



Synthesis and Dyeing Performance of Azo Acid Dyes Derived From P-Nitroaniline on Semi- Chrome and Vegetable Tanned Leather

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ABSTRACT

P-nitro aniline dye was synthesized by coupling reaction of diazonium salt with 2-amino-8-naphthol Sulphuric acid (J-acid) and 8-amino-1-naphthol 3-6 disulphuric acid (H-acid). Scheme (1) showed the reaction of p-nitro aniline with sodium nitrite in the presence of hydrochloric acid for the production of dye intermediate. Scheme (2) showed the reaction between the dye intermediate and J.acid to generate dye A. Scheme (3) showed the reaction between the dye intermediate and H.acid to yield dye B. The synthesized dyes gave a maximum absorption within the UV- a visible region with λ_{max} 465-500 nm which indicate bathochromic shift and the infra-red spectra showed peaks at $1582-1421\text{cm}^{-1}$ (due to azo group (N=N) stretching vibration), at $3400 - 3200\text{cm}^{-1}$ (due to (OH&NH) medium & broad stretching vibration), at $2830-26-95\text{cm}^{-1}$ (due to aromatic group (C-H) stretching vibration), at $1760-1640\text{cm}^{-1}$ (due to carbonyl group (C=O) stretching vibration), at $1342-1266\text{cm}^{-1}$ (due to aromatic amine group (C-N) stretching vibration) and at $2260-2222\text{cm}^{-1}$ (due to nitrile (C=N) stretching vibration) Fastness properties to light and wash fastness rating of both substrate were (4-5) generally indicating very good to excellent which is attributed to proper penetration, levelness and solubility were achieved. The good shades observed such as light brown and plumb purple may be due to better substantivity, affinity as well as good solubility of the dyes on semi-chrome and vegetable-tanned leather.

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INTRODUCTION

Dyes may be seen as a colourant that has substantively for a substrate, either by reactants or more correctly as a coloured substance capable of application in aqueous or non-aqueous solution or an aqueous dispersion to a substrate so that the substrate acquires a coloured appearance. The substrate usually textile fibre but will also be paper, leather, hair, plastic material. This characteristic is promoted by the existence in the molecule of an organic compound of one or more certain unsaturated groups of atoms called "chromospheres".

C=C -ethylenic group

C=O - keto group

-N=O -nitroso group

-N=N -azo group

NO₂ -nitro group

These are the most important of them. When these chromophores are introduced into an organic compound that absorbs light, only in the ultraviolet region, these groups bring about absorption at lower frequencies and the new compound are coloured. For instance, Anthracene is colourless and anthraquinone is pale-yellow compound because anthraquinone contains two keto group C=O. also, certain substituents such as hydroxyl, amino and substituted amino groups greatly enhance the colour, yielding properties of

chromophores but do not themselves result to absorption in the visible spectrum. These substituents are known as "auxochrome" Synthetic azo dyes are extensively used in textile dyeing, paper printing, colour photography, pharmaceutical, food, cosmetics and leather industries [1] and [2]. Azo compounds are a class of chemical compound that is continuously receiving attention in scientific research [3] and [4]. They are usually strong coloured compounds which can be intensely yellow, red, orange, blue, green etc. depending on the exact structure of the molecule. [5] However, the main focuses of this research is a synthesis of azo acid dyes derived from p-nitro aniline and their application on semi chrome and vegetable-tanned leather for shoe upper production of leather.

MATERIALS AND METHOD

All commercial products were purchased from Sigma-Aldrich. Melting points were determined by the open capillary method using the Gallenkamp melting apparatus. The visible absorption spectra were measured using Agilent CARY 300 UV/Vis spectrophotometer; IR was measured and recorded in KBr pellets

using the Agilent CARY 630 Fourier Transform Infra-red Spectrometer.

METHODOLOGY

Synthesis of Diazonium Salt Solution

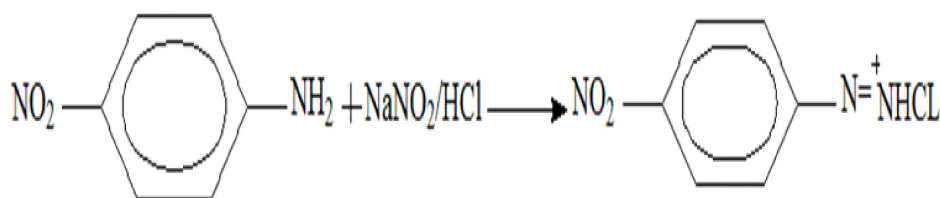
P-nitro aniline (2.0 g) was added to a portion of (1.7 g) of sodium nitrite in the presence of concentrated hydrochloric acid at 0-5°C in an ice bath. The reaction mixture was cooled in an ice bath and stirring for 30 min to obtain the diazonium salt which is the dye intermediate [6]

Coupling of Diazonium Salt Solution

J acid (1.5g) was dissolved in 7cm³ of ethanol and the solution was cooled in ice bath 0-5°C the freshly prepared diazonium salt solution was added drop wise for 15min maintaining the temperature between 0-5°C with vigorous stirring. The dye obtained was collected to wash several times with distilled water and dry in an oven at 40°C. Using the same coupling procedure, control condition and reaction azo acid dye (1-2) was synthesized using J and H- acid as coupling component [7].

Diazotization reaction

Scheme 1; shows the reaction of P-nitro aniline with Sodium Nitrite in the presence of Hydrochloric acid to produce the dye intermediate.



P-nitro aniline

Sodium Nitrite/
Hydrochloric acid

Dye intermediate

Fig. 1: Hydrochloric acid

Coupling Reaction

Scheme 2; shows the reaction between the dye intermediate and 2-amino-8-

naphthol Sulphuric acid to generate dye (1a).

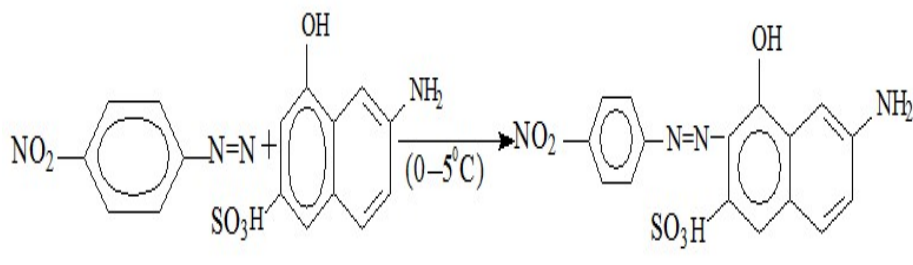


Fig. 2: Structure of Dye 1

Scheme 3; shows the reaction between the dye intermediate and 8-amino-1-naphthol 3-6 disulphuric acid to yield dye (2b).

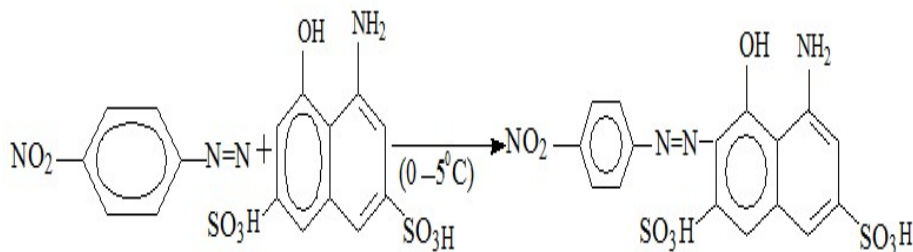


Fig. 3: Structure of Dye 2

Purification of the Dyes

The dyes were purified through the same process of recrystallization as highlighted above for the intermediates. Some of the dyes required the mixed solvent of ethanol, methanol /DMF (9/1 solvent mixture) according to a procedure suggested by [8]. The purity of each synthesized dyes was confirmed by melting point.

