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Properties and Evaluation of Azo Acid Dyes Based From 2-Aminothiophene on Chrome Tanned Leather and Nylon 6,6 Substrate

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Abstract

A series of new azo acid dyes have been synthesized in moderate yield by diazotizing 2-amino-thiophene and coupling with R,H,J and ɣ acid. The dyes were characterized by spectroscopic studies. The dyeing capabilities were assessed by applying them on chrome tanned leather and nylon 6,6 substrates. The dyes were found to produced shades of red, dark blue and dark maroon. The synthesized dyes gave a maximum absorption within the UV- visible region with λ_{max}515-597 nm and molar extinction coefficient ranging from (3.217-4.221 x 10^4 l/mol^{-1} cm^{-1}). The chrome tanned leather gave a wash fastness rating ranging from 3(good) 4(very good) to 5(excellent) respectively, and nylon 6,6 gave a wash fastness rating ranging from 4(very good) to 5(excellent) fastness properties and the light fastness properties of chrome tanned leather gave a fastness rating 4(moderate), 5(good), 6(very good) and 7 (excellent) and rubbing fastness rating 4(very good) to 5(excellent) on both substrates. The synthesized azo acid dyes derived from 2-aminothiophene exhibit promising dyeing performance and fastness properties, demonstrating their potential suitability for application on both chrome tanned leather and nylon 6,6 substrates.

Key Words: Azo dyes, Synthesis, Spectroscopic studies, Fastness properties, Diazotization

Introduction

Azo-functionalized dyes bearing aromatic heterocyclic components [1] have attracted ever increasing attention in recent years due to their range of colour, brightness, simplicity, ease of manufacturing, good dyeing performance [2]. Azo compounds are a class of chemical component that are continually receiving attention in scientific research [3-5]. They are usually strong coloured compounds which can be intensely yellow, red, orange, blue and green etc. depending on the exact structure of the molecule. These dyes have

characteristically good tinctorial strength as well as stability. Their preparation procedures by the classic diazotization and coupling reactions, are very simple and of low cost. They have found wide application in dyeing of protein fibers such as wool, angora, cashmere, and silk, as well the milk protein fiber called "Silk Latte", the soy protein fiber called "Soy Silk", and the synthetic polyamide fiber nylon [6-10].

As a result of their colour, azo compounds are tremendous important as dyes and as pigments for a long time [15]. Infact, about half of the dyes in industrial use are azo dyes which are mostly prepared from diazonium salt [16]. Azo dyes, account for more than half of the dye which contain phenol as intermediates. "The aim of the study was to synthesized novel monoazo acid dyes" and the assessment of their fastness properties on chrome tanned leather and nylon 6,6 derive from 5-amino-4-cyano-2-methyl-N-phenylthiophene-3-carboxamide using coupling component such as R ,H, J and ɣ acid.

Material and Methods

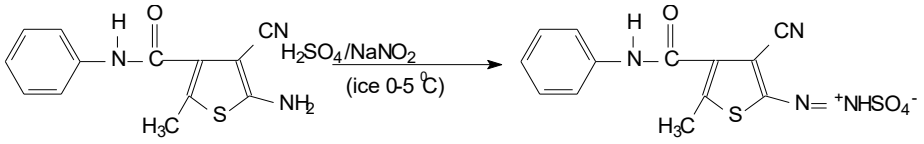
Materials

All commercial products were purchased from Sigma-Aldrich. Such as H-acid, R-acid,J-acid. Gamma-acid, acetic acid, anionic detergent and all reagent are purified.

FT-IR spectrophotometer (Agilent CARRY 630 FT-IR Spectrophotometer, GC-MS spectrometry (7890B GC System).

Synthesis of dye diazonium salt solution Zollinger, [11]

Sodium nitrite (1.38 g, 0.02 mol) was added in portion wise to a 10 cm^3 portion of nitrosyl sulphuric acid added to propionic acid and acetic acid 2:1 and was cooled to 0-5^{o}C in an ice bath. And the mixture was added to the (2.57g, 0.01 mol) intermediate. The reaction mixture was then cooled to 0-5^{o}C and then added in portion wise, stirring continued for 2 hrs at 0-5^{o}C to avoid excess heat that will destroy the diazonium salt. The resulting dye intermediate solution was then obtained.

