Original Research Article

UV and IR Characterization of Monoazo Disperse Dyes Synthesized from Aminobenzene and its Derivatives

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Abstract

The potential of amino benzene and its derivatives in the synthesis of monoazo disperse dyes was studied. The dyes were synthesized by the diazotization of amino benzene and its derivatives and subsequent coupling with salicylic acid. The synthesized dyes were subjected to UV and IR characterization and the UV-VIS absorption spectra of the dyes in methanol, ethanol and ethyl acetate revealed that the dyes have absorption bands within the visible region of the electromagnetic spectrum and that the λmax of the dyes increases with increase in polarity of the solvents. The FTIR characterization of the dyes revealed the presence of C – O from phenol, C – N and N – H from amines, C – H from alkane, N = O from nitro compounds and – OH from alcohol and the proposed structures of the dyes revealed the presence of chromophoric, auxochromic and azodic groups which may help to explain why the dyes have excellent colourations. The dyeing and fastness properties of the dyes on nylon, wool, polyester and cotton revealed that the dyes will have commercial importance within the textile industries.

Keywords: Monoazo disperse dyes, azodic groups, characterization, diazotization, coupling.

1.0 INTRODUCTION

Dyes are coloured substances which have the ability to form chemical bond with the substrate to which they are being applied. The colour of a dye is dependent upon the ability of the substance to absorb light within the visible region of the electromagnetic spectrum (380-750 nm). An earlier theory known as Witt's theory (McGraw, 2003) stated that a coloured dye had two components; a chromophore, which is responsible for the colour of the dye (eg. NO_2, -CO, -N=N-, -C=C- groups) and an auxochrome which serves to deepen the colour of the chromogen (e.g. –OH, -NH_2, -NHR, -COOH, -SO_3H) (Taura, 2014).

Disperse dyes are class of sparingly water soluble dyes originally introduced for dyeing cellulose acetate and usually applied from fine aqueous dispersion. Though originally developed to dye cellulose acetate, disperse dyes are now usefully applied to other hydrophobic fibres such as polyester (Meena, 2013). Azo dyes are chemical compounds whose behaviours are characterised by the presence of the azo group (R – N=N –R'), where R and R' are usually aryl groups. They are commercially important dyes, especially, in the treatment of leather and textile materials as well as some food stuff. Because of their increased demand and large production volume, azo dyes play important role in the governing policies of the dye and printing industries (Shankarling, 2017). They are usually synthesized by diazotization and coupling reactions through a different route and modifications in order to obtain a desired colour property, yield and particle size of the dye for improved dispersibility (Shankarling, 2017). And their colours depend on the associated chromophores and auxochromes (Gurses, 2006 and Rauf, 2011).

1.1 Diazotization and Coupling of Azo Compounds

Diazotization is the process of converting aromatic amines into diazonium salst. When a cold solution of a primary aromatic amine in a dilute mineral acid such as hydrochloric acid (HCl) is treated with a cold solution of nitrous acid at about $0 – 5^0C$, a diazonium salt is formed. Nitrous acid (HNO_2) is usually formed when sodium nitrite ($NaNO_2$) and mineral acid (HCl) react together.

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$
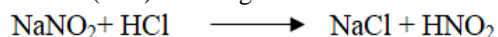
Generally, the preparation of these diazonium salts involves the reaction of an aromatic amine with nitrous acid in the presence of a mineral acid. An example of a diazotization reaction is given below.

$$ArNH_2 + HNO_2 + HCl \longrightarrow ArN_2^+Cl^- + 2H_2O$$
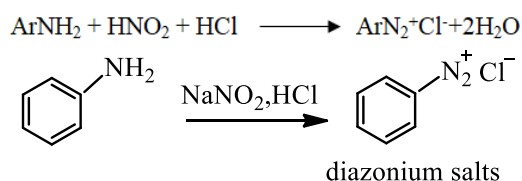
Diazonium salts are a group of organic compounds which share as a common functional group $R - N_2^+ X^-$ where R denotes any organic residue (such as an alkyl or aryl group) and X is an organic or inorganic anion (a halogen, for example).

1.2 Mechanism of Diazotization Reaction

When a nitrous acid is reacted with another mineral acid, a nitrosonium ion is formed.

The positive charge of the nitrosonium ion moves to the electron rich nitrogen, which is directly attached to the aromatic specie to form a new nitrogen – nitrogen bond. This is followed by a subsequent deprotonation to give the n – nitrosamine and in the presence of excess acid, the n – nitrosamine can be converted into a diazohydroxide by protonation and subsequent deprotonation. Diazohydroxide is now protonated and water is removed from the compound to give the required aryl diazonium ion (which can easily be converted into a diazonium salt).

