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Author Affiliation:
[1]Department of Chemistry/ Biochemistry, Abia State Polytechnic, Abia State, Nigeria
[2]Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, Chukwuemeka Odumegwu Ojukwu University, Anambra State, Nigeria
[3]Department of Biochemistry, Ebonyi State University, Ebonyi State, Nigeria
[4]Department of Chemistry, Alex Ekwueme Federal University, Ebonyi State, Nigeria
[5]Department of Petroleum Chemistry, American University of Nigeria, Adamawa State, Nigeria
[6]Chemistry Department, Federal University of Technology, Imo State, Nigeria
[7]Medical Laboratory Science, Delta State University, Delta State, Nigeria
[8]Department of Medical Biochemistry, Delta State University, Delta State, Nigeria
[9]Department of Biology/ Microbiology, Abia State Polytechnic, Abia State, Nigeria

[*]**Corresponding Author**
Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, Chuekwuemeka Odumegwu Ojukwu University, Uli, Anambra State,
Nigeria
E-mail: iemmanuel385@gmail.com

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Synthesis, spectroscopic studies and fastness evaluation of disperse dyes derived from aniline derivatives on polyester fabric

Emeka Onuh Friday[1], Emmmanuel Ifeanyi Victor[2*], Nwuruku Olisa Alfred[3], Linus N Okoro[4], Bolade O Agboola[5], Yahaya Muhammadu[5], Okolo Azubuike Jeremiah[2], Ugariogu Nnaemeka Silvester[6], Okoro Edith Omozefe[7], Mordi Joseph Chukwufumnaya[8], Ndulaka JC[1], Chukwu Henry Chima[1], Ogonna Chinyere Roseline[9]

ABSTRACT

Monoazo disperse dyes were synthesized via the diazo-coupling method by using 4-sulfanilic acid and 4-chloroaniline as diazonium components and were individually coupled with 1-napthol, 2-naphthol, phenol and salicyclic acid. The absorption wavelengths of these dyes were measured in solvents of different polarities (methanol, ethanol and ethyl acetate). The maximum wavelength (λ_{max}) in methanol and ethyl acetate were found to be the highest and lowest respectively. This showed that solvatochromic effect occurred. Dyes with 2-naphthol ring exhibited a higher wavelength than the rest of the dyes. More so, the various auxochromes in the dye structures displayed remarkable effects on the λ_{max} of the synthesized dyes. All the dyes were applied on polyester fabric via the High Temperature High Pressure (HTHP) dyeing method and their fastness evaluation revealed that they all had outstanding fastness ratings.

Keywords: Polyester, disperse dyes, solvatochromic effect, wash fastness, light fastness, heat fastness

1. INTRODUCTION

Polyesters are made up of at least 85% by weight of an ester and a dihydric alcohol and a terephthalic acid. They are regarded as one of the most important classes of a poly condensation polymer (Jeyakodi et al., 2021). Among synthetic fibres, polyester, specifically polyethylene terephthalate (PET), is the most widely used material in the textile industry because of its excellent physical properties, processability, lower price (Yoon et al., 2019; Kaminska et al., 2019), ability to integrate different types of products that unfold in the textile chain (Burkinshaw

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et al., 2019), low water absorption, non-ionic character and high crystallinity (Gabardo et al., 2021); and therefore are a prominent topic of research.

Disperse dyes have been reported to show potential research values in the development of high light resistant and functional dyes (Song et al., 2020). They contain auxochromes such as amino and hydroxyl groups, are of low water solubility (Al-Etaibi & El-Apasery, 2020), non- ionic and hydrophobic in nature. Some have also been noted to exhibit impressive antioxidant and antimicrobial activities (Huda et al., 2019). Disperse dyes are unarguably the most important class of dyes used in dyeing polyesters (Kaminska et al., 2019; Karim et al., 2021), as most have shown very good to excellent light and washing fastness properties (Ghanavatkar et al., 2020). This explains the ever-increasing demand for more disperse dyes especially via the synthetic route. Conventional polyester dyeing is an energy intensive process as the dyeing is carried out above 120 ^{o}C in a weakly acidic aqueous dye bath in order to obtain an efficient diffusion of the dye. This is because imparting colour to polyester is extremely difficult and this can be attributed to its highly compact and crystalline structure. This process of dyeing is referred to as High Temperature High Pressure (HTHP) dyeing method (Yoon et al., 2019).

Polyesters can also be dyed using the Low Temperature (LT) dyeing method at 100 ^{o}C. However, in this case, a carrier must be used. These carriers are organic compounds usually of smaller sizes than the dyes which help to quicken dyeing. They do this by penetrating the internal regions of the fibre and open up the macromolecular structures at a temperature higher than the Glass Transition Temperature (T_g). They do this by dissolving dye aggregates and carry them to the fibre water interface in little amounts that are enough to be absorbed by the polyester fibre. However, studies have shown that polyester dyeing at 120 ^{o}C makes the swelling of the fibre even and enables dye molecules to penetrate the fibre polymer more than is accomplished in the LT dyeing method (Al-Etaibi & El-Apasery, 2020).

This research work sets out to

Synthesize monoazo disperse dyes by using 4-sulphanilic acid and 4-chloroaniline (as diazonium components); and naphthols, salicylic acid and phenol (as coupling components).

Apply the synthesized dyes on polyester fabrics via the HTHP dyeing method and compare the fastness properties of the synthesized dyes on the polyester fabric being dyed.

2. MATERIAL AND METHOD

Experimental Design

The dyes were synthesized via a diazo-coupling method as outlined in Obi et al., 2022 and grouped into series based on their diazonium components. The diazonium components used were 4-chloroaniline and 4-sulphanilic acid. These were separately coupled to the various coupling components. Coupling components used were phenol, 1-naphthol, 2-naphthol, and salicylic acid.

Preparation of Coupling Components

A weighed amount of 0.94 g of phenol was added into a beaker which contained 5 cm^3 of 2.50 M NaOH. The solution was maintained below 4^{o}C by placing it in an ice bath. This is the phenol coupling component. The coupling components of 1-naphthol, 2-naphthol and salicylic acid were prepared separately by following the above procedures and using 1.44 g, 1.44 g and 1.38 g of 1-naphthol, 2-naphthol and salicylic acid respectively.

Synthesis of 4-sulphanilic acid series (Dye 1 series)

A weighed mass of 1.73 g of 4-sulphanilic acid was added into a beaker containing 10 cm^3 of concentrated hydrochloric acid. This was kept in an ice bath to reduce and maintain the temperature below 4^{o}C and was labeled 'A'. 5 cm^3 of water containing 0.69g of $NaNO_2$ was added drop-wise to solution 'A' by using a dropper, while continually stirring for another 10 minutes to give the diazonium salt. This was labeled 'B'. The temperature of solution 'B' was maintained at below 4^{o}C by placing it in an ice bath and was added slowly to the solution of the coupling component to produce the dye. The synthesized dye was kept in an ice bath for an additional 20 minutes to ensure the reaction is completed. Thereafter, it was filtered, recrystallized from ethanol, washed using water and dried in an oven operated at 42^{o}C.

Synthesis of 4-chloroaniline series (Dye 2 series)

A weighed amount of 1.28 g of 4-chloroaniline was poured into a beaker containing 10 cm^3 of concentrated hydrochloric acid and was immediately placed in an ice bath to reduce the temperature below 5^{o}C. In another beaker, 0.69g of sodium nitrite was added to 5cm^3 of water. This solution was added slowly to the chloroaniline solution by using a dropper and was continuously stirred. This

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generated the diazonium salt which was added slowly to the coