikfar and Jaberidoost, 2014). The wider applications of these dyes result from a combination of the properties of azo groups and several types of the aromatic- substituted ligand that confer to them intense color over the whole visible range. Azo dyes that contains substituents group on the aromatic rings have also been found to be useful for non-linear optical usage while others have excellent thermal and optical properties that promotes their applications as optical recording medium, toner, inkjet printing, oil soluble light fast dyes, photoconductors for laser printers, nonlinear optics, singlet oxygen generators, dark oxidation catalysts, and high-density memory storage devices (Taura *et al.,* 2014).

Metal complex dyes are complexes synthesized through coordination of bi or polyvalent transition metal ions with dyes (Chakraborty, 2011;). Premetallised dyes (metal complex dyes) are broadly divided into 1:1 and 1:2 meta Zarkogianni *et al.,* 2012l complexes. According to Chavan (2011), the dye molecules are mostly a monoazo structure containing additional groups (such as carboxyk, amino or hydroxyl groups) that are capable of forming strong coordination complexes with transition metal ions (such as Co, Cr, Cu, etc). They are widely applied to wool, silk, polyamides (1:2 complexes) and nylon in order to enhance improved fastness than the parent dye (Hussain, 2011). According to Chavan (2011), metal-complex dyes have good affinity for protein fibres. Most of them have low solubility in water and the solubility decreases from 1:1 to 1:2 complexes (Taura *et al.,* 2014).

In view if the wider application of metal azo dye complexes, there is need to extend synthetic approached to those complexes are have not been adequately studied. Therefore, the present study is aimed at synthesizing 1:2 cobalt complex of azo dye and to characterize it using Fourier transformed infrared and ultraviolet visible spectrophotometers.

2.0. Methodology

2.1. Diazotization of 3-aminophenol

2.50g of 3-aminophenol was weighed and dissolved in a conical flask containing distilled water.5ml of HCl was added slowly and stirred till a complete dissolution was achieved. The solution was allowed to cool on an ice-water bath till its temperature decreases to 5 °C.

2.2. Coupling with 1-Naphthol

i. 3.0g of 1-naphthol was weighed and transferred into a 250 ml conical flask containing 20ml of 1M NaOH. The mixture was warmed on a steam-water bath for complete dissolution. The flask content was allowed to cool on an ice-bath.

ii. 0.3g of $NaNO_2$ was added into 5 ml of distilled water in a conical flask and shaken until it dissolved.

iii. The solution of $NaNO_2$ was transferred into the diazonium salt that was prepared in (A).

iv. 10g of crushed ice was placed into a 250 ml conical flask and 5ml of concentrated HCl was added.

v. The solution that was prepared in (iii) was transferred into (iv) and stirred for 7mins.The solution was allowed to cool in an ice-water bath at a temperature below 5 ºC.

vi. The solution in (i) was poured into and stirred thoroughly

vii. The product was filtered and dried

2.3. Metal complex synthesis

i. 0.35g of unmetalized azo dye was weighed and transferred into a 50ml beaker and 30ml of methanol was added to it.

ii. 0.45g of $CoCl_2$ was dissolved in 30 ml of methanol in a 50 ml beaker.

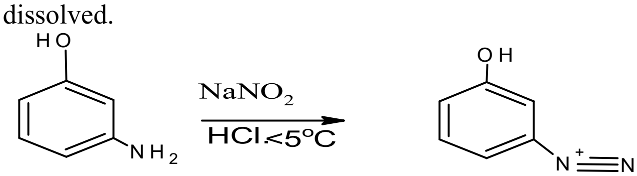
iii. The two solutions were mixed together while adjusting pH to 8 using 0.1M NaOH.

iv. The solution was stirred and heated on a hot plate at 70ºC for 30minutes.

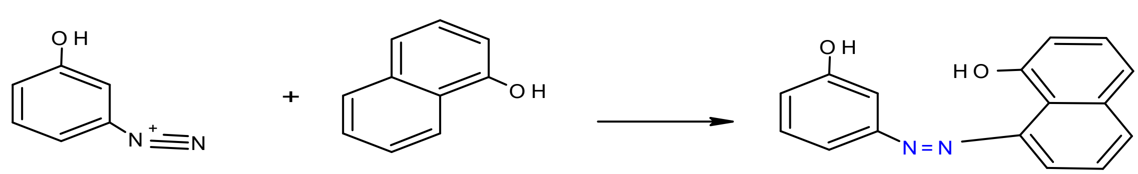
v. The mixture was kept for 24hrs before it was filtered and then wash with methanol and dried.