Diazonium salts are important synthetic intermediates that can undergo coupling reactions to form azo dyes and electrophilic substitution reactions to introduce functional groups (Smith, 2007).

2.0 EXPERIMENTAL

The monoazo disperse dyes were produced by the general methods of diazotization and coupling reactions as described by Sharma (2014).

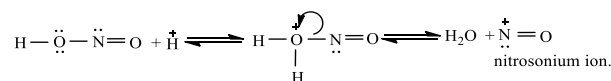### 2.1. General Methods for the Preparation of Diazonium Salt

The diazonium salt was prepared by dissolving 1.73g (0.01M) of 4 – nitroaniline in 10 ml of conc. Hydrochloric acid. The mixture was stirred until the 4 – nitroaniline was completely dissolved. The mixture was gradually added with stirring into another beaker containing 20 ml of 2 M sodium nitrite (which has been previously cooled to below 5℃ in an ice bath) to form a diazonium salt (Diazotization reaction). The mixture was allowed to remain in the ice bath to maintain the temperature at 5℃ prior to the coupling reaction.

2.2. General methods of Coupling Reaction

In order to carry out coupling reaction, 1.38g (0.01 M) of the coupling agent (salicylic acid) was dissolved into a beaker containing 10 ml solution of 2 M sodium hydroxide. The mixture was stirred until complete dissolution was achieved. The beaker was immersed in an ice bath and the temperature allowed to cool below 5℃. While the content of the beakers were still below 5℃, the mixture was coupled by slowly adding the diazonium salt with constant stirring into the mixture of the salicylic acid using a dropping funnel. After the addition, the mixture was left in the ice bath for extra 10 minutes before filtration under vacuum. The solid product was re-crystallized by dissolving in a 30 ml of ethanol, heated to near boiling and allowed to cool to room temperature before immersing in an ice bath for re-crystallization. The solid product was filtered under vacuum, dried and weighed. The dye was stored in a small sample bottle prior to other analysis. These methods were used in synthesizing other dyes.

2.3 Dyeing of fabrics

The dyeing process employed 1: 50 material to dye ratio. For cotton, wool and nylon, a fabric material weighing 1.0 g was wetted with water and the excess water squeezed off with a filter paper, after which, it was introduced into 50 ml of 2% dye solution which has been pre-heated to about 50 ℃. The mixture was

allowed to be heated up to 100℃ and the dying process continued for about 1hr. with occasional gentle stirring. After the dyeing process, the fabric was removed from the dye bath, rinsed with water, air dried and stored in a polyethylene bag prior to the fastness tests (Salah and El-Badry, 2012).

2.4 Dyeing of polyester fabric

Dyeing was carried out by using high temperature high pressure (HTHP) Method. Dyeing solution of 1% stock was prepared by dissolving 1.0 g of the dye in 100.0 g of dimethylformamide solvent. Material to liquor ratio of 1:50 was maintained all through the dyeing process. The fabric was immersed into the dye bath at 50℃ after being wetted in the aqueous solution and dried. The temperature was increased to 130 ℃ and dyeing continued at this temperature for 45 minutes while pH of 4.5 – 5.5 was maintained by using glacial acetic acid. The dyed sample was rinsed in cold water, air dried and presented for fastness tests (Ashitosh, Sandeep and Adivarekar, 2018).

2.5 Wash Fastness Test

The wash fastness was determined according to the International Standard Organization (ISO) washing test number 3. The dyed fabric measuring 10 X 5 cm was removed and treated at $60^{\circ}c$ for about 45 minutes with a mixture that contains 0.5% of soap solution and 0.2% of sodium carbonate solution in the ratio of 50:1. After which, the fabric was washed in a running water and air dried. The change in shade of the material was related to the standard grayscale rating whose indications are 1 to 5 (where 1 is poor and 5 is excellent) (Ukponmwan, Odilora, Offor and Freeman, 1999).

2.6 Light Fastness

The light fastness test was carried by exposing the dyed fabric to sun light for about 35 hours and the change in shade of the material was evaluated according to the standard blue wool fabrics (grade 1 to 8) where 1 is poor and 8 is excellent (Odilora and Omatseye, 2000).

2.7 Heat Fastness

The heat fastness examination was assessed according to ISO 105-PO1 1993. The dyed fabric was exposed to a heat source of about $170^{\circ}c$ for 30 seconds and the change in shade was related to the standard grayscale (grade 1 to 5) where 1 is poor and 5 is excellent (Odilora and Omatseye, 2000).