Dyeing of Leather

The synthesized dyes were used in the dyeing of semi- chrome and vegetable-tanned leather. The standard method of dyeing leather was followed using the recipe.

- i. 120 % of water (60 °C)
- ii. 2 % of the dye
- iii. 0.1 % of formic acid

A solution of the dye sample (2%) was made with distilled water using heating mantle and the temperature of the medium was raised to 60 °C. The pH of

the bath was adjusted to 5.5 with formic acid. The leather samples were introduced into the bath and run for 1 hour in a mechanical shaker at a controlled speed [9]

Application of Dyes Solution

A solution was prepared by dissolving about 1g of dried dye powder in 100 mls of distilled water. To determine the qualities required for the experiment the following parameter was utilized.

$$\text{Number of ml of stock solution required} = \frac{W \times P}{C}$$

Where W = weight (in grams) of sample to be dyed

P = percentage of dye to be used

C = concentration (%) of stock solution [10].

The general procedure of dyeing chrome tanned leather

1 % of dye (on the weight of the materials)
50 + 2°C dyeing temperature

0.1 % of formic acid on the weight of the dye

Time of dyeing: one hour

Liquor ratio 20:1

Wash Fastness Test Using International Standard Organization 3 (Iso3)

This is to assess the leather resistance to prolong the action of water. 2 x 2 cm of the dyed leather was dipped into the solution made by 5 g (0.5%) of detergent powder into 200 cm³ of distilled water. This was placed in a water bath and the temperature allowed rising to 40 °C. Then it was agitated for about 30 minutes, and the leather was transferred to 100 cm³ distilled water for washing and rinsing for about 5 times and then dried. The colour change was assessed by the standard greyscale.

Light Fastness Test

This method is to determine the resistance of the colour of the leather to the action of ordinary daylight. A piece of dyed leather of size 3 by 3cm was half-covered with a black polythene sheet such half of the length 1.5 by 1.5 cm was half-covered and the remaining half will be left uncovered. This was exposed to daylight

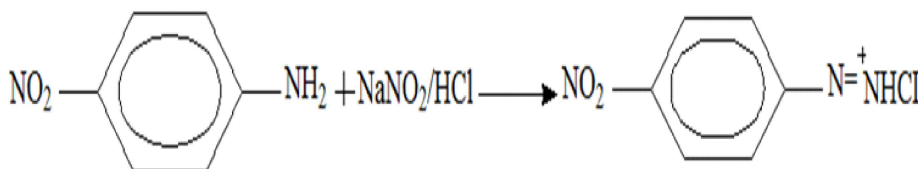
for 5 consecutive days between the hours of 9.00 am-3.00 pm (6 hours); after which the colour change was compared to the uncovered and unexposed leather respectively; using the standard grey scale.

Ultra Violet- Visible Spectroscopic Analysis

1g of the dye sample was obtained using an analytical weighing balance and dissolved in 10 cm³ distilled water in a test-tube respectively. Each of the dye solutions was diluted in the following order; 1 cm of the dyed sample was measured in each case into different test-tube and 9cm³ of distilled water was added respectively. The UV-Visible spectrophotometer (Jenway 6305 spectrophotometer) was used to determine the different absorbance of the different dye sample at a different wavelength from 400-750 nm with an interval of 10 minutes.

RESULT AND DISCUSSION

Scheme 1; shows the reaction of P-nitro aniline with Sodium Nitrite in the presence of Hydrochloric acid to produce the dye intermediate.



P-nitro aniline

Sodium Nitrite/

Dye intermite

Fig. 4: Hydrochloric acid

Coupling Reaction

Scheme 2; shows the reaction between the dye intermediate and 2-amino-8-

naphthol Sulphuric acid to generate dye (A).