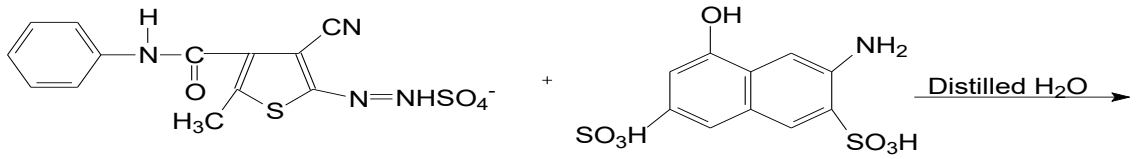


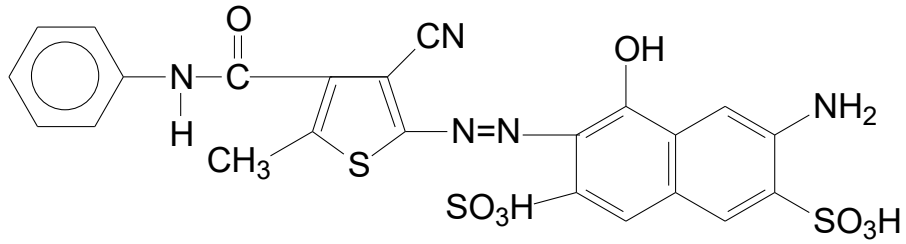
Scheme 1: Schematic route for the synthesis of diazonium salt

Coupling of diazonium salt solution Maradiya, [12]

H-acid (2.0 g, 0.01 mol) was dissolved in 10 cm^3 of distilled water and the solution was cooled to 0-5^{o}C. To the well stirred solution, the freshly prepared diazonium salt solution was added drop wise over 45 minutes maintaining the temperature below 0-5^{o}C with vigorous stirring. The stirring was

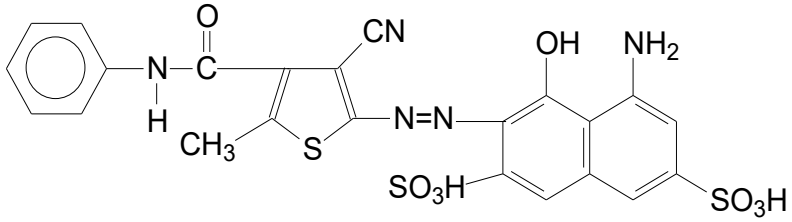
done for 1 hour at 0-5°C, maintaining a pH of 4-5, using sodium carbonate solution (10%$^{w}/_{v}$). The resulting dye was collected, washed several times with water to ensure a free acid and dried in an oven at 40 °C. The result was repeated for R acid.





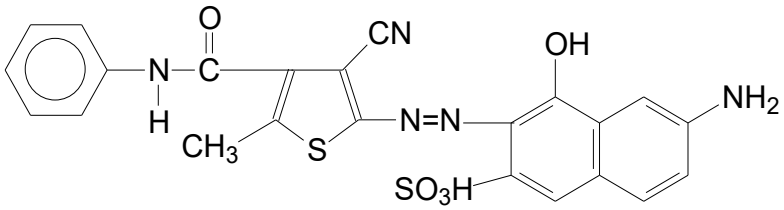
Dye 1a

3-amino-6-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)naphthalene-2,7-disulfonic acid



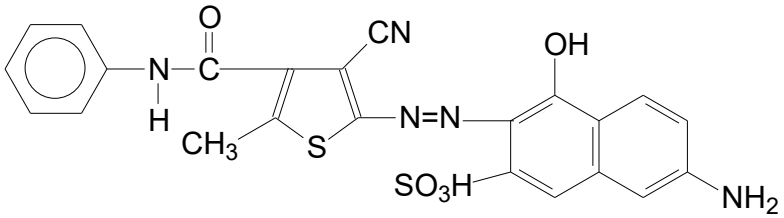
Dye 1b

5-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonic acid



Dye 1c

6-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid



Dye 1d

7-amino-3-((3-cyano-5-methyl-4-(phenylcarbamoyl)thiophen-2-yl)diazenyl)-4-hydroxynaphthalene-2-sulfonic acid

Structures of Synthesized Dyes

Dyeing of nylon 6, 6 fabric

For the nylon 6,6 fibre, a dispersing agent (anionic detergent) was used to facilitate the dyeing process. The fabric was wetted and thoroughly squeezed to remove excess water. It was then immersed into the bath at 70°C and allowed to reach boiling within 15 min.