2.8 Determination of Wavelength of Maximum Absorption ($Λ_{max}$) of The Dyes

The wavelength of maximum absorption of the dyes in methanol, ethanol and ethyl acetate were determined using Drawell D-8 UV-VIS spectrophotometer.

2.9 Determination of the Functional Groups Present in the Dyes

The functional groups present in the dyes were determined using Bulk Scientific M530 USA FTIR spectrophotometer.

2.10 Determination Molar Absorptivity of the Dyes

The molar absorptivity of the dyes were determined according to the method described by Joseph (2020). The absorbance of 1M of the dye in a 1 cm cuvette (path length) was measured and the molar absorptivity calculated using the relationship:

$A = \varepsilon cl$

Where:
A = absorbance
ε = molar absorptivity
C = concentration
l = path length

3.0 RESULTS AND DISCUSSIONS
3.1 RESULTS

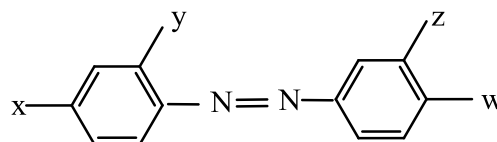The synthesized monoazo disperse dyes can be represented by the general structure.

Fig 1: General structure of the synthesized monoazo dispersed dyes

Where for;
Dye 1: x = H, y = H, z = CO2H, w = OH
Dye 2: x = H, y = NO$_2$, z = CO$_2$H, w = OH
Dye 3: x = NO$_2$, y = H, z = CO$_2$H, w = OH
Dye 4: SO$_3$H, y = H, z = CO$_2$H, w = OH

The molecular formula and the IUPAC nomenclature of the synthesized dyes are presented in the table 1 below; while the physical properties are presented in Table 2.

Table 1: The IUPAC names of the dyes

Dyes	Molecular Formula	IUPAC
Dye 1	C$_{13}$H$_{10}$O$_3$N$_2$	5-(phenylazo) salicylic acid
Dye 2	C$_{13}$H$_9$O$_5$N$_3$	5-[(2-nitrophenyl)azo]salicylic acid
Dye 3	C$_{13}$H$_9$O$_5$N$_3$	5-[(4-nitrophenyl)azo]salicylic acid
Dye 4	C$_{13}$H$_{10}$O$_6$N$_2$S	5-[(sulphanilic acid)azo]salicylic acid

Table 2: Physical properties of the synthesized monoazo disperse dyes

Dyes	MW (g)	Melting Point (°c)	% yield	Colour	Texture
Dye 1	242	311	34.4	Caramel yellow	powder
Dye 2	287	148	61.5	Golden Yellow	powder
Dye 3	287	294	57.9	Maroon Red	powder
Dye 4	322	318	58.6	black	crystalline

The diazotization of aminobenzene and its derivatives and subsequent coupling with salicylic acid produced 4 monoazo disperse dyes. From table 1, the IUPAC names of the dyes are 5-(phenylazo) salicylic acid, 5-[(2-nitrophenyl)azo]salicylic acid, 5-[(4-nitrophenyl)azo]salicylic acid and 5-[(sulphanilic acid)azo]salicylic acid. The dyes have 34.4%, 61.5%, 57.9% and 58.6% yield respectively as shown in Table 2. The proposed structures of the dyes as shown in the figures 1 above revealed the presence of –NO$_2$ and –N=N– which represent the chromophoric and the azodic groups respectively, while the –COOH and –OH represent the auxochromic group. These explain why the dyes have brilliant caramel yellow, golden yellow, maroon red and black colourations respectively. The dyes were synthesized as crystalline solid materials with melting points of 311℃, 148℃, 294℃ and 318℃ respectively.

Table 3: Results of the λmax of the dyes in solvents of different polarity (Methanol, Ethanol and Ethyl acetate)

Dyes	λmax (nm)			Molar Absorptivity
	Methanol	Ethanol	Etheyl acetate	ɛ (dm^{3}mol^{-1}cm^{-1})
Dye 1	432	428	418	2.45 x 10^4
Dye 2	459	451	421	2.32 x 10^4
Dye 3	463	458	446	3.10 x 10^4
Dye 4	431	426	422	2.78 x 10^4

The UV – VIS absorption spectra of the dyes in methanol, ethanol and ethyl acetate are presented in Table 3. The results revealed that the dyes show high λmax of 432nm in methanol which is a more polar solvent than the ethanol and ethyl acetate where the λmax are 428nm and 418nm respectively for dye 1. This trend was also observed in all the dyes and the bathochromic effects observed in the λmax of the dyes in the different solvents is as a result of the lowering of the energy level between $\pi – \pi*$ associated with polarity of solvents. The results also revealed that the dyes absorb at the visible region of the electromagnetic spectrum. However, this explains why the dyes are coloured.

