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Synthesis of Monoazo Dyes From Halogenated Arylamines and Fastness Properties on Cotton and Nylon

Juliana Chineze Obi
Department of Pure and Industrial Chemistry, Faculty of Physical Sciences,
Chukwuemeka Odumegwu Ojukwu University,
Uli, Anambra State, Nigeria

***Emmanuel Ifeanyi Victor**
Department of Pure and Industrial Chemistry, Faculty of Physical Sciences,
Chukwuemeka Odumegwu Ojukwu University,
Uli, Anambra State, Nigeria
iemmanuel385@gmail.com

Azubuike Jeremiah Okolo
Department of Pure and Industrial Chemistry, Faculty of Physical Sciences,
Chukwuemeka Odumegwu Ojukwu University,
Uli, Anambra State, Nigeria
zube4success@yahoo.co.uk

Emeka Friday Onuh
Department of Pure and Industrial Chemistry, Faculty of Physical Sciences,
Chukwuemeka Odumegwu Ojukwu University,
Uli, Anambra State, Nigeria
alphamekonus@gmail.com

Collins C. Osuagwu
Chemical Engineering Department, Faculty of Engineering,
Imo State University,
Owerri, Imo State, Nigeria
mosion22@yahoo.com

Nnaemeka J Okorocha
Department of Pure and Industrial Chemistry,
University of Calabar,
Calabar, Cross River State, Nigeria
emybeck@yahoo.com

Olisa Nwuruku Alfred
Department of Biochemistry (Medical),
Faculty of Sciences,
Ebonyi State University,
Abakaliki, Ebonyi State, Nigeria
nwurukualfred1@gmail.com

James Onyeka Okechukwu
Department of Chemistry
Modibbo Adama University of Technology,
Yola, Adamawa State, Nigeria
okechukwujames298@gmail.com

Abstract: Some varieties of monoazo disperse dyes derived from halogenated arylamines were synthesized by simple diazotization and coupling to 1 and 2-naphthols. The impure dyes were recrystallized from ethanol solvent. Interestingly, all the dyes synthesized have colouristic properties. The purity and structural identities of the dyes obtained were confirmed by melting point, UV and IR spectrometry. The UV spectra of all the dyes synthesized revealed solvatochromism in solvent of different polarities and also halochromism. Fastness properties showed that all the dyes had better fastness properties on cotton than on nylon fabric, although deep dyeing was obtained on nylon fabric.

Keywords— azo dyes; solvatochromism; fastness properties; wavelength.

1. INTRODUCTION

Dyes are substances, usually, organic, which are designed to be absorbed or adsorbed by, made to react with, or deposited within a substrate in order to impart colour to that substrate with some degree of permanence [1]. They also possess auxochromes which help to influence the colour of the chromogen [2]. The history of dyeing can be generally divided into two great periods, the 'pre-aniline', extending to 1856 and the 'post-aniline' periods [3].

Worldwide, vast quantities of dyes are annually produced and consumed, with more than 100,000 different synthetic dyes available in the market [4]. However, the three most common chemical groups used in the production of these dyes are azo, anthraquinone and phthalocyanine groups [5], with azo being the largest [6]. These types of dyes are suitable for the dyeing of polyester, nylon and cotton fabrics [7].

Azo dyes are the largest group of coloured organic compounds [8], and this is due to the large number of variations in their chemical structures and their wide chemical applications [9]. They are diazene-containing compounds. They can also be called diamine or diimide and have the azo moiety (-N=N-) [10]. Monoazo dyes have only one azo group [11], but are known to have various sub groups [12].They are known to have great environmental stability, electrical and optical properties, and some are reported to have shown biological activities against bacteria like digestive tract bacteria, staphylococcus aureus etc. [10].

Without exception, all azo dyes are synthesized by the diazotization of a primary aromatic amine followed by the coupling of the resultant diazonium salt with an electron rich nucleophile.

Generally, azo dyes possess good all round fastness properties, and are highly useful for colour impartation [13] on textile fibres, printing systems, foods, etc. [14]. More so, some can be used for biocidal treatment of textile materials [15].