Dyeing was carried out for one hour at a temperature of 100°C with agitation. At the end of the dyeing process, the substrate was removed, squeezed and rinsed thoroughly under running tap water and allowed to dry at room temperature [13].

Dyeing of leather

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

i. 120 % of water (60 ^{0}C)
ii. 2 % of dye
iii. 0.1 % of formic acid

A solution of the dye sample (2%) was made with distilled water using a heating mantle and the temperature was raised to 60 ^{0}C. The pH of the bath was adjusted to 5.5 with formic acid. The leather samples were introduced into the bath and ran for 1 hour in a mechanical shaker at a controlled speed [14].

Application of dyes solution

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

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 [15]

General procedure of dyeing chrome tanned leather

1 % of dye (on weight of the mater

50 + 2^{o}C dyeing temperature

0.1 % of formic acid on weight of the dye

Time of dyeing: one hour

Liquor ratio 20:1

Determination of dye bath exhaustion

The percentage dye bath exhaustion (%E) for each substrate was calculated using equation below:

$$\% E = \frac{A_o - A_1}{A_o} \times 100$$

Where A_o and A_1 are the absorbance at λ_{max} of the dye bath prior to dyeing and after dyeing respectively.

Fastness Properties of the Substrate

Light, wash and rubbing fastness of dyed substrates according to SLT 401 (IUF 401), by the standard grey scale and rub fastness tester (Machine Model STM) respectively.

Results and Discussion

Table 1: Physical properties of the synthesized dye intermediate

Name of intermediate	Colour	Melting point (°C)	Percentage yield (%)	Molecular weight(g/mol)	Molecular formula
2-aminothiophene	Darkbrown	188-194	97	257	$C_{13}H_{11}ON_3S$

Table 2: Physical properties of the synthesized mono azo acid dyes

Dye no	Molecular formula	Shade crystal	Molecular weight(g/mol)	Melting point (°C)	Percentage yield (%)
1a	$C_{23}H_{17}O_8S_3N_5$	Red	587	200-202	76
1b	$C_{23}H_{17}O_4\ S_3N_5$	Darkblue	587	191-194	62
1c	$C_{26}H_{17}O_5S_2N_5$	Dark maroon	507	120-122	68
1d	$C_{26}H_{17}O_5S_2N_5$	Red	507	212-214	82

Table 3: Spectra data of the synthesized mono azo acid dyes using dimethylformamide and ethanol

Dyes no	λ_{max} in (nm) DMF	λ_{max} in (nm) Ethanol	Molar Extinction Coefficient in(DMF) x 10^4 ($l/mol^{-1}cm^{-1}$)
1a	530	515	4.181
1b	597	572	4.176
1c	580	577	3.217
1d	565	527	4.145

The spectral data analysis of synthesized monoazo acid dyes

The synthesize monoazo acid dye shown in Table 3: 1a, 1b, 1c and 1d absorbed at 530, 597, 580 and 565 nm respectively in dimethylformamide. Dye 1b for instance is more bathochromic compared with dye 1a, 1c and 1d. dye 1b was synthesized from the coupling component of 8- amino-1- naphthol 3-6-disulphuric acid. This is followed by dye 1c containing 2, amino–8–naphthol sulfuric acid as coupling component which absorbed at 580nm and is bathochromic compound with dye 1a and 1d which absorbed at 530 and 565 nm containing 2–naphthol–3–6 disulfuric acid and 2-amino-5-naphthol-7-sulfuric acid respectively, The substituent shifts of maximum wavelength (λ_{max}) absorption to shorter wave length, with reduced absorbance energy, intensifed the colour of dyes.

The colour change observed for each dye is due to the oscillation of electrons and the presence of additional substituents Maximum absorption moves to longer wavelength as the amount of delocalization increases, therefore the maximum absorption moves to shorter frequency, the absorption needing less energy gap between the bonding and anti-bonding orbitals [15].