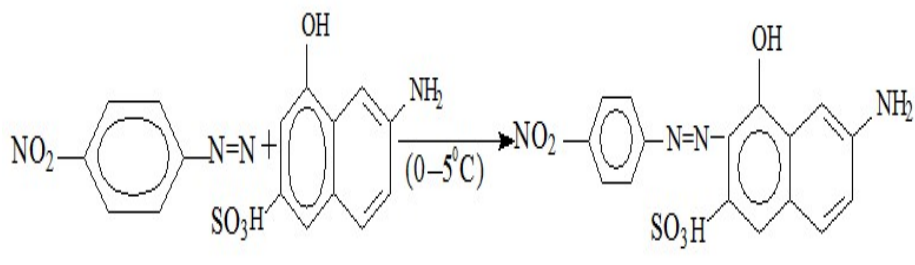


Fig. 5: Structure of Dye A

Scheme 3; shows the reaction between the dye intermediate and 8-amino-1-naphthol 3-6 disulphuric acid to yield dye (B).

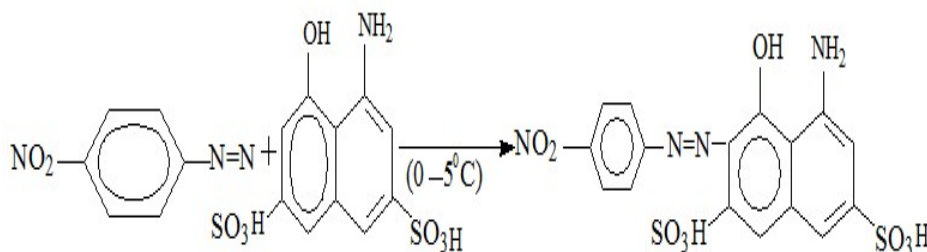


Fig. 6: Structure of Dye B

Synthesis of Diazonium Salt Solution

2.0g of p-nitro aniline was added into the portion of 1.7 g of sodium nitrite that was dissolved with concentrated hydrochloric acid at 0-5 °C in an ice bath. This reaction mixture was carried out in an ice bath, with continuous stirring for 30min. to obtain the diazonium salt which was the dye intermediate.

Coupling of Diazonium Salt Solution

1.5g of J. acid was dissolved in 7 cm³ of ethanol and was cooled in an ice bath between 0-5°C. The freshly prepared diazonium salt solution was added into the dissolved solution of J. acid with vigorous stirring and maintaining the temperature between 0-5°C. A light brown dye was obtained, after which it was filtered and dry the dye an oven at 40°C.

1.5g of H. acid was dissolved in 7cm³ of ethanol and was cooled in an ice bath between 0-5°C. The freshly prepared diazonium salt solution was added into the dissolved solution of J. acid with vigorous stirring and maintaining the temperature

between 0-5°C. A purple dye was obtained, after which it was filtered and oven-dry the dye at 40°C.

The Spectral Data Analysis of Synthesized Azo Acid Dyes

All the compounds showed absorption in the visible region greater or equal to 400 nm which were characteristic of all compound of the dye studied. The azo acid dye: A and B absorbed at 500, 465 nm respectively in distilled water. Both dyes have a bathochromic effect. Maximum absorption moves to longer wavelength as the number of delocalization increases, therefore the maximum absorption moves to shorter frequency, the absorption needing less energy gap between the bonding and antibonding orbitals [11]. The energy difference between the ground and the excited state is reduced leading to a bathochromic shift in the visible absorption band



Assessment of FT-IR Group Absorption Spectroscopic Properties of Synthesized Acid Dye.