The beginning of synthetic fibres like nylon, polyester, etc. created significant challenges in the dyeing ability of hydrophobic fibres to dyestuff chemists. Consequently, over the last three decades, dye chemists and researchers focused their efforts in the synthesis of dyes for these fibres [16].

In this research work, eight monoazo disperse dyes were synthesized from 2-bromoaniline, 3-chloroaniline, 4-chloroaniline and 4-fluoroaniline, using 1- naphthol and 2-naphthol as coupling components. Thereafter, each of these dyes were used to dye a natural textile fibre (in this case, cotton) and a synthetic textile fibre (in this case, nylon). The coloured fabrics were subjected to various fastness tests in order to ascertain their fastness properties.

2. MATERIALS AND METHODS

The monoazo disperse dyes were prepared by diazotization of the different aminobenzene derivatives and coupled with 1 and 2-naphthol as outlined in the general procedure (Method A and B). All the reagents used were obtained from commercial sources. Melting point was measured using a Sanyo GallenKamp MPD. 350 variable heater instrument and are uncorrected. IR and UV spectra were recorded using Buck scientific infrared spec M530 and Jenway 6850 UV-VIS respectively.

2.1 Method A: General Procedure for Diazotization

0.1 mole of the halide benzene derivative was added into a beaker containing 100 cm3 of concentrated HCl solution and this was immediately placed in an ice bath to maintain the temperature below 5 oC. 6.9 g of $NaNO_2$ was dissolved in 50 cm3 of water and the solution was added slowly using a dropper while stirring continually for about 10 minutes to give a solution of diazonium salt. The solution was then kept below 5 oC in an ice bath [15]. This was repeated for each of the halide benzene derivatives.

2.2 Method B: General Procedure for Coupling

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0.1 mole of naphthol was dissolved in a beaker containing 50 cm3 of 2.50 M NaOH. The solution was maintained below 5 oC. The diazonium salt solution was added slowly to the coupling component solution using a dropper while stirring for about 30 minutes. This was left in an ice bath for an additional 20 minutes to ensure the reaction is completed. The dyes were filtered, recrystallized from ethanol, washed thoroughly and dried in an oven at a temperature of about 42 oC [15]. Thereafter, they were presented for melting point, ultra violet/ visible spectroscopy (UV/VIS), infra-red (IR) spectroscopy and dyeing.

2.3 Molar Extinction Coefficient Calculation (ε)

The molar extinction coefficient (ε) of the dyes was calculated from the results obtained from UV/VIS via the formula;

$A=\varepsilon CL$

Where A= absorbance at maximum wavelength

C= concentration of the dye solution

L= path length of the sample cell (in this case, 1.0 cm) [17].

2.4 Dyeing of the Fabric

2.0 g of the dye was dissolved in 100 cm3 of water to give a liquor ratio of 1:50 at room temperature. After the dye bath was set, 2.0 g of the fabric was wetted and excess water squeezed out with the aid of a filter paper. Thereafter, the fabric was introduced into the dye bath at a temperature of 50 oC. The temperature was later increased to 100 oC for 20 minutes and dyeing continued at this temperature for 60 minutes. After dyeing, the fabric was removed, rinsed thoroughly with water and air dried [18].

2.5 Wash Fastness Test

The dyed fabric was immersed in a detergent solution containing 0.50 g of detergent and 30 cm3 of distilled water. The fabric was stirred gently for 30 minutes and then removed and washed thoroughly with water. The fabric was air dried and the changes in shades were related to the standard gray scale rating (grade 1-5) where 1 is poor and 5 is excellent [19].

2.6 Light Fastness Test

The dyed fabric was firmly attached to a white cardboard paper and exposed to sunlight for 3 hours. The changes in shades were related to the standard gray scale rating (grade 1-5) where 1 is poor and 5 is excellent [20].

2.7 Heat Fastness Test

The dyed fabric was firmly placed on a white background (in this case, a cardboard paper) and ironed for about 30 seconds using a pressing iron set at 60 oC. The ironed sample was compared with the control to see if any colour change had occurred. The changes in colour shade were related to the standard gray scale (grade 1-5) where 1 is poor and 5 is excellent [19], [20].