Table 4: Infrared spectra of mono azo acid dyes

Functional group	OH & NH	Aromatic C-H	Carbonyl C-O	Aromatic amine C-N	Azo N=N
Types of vibration	Stretching	Stretching	Stretching	Stretching	Stretching
1a	3347.1		1636.3	1315.8	1488.6
1b	3377.0		1636.3	1367	1499.4 1529.2
1c	3373.2		1703.4 1654.9	1319.5	1468.5
1d	3410.5		1636.3		1535.7 1468.6

Assessment of FT-IR group absorption spectroscopic properties of synthesized acid dye

It is obvious as shown in Table 4 that Dye 1a – d were obtained by diazotization of 2–aminothiophene and coupling with 2–naphthol–3–6 disulfuric acid, 8–amino–1–naphthol-3-6, disulfuric acid, 2–amino–8–naphthol sulfuric acid and 2–amino–5–naphthol–7 sulfuric acids respectively. The absorption peaks due to (O–H and N–H) group at 3347 cm^{-1}, (C=O) at 1636.3 cm^{-1}, (C–N) at 1315.8 cm^{-1}, and (-N=N-) group at 1488.6 cm^{-1}, stretching vibration in dye 1a. dye 1b which is

obtained by diazotization of diazonium salt coupling with 8–amino–1-naphthol–3-6–disulfuric acid showed absorption peaks due to (O–H and N–H) group at 3377.0 cm^{-1}, (C=O) group at 1636 cm^{-1}, (C–N) at 1367 cm^{-1}, and (-N=N-) group at 1499.4 and 1529.2cm^{-1}, stretching vibration. Dye 1c which is obtained by coupling diazonium salt with 2–amino–8–napthol sulfuric acid gave absorption peak due (O – H)\ and N –H) group at 3373.2 cm^{-1}, (C=O) group at 1703.4 cm^{-1}, and 1654.9cm^{-1}, (C–N) group at 1319.5 cm^{-1}, and (N=N) group at 1468.5 cm^{-1} stretching vibration. Dye 1d which is obtained by coupling diazonium salt with 2–amino–5–naphthol–sulfuric acid showed absorption peak due to (O –H and N – H) group at 3410.5cm^{-1}, (C = O) group at 1636.3 cm^{-1}, (-N=N-) group at 1535.7 cm^{-1}, and 1468.6 cm^{-1}, stretching vibration.

Table 5: Light and wash fastness properties of chrome tanned dyed leather

Dyed no	Light fastness rating	Wash fastness rating
1a	5-6	4-4
1b	5	4-5
1c	5-6	4-5
1d	3-4	3-4

Table 6: Rubbing fastness properties on chrome tanned dyed leather

Dyed no	number of rubs	Fastness rating	Staining of adjacent un-dyed cotton
1a	100	5	4
1b	100	5	4
1c	100	5	3
1d	100	5	3

Tables 6 and 8 show the wash fastness of the dyes coupled with diazoniun salt, 2-naphthol, 3-6 disulfonic acid, 8–amino-1-naphthol; 3-6. Disulphonic acid, 2-amino-8-naphthol sulphonic acid and 2-amino -5- napthol -7- sulphonic acid. These dyes gave purple, brown, pink , deep blue to khaki hues with brighter and deeper shades, high tinctorial strength and excellent levelness on the substrates ranging from good (3), very good (4),to excellent (5) Dye 1a-1d gave a wash fastness rating on chrome tanned leather (3-5) good, very good and excellent which is attributed to dyed in difficult to wash out , while on nylon 6,6 gave a wash fastness rating (3-4) good to very good . It could be seen that chrome tanned leather gave better wash fastness than nylon 6,6. which could

be as result of the texture of the fabric, which in nylon 6,6 involved high diffusion and penetration, and in chrome tanned leather its interweave involve slow diffusion and penetration [16].

Conclusion

A series of new monoazo acid dyes have been synthesized in moderate yield by diazotizing "2-amino-thiophene" and coupling with R , H, J and ɣ acid .The dyes were characterized by spectroscopic studies. The dyeing capabilities were assessed by applying them on chrome tanned leather and nylon 6,6 substrates.

The dyes were found to produce shades of red, dark blue and dark maroon . The synthesized dyes gave a maximum absorption within the UV-visible region with λ_{max}515-597 nm and molar extinction coefficient ranging from (3.217-4.221 x 10^4 l/mol^{-1} cm^{-1}). The chrome tanned leather gave a wash fastness rating ranging from 3(good), 4(very good) to 5(excellent) respectively and nylon 6,6 gave a wash fastness rating ranging from 4(very good) to 5(excellent) fastness properties and the light fastness properties of chrome tanned leather gave a fastness rating 4(moderate), 5(good), 6(very good) and 7(excellent) and rubbing fastness rating 4(very good) to 5(excellent) on both substrates.

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