The absorption of infrared radiation from the vibrations of atom constituting the molecules showed the functional group present in the molecules of the compound synthesized [12]. It is obvious dye A and B were obtained by diazotization of P-nitroaniline and coupling with 2-amino-8-naphthol sulfuric acid and 8-amino-1-naphthol-3-6, disulfuric acid respectively. The infra-red spectra showed peaks at $1582-1421\text{cm}^{-1}$ (due to azo group (N=N) stretching vibration), at $3400 - 3200\text{ cm}^{-1}$ (due to (OH&NH) medium & broad stretching vibration), at $2830-26-95\text{cm}^{-1}$ (due to aromatic group (C-H) stretching vibration) , at $1760-1640\text{ cm}^{-1}$ (due to carbonyl group (C=O) stretching vibration), at $1342-1266\text{ cm}^{-1}$ (due to aromatic amine group (C-N) stretching vibration) and at $2260-2222\text{ cm}^{-1}$ (due to nitrile (C=N) stretching vibration)

Light Fastness

Lightfastness rating of the dye substrate A and B The test is carried out by exposing each dyed sample to daylight alongside eight blue wool standards. It was observed that lightfastness of dye A and B which is obtained by coupling diazonium salt with 2-amino-8-naphthol sulfonic acid and 8-amino-1-naphthol -3-6 disulfonic acid to obtained azo acid dyes gave a lightfastness rating (4-5) very good to excellent on semi chrome and vegetable-tanned leather, Other dyes gave very well to excellent fastness this, may be attributed to the molecular structure of the dyes, planarity and dye substituents that provided a shield from radiant energy on azo chromophores, therefore, this effect conferred good light fastness properties on the dyes [13]

Washing Fastness

It is a very important requirement that coloured fibres withstand conditions which it may encounter during processing

the following colouration and their subsequent daily use and wash fastness test is important when azo acid dyes are used the dyes are soluble in water. It was observed that wash fastness of dye A and B which is obtained by coupling diazonium salt with 2-amino-8-naphthol sulfuric acid and 8-amino-1-naphthol-3-6 disulfonic acid to obtained azo acid dyes gave a wash fastness rating (4-5) very good and excellent on semi chrome and vegetable-tanned leather. The light brown and plumb purple hues with brighter and deeper shades, high tinctorial strength and excellent levelness on the substrates ranging from very good (4), to excellent (5). The remarkable degree of levelness and brightness after washing indicates good penetration and excellent affinity of the dyes to the substrate and this is necessary for spite the fact that the substrate is quite often very uneven in structure [14]

CONCLUSION

P-nitro aniline dye was synthesized by coupling reaction of diazonium salt with 2-amino-8-naphthol Sulphuric acid (J-acid) and 8-animo-1-naphthol 3-6 disulphuric acid (H-acid). Scheme (1) showed the reaction of p-nitro aniline with sodium nitrite in the presence of hydrochloric acid for the production of dye intermediate. Scheme (2) showed the reaction between the dye intermediate and J.acid to generate dye A. Scheme (3) showed the reaction between the dye intermediate and H.acid to yield dye B. The synthesized dyes gave a maximum absorption within the UV- a visible region with $\lambda_{\text{max}}465-500\text{ nm}$ which indicate bathochromic shift and the infra-red spectra showed peaks at $1582-1421\text{cm}^{-1}$ (due to azo group (N=N) stretching vibration), at $3400 - 3200\text{ cm}^{-1}$ (due to (OH&NH) medium & broad stretching vibration), at $2830-26-95\text{cm}^{-1}$ (due to aromatic group (C-H) stretching vibration) , at $1760-1640\text{ cm}^{-1}$ (due to carbonyl group (C=O) stretching vibration), at $1342-1266\text{ cm}^{-1}$ (due to aromatic amine group



(C-N) stretching vibration) and at 2260-2222 cm^{-1} (due to nitrile (C=N) stretching vibration) Fastness properties to light and wash fastness rating of both substrate were (4-5) generally indicating very good to excellent which is attributed to proper penetration, levelness and solubility were achieved. The good shades observed such as light brown and plumb purple may be due to better substantivity, affinity as well as good solubility of the dyes on semi-chrome and vegetable-tanned leather.

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