3. RESULTS

The monoazo disperse dyes of the general structure (Figure 1) were synthesized by the diazotization of an appropriate amine and coupled to 1 and 2-naphthols (Scheme 1).

Diazotization: $RNH_2 + HCl + HNO_2 (NaO_2 + 2HCl) \rightarrow R\text{-}N_2^+Cl^- + 2H_2O$

Coupling: $R\text{-}N_2^+Cl^- + RHOH \rightarrow RN{=}NROH + HCl$

Scheme 1: General Reactions for the Diazotization and Coupling [14], [21].

The impure monoazo dyes were recrystallized from ethanol and their purity was monitored by thin layer chromatography (TLC). All the dyes were obtained in good yields (60-76 %). The physical characteristics of the dyes synthesized are presented in table 1.

The structure of the monoazo disperse dyes synthesized were verified by IR spectrometry and the spectra confirmed the presence of aromatic rings, -OH, C=C, and the halogen groups as shown in table 2.

The molar extinction coefficient (ε) values of the dyes as shown in table 3 which ranges from 1.47 x 104 to 5.72 x 104, is an indication that all the dyes are suitable for commercial dyeing with the exception of dye 8, as dyes suitable for commercial dyeing must have a molar extinction coefficient value above 20,000 [17].

4. DISCUSSION

The maximum absorption wavelength (λmax) of all the synthesized monoazo disperse dyes were carried out in ethanol, acetone and toluene solvent as illustrated in table 3. The data revealed that solvent had a marked effect on the λmax value of the monoazo disperse dyes. The dyes in ethanol showed a significant increase in the λmax value when compared to that of acetone and toluene. This increase in λmax value (bathochromic shift) with change in solvent polarity may be due to $\pi \rightarrow \pi^*$ transition which occurs when the dielectric constant (or polarity) of the solvent increases. For example, the dielectric constants of toluene, acetone and ethanol are 2.40, 20.70 and 25.90 respectively [7].

Also, when halogens (-Br, -Cl and -F) which are electron withdrawing groups are introduced into the benzene component of the dyes, there is an observed increase in the wavelength. Dyes containing groups

with more electron withdrawing inductive ability had lower wavelength value compared to those with less electron withdrawing inductive ability as depicted in table 3.

Comparing dyes 3 and 5, the only difference is the position of the haloen group (Cl). In dye 3, the Cl group is in meta position to the azo (-N=N-) group but in para position to the azo group in dye 5. There is an observed increase in the wavelength of dye 5 as compared with dye 3. Again, this could be attributed to the farther distance of the Cl group in dye 5 as compared with dye 3. This farther distance helped to reduce the inductive effect of the halogen group on the azo group and thus caused a bathochromic shift.

Likewise, dyes having 2-naphthol rings in which the hydroxyl (-OH) is at the ortho position to the azo group had higher wavelength than those with 1-naphthol ring with the -OH at para position as seen in table 3. This suggests that hydrogen bonding between the -OH group and azo group might have played a significant role in the increase in the λmax values.

Similarly, the effect of few drops of concentrated hydrochloric acid on the λmax of the monoazo disperse dyes were also studied and the result revealed that all the dyes showed positive halochromism as a result of the protonation of β-azo nitrogen atom of the dye.

Dyeing was carried out on both nylon and cotton fabrics at such a concentration as to attain equal depth of 1/1. It was observed that the colour strength of the dyed cotton was not as solid as that of nylon. Nylon absorbs more dye molecules than cotton in simultaneous dyeing and this may be due to the crystalline nature of cotton which makes dye diffusion more difficult. Nylon is amorphous and therefore very easy for dye molecules to diffuse.

The light fastness of the dyes as presented on table 4 is comparatively close for both fabrics, while the wash and heat fastness of the dyes on cotton is better than that of nylon. This could be again due to the crystalline nature of cotton which disallowed outward migration of dye molecules from the fabric during washing and heating. Nylon being amorphous, therefore, “easy in easy out”.