The results also showed the effects of substituents on the λmax of the dyes. The introduction of electron withdrawing groups like NO$_2$ and SO$_3$H causes a bathochromic effects as shown in table 3 above. The higher λmax of dye 3 can be ascribed to the more electron withdrawing tendency and orientation of the NO$_2$. The substituents distort the stability constant of the ring by increasing the HOMO and the LUMO of the dyes. (Soleimani and Taylor, 2008). Also, from the table above, the molar absorptivity of the dyes are within the range of 2.32 x 104 – 3.10 x 10^4 (dm^{3}mol^{-1}cm^{-1}). This according to Efurhievwe (2014), shows that the dyes have commercial importance.

Table 4: The results of IR analysis of functional groups present in the dyes

IR peaks (cm^{-1})									
V$_{O-H}$	V$_{N-H}$	V$_{C-H}$	V$_{C=O}$	Ar-H	V$_{C-NO2}$	V$_{S=O}$	V$_{C-N}$	V$_{C-O}$	V$_{N=N}$
3200-3500	33100-3300	2600-2800	1800-1600	1600-1475	1550-1700	1400-1500	1200-1350	1150-1200	1450-1500

The FTIR characterization of the dyes shows absorption bands that covers a broad range of wavenumbers (1200 – 3500 cm^{-1}). These revealed the peak at 3200-3500 cm^{-1} of O – H groups from both alcohol and carboxylic acids (Otutu, 2014), 3310 – 3300 of N – H from amines, 2600 – 2800 of C – H from alkanes, 1600 – 1800 of C = O groups from COOH, 1475 – 1600 of Ar – H from aromatic group, 1550 – 1700 of N = O from Nitro group, 1400 – 1500 of S = O from sulfonic acid, 1200 – 1350 of C – N from amines, 1150 – 1200 of C – O from phenol and 1450 – 1500 of N=N of the azo group (Mohammed, 2011). The functional groups observed in the dyes conformed to the presence of the chromophoric and the auxochromic groups observed in their structures.

Table 5: Results of fastness properties of the dyes on fabrics

Dye	Fabrics	Colour on Fabrics	Fastness Rating		
			Wash fastness	**Light fastness**	**Heat fastness**
1	cotton	golden	4/5	4/5	4/5
	nylon	golden	4/5	4/5	4/5
	polyester	golden	4/5	4/5	4/5
	Wool	golden	2/5	4/5	3/5
2	cotton	peach	4/5	4/5	4/5
	Nylon	peach	4/5	4/5	4/5
	polyester	peach	4/5	4/5	4/5
	Wool	peach	3/5	4/5	3/5
3	cotton	butter	4/5	4/5	4/5
	Nylon	butter	4/5	4/5	4/5
	polyester	butter	4/5	4/5	4/5
	Wool	butter	3/5	4/5	3/5
4	Cotton	flamingo	4/5	4/5	4/5
	Nylon	flamingo	4/5	4/5	4/5
	Polyester	flamingo	4/5	4/5	4/5
	Wool	flamingo	3/5	4/5	3/5

The results of wash, heat and light fastness of the dyes on wool, cotton, nylon and polyester fabrics are shown in Table 5. The colours of the dyes on the fabrics include golden, peach, butter and flamingo, which show different shades on different fabrics. The colour strength of the dyes was more solid on nylon, followed by cotton, wool and then the polyester. The excellent colour strength as shown by nylon was an indication that the nylon has better affinity for the dye molecules which may be due to non-crystalline nature of the nylon fabric which makes it easier for the dye molecules to penetrate into the material.

The wash, heat and light fastness rating of the dyed fabrics on fabrics are shown on table 5 as well. From the results, the dyes have good fastness properties except for wool which shows a poor wash and heat fastness. The good fastness properties can be attributed to the substituents on the benzene ring. The excellent fastness properties as shown in the results indicate that the dyes can be used in the textile industries for dyeing of nylon, polyester and cotton.

3.0 CONCLUSION

From the results of this work, amino- benzene and its derivatives can be used in the synthesis of monoazo disperse dyes with excellent dyeing, spectra and fastness properties on fabrics like Nylon, Wool, Polyester and Cotton. The dyed fabrics showed excellent colourations and the fastness properties as exhibited by the dyes on fabrics as well as their molar absorptivity of the dyes are good indicators that the dyes will have great industrial application in the textile industries.

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