3.0 Results and Discussion

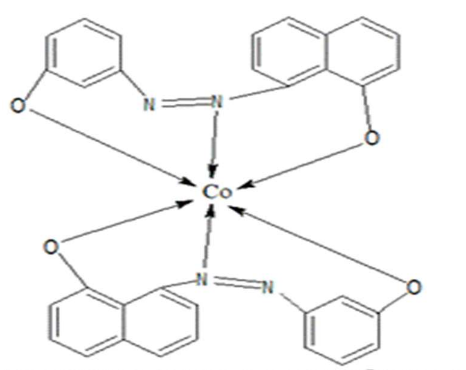
The equation for diazotization of 3-aminophenol is shown in scheme 1 while scheme 2 shows the coupling with naphthol. The proposed structure of the synthesized compound is shown in Scheme 3. In Table 1, names and properties of synthesized metallized and unmetallized dyes are presented



Scheme 1: Equation for diazotization of 3-aminophenol



Scheme 2: Coupling with naphthol



Scheme 3: Proposed metal complex structure

The solubility test results of the synthesized ligand and the metal complex is presented in Table 2

The dye and its metal complex were soluble in methanol and acetic acid. The azo dye was slightly soluble in chloroform and insoluble in water. The metal complex dye was insoluble in both chloroform and water.

Ultra violet visible spectroscopy was employed in order to determine the wavelength of maximum absorption (λ max) for the synthesized dyes. Results obtained are presented in Table 3

Table 1: Names and properties of metallized and un-metallized dye synthesized

Name of dyes	Texture	Colour	Percentage yield	Molecular formula	Molecular weight (g/mol)	M.p (^{O}C)
8-[(*Z*)-(3-hydroxyphenyl)diazenyl]naphthalen-1-ol	Powdery solid	Deep brown	84	$C_{16}H_{12}N_2O_2$	264.28	120
1:2 Cobalt complex of azo dye	Powdery solid	Reddish brown	59	$C_{32}H_{22}CoN_4O_4$	585.47	>360

Table 2: Results of solubility test

Solvent	Unmetallized dye	Metallized dye
Methanol	Soluble	Soluble
Chloroform	Slightly soluble	Insoluble
Acetic acid	Soluble	Soluble
Water	Insoluble	Insoluble

Moreover, the functional groups associated with the dye and the metal dye complex were also determined, and the results obtained are presented in Table 4 and 5 respectively.

Table 3: Wavelength of maximum absorption for the dye and synthesized metal dye complex

Compound	λmax (nm)	Absorbance
Dye	470	1.067
Cobalt complex	473	0.781

Table 4: Functional groups and assignment of the azo dye

Functional group	Experimental peak(cm^{-1})	Proposed functional group
O-H	3280.1	3550-3200 (alcohols and phenols)
C=O	1654.9	1760-1690 (carbonyl stretch)
N=N	1513.3	1450-1600(Azo group)
C-H	1908.4	1650-1600 (alkanes)
C=C	1576.7	1650-1600 (in ring stretch)
C-N	1267.3	1342-1266 (aromatic amines)

Table 5: Functional groups and assignment for the synthesized metal dye complex

Functional group	Experimental peak(cm^{-1})	Proposed functional group
O-H	3330.0	3550-3200(alcohols and phenols)
C=O	1654.9	1760-1690 (carbonyl stretch)
N=N	1457.4	1450-1600(Azo group)
C=C	1625.1	1650-1600 (in ring stretch)
C-N	1300.0	1342-1266 (aromatic amines)

An azo dye was synthesized by coupling diazotized 3-aminophenol with 1-naphthol. Its metal complex was formed by reacting the dye which serves as a ligand with cobalt (II) chloride. The infrared spectra of the azo dye and its cobalt complex were obtained. The appearance of the azo band at (1450-1600 cm-1) confirmed that the synthesized dye and its iron complex contained azo group (Myek *et al.,* 2015).

The FTIR of the azo dye and its metal complex shows the presence of the azo group (-N=N-) at about 1513.3 cm^{-1} and 1457.4 cm^{-1} respectively. C-H aromatic alkenes values were obtained at 1908.4 cm^{-1} for the dye. The phenolic O-H was observed at 3280.1 cm^{-1} for the dye and 3330.0 cm^{-1} for the metal complex. The carbonyl (C=O) stretches were found at 1654.9 cm^{-1} for both azo dye and its metal complex. The ring C=C stretches were observed at 1576.7 cm^{-1} for the dye and 1625.1 cm^{-1} for the metal complex. The ligand (azo dye) exhibited an absorption maximum in methanol solution at 470 nm, upon binding with the Co (II), forming complex, the maximum absorption band was shifted to 473 nm, suggesting an interaction of the Co(II) with the ligand. These results are in agreement with those reported in the literature (Escandar and Sala, 1991; Yogeeswaran *et al.,* 2000; Budzisz et al., 2004; De Giovani and De Souza, 2005) which indicates that the band shift is caused by the binding of the metal ion. The calculated percentage yield of the azo dye was found to be 84% while that of the cobalt complex, 59%. The decreased in yield for iron complex may be due to some interferences during the course of the experiment. Similar result has been reported (Myek *et al.,* 2015).

4.0 Conclusion

At the end of the experiment, an azo dye with proposed name, 8-[(Z)-(3-hydroxyphenyl)diazinyl-naphthalen-1-ol, was synthesized by coupling diazotized 3-aminophenol with 1-naphthol. Its cobalt complex was also produced and characterized using UV and FTIR. The proposed structure of the dye and its metal complex were established based on the results of FTIR analysis. Therefore, a 1:2 cobalt complex can be produced from azo dye.

5.0 References

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