5. CONCLUSION

These studies have shown that the introduction of halogen groups on the benzene component of monoazo disperse dyes played a significant role in the wavelength and colour shade of the dyes. All the dyes synthesized have moderate to good fastness properties with the exception of dye 8. This implies that dye 8 may need a mordant to improve its fastness properties. Finally, the amazing fastness properties and good colour shade of these groups of dyes could play a vital role in synthetic dye technology.

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Table 1: Physical Characteristics of the Synthesized Monoazo Disperse Dyes

Dye No.	Percentage Yield (%)	Colour	Texture	Molecular weight (g/mol)	Melting point (°C)
1	72.51	Mulberry purple	Crystal	327.18	136.00
2	76.84	Brick red	Powdered	327.18	172.00
3	62.41	Penny brown	Crystal	282.73	139.00
4	65.52	Wine	Crystal	282.73	177.00
5	60.41	Pecan brown	Crystal	282.73	150.00
6	62.55	Dark brick red	Powdered	282.73	170.00
7	75.20	Orange purple	Crystal	266.28	154.00
8	71.31	Dark red	Powdered	266.28	174.00

Table 2: Infra-red Spectra of the Monoazo Disperse Dyes (IR peaks (cm^{-1}))

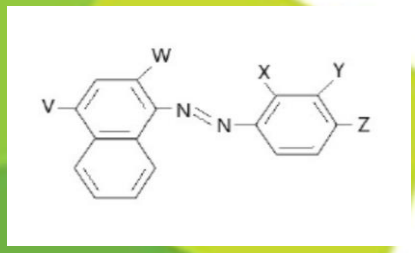
Functional Group	Vibrational Frequency (cm^{-1})
V_{O-H}	3650-3640
V_{C-H}	3070-3060
V_{Ar-H}	1617-1580
$V_{C=C}$	1600-1560
$V_{N=N}$	1500-1400
V_{C-N}	1400-1370
V_{C-Br}	660-600
V_{C-Cl}	800-730
V_{C-F}	150-140

Table 3: UV Spectra of Dyes in Solvents of Different Dielectric Constants

Dye No.	λ_{max} in Ethanol (nm)	λ_{max} in Acetone (nm)	λ_{max} in Toluene (nm)	λ_{max} in Ethanol + HCl (nm)	Molar Extinction Coefficient (ε) ($Lmol^{-1}cm^{-1}$)
1	472.00	461.00	458.00	486.00	3.64×10^4
2	474.00	470.00	459.00	483.00	3.25×10^4
3	465.00	455.00	450.00	476.00	3.87×10^4
4	468.00	459.00	453.00	473.00	2.44×10^4
5	469.00	461.00	457.00	479.00	5.52×10^4
6	471.00	464.00	459.00	472.00	5.72×10^4
7	461.00	451.00	448.00	463.00	5.11×10^4
8	467.00	458.00	453.00	473.00	1.47×10^4

Dye No	Wash Fastness		Light Fastness		Heat Fastness	
	Nylon	Cotton	Nylon	Cotton	Nylon	Cotton
1	3	4	3-4	3-4	4	4-5
2	2-3	3-4	4	4-5	3	4
3	3	3-4	2-3	3	3-4	4-5
4	3	3-4	3	3	3-4	4-5
5	3	4	3-4	3	4	4-5
6	2-3	3-4	3	3-4	3	4
7	3	4	3-4	4	3-4	4-5
8	1	2	1-2	2	2	2-3

Table 4: Wash Fastness, Heat Fastness and Light Fastness on Dyed Nylon and Cotton Fabrics



Where

Dye 1: X=Br; W=Y=Z=H; V=OH

Dye 2: X=Br; V=Y=Z=H; W=OH

Dye 3: Y=Cl; W=X=Z=H; V=OH

Dye 4: Y=Cl; V=X=Z=H; W=OH

Dye 5: Z=Cl; W=X=Y=H; V=OH

Dye 6: Z=Cl; V=X=Y=H; W=OH

Dye 7: Z=F; W=X=Y=H; V=OH

Dye 8: Z=F; V=X=Y=H; W=OH

Fig. 1. General Structure of the Synthesized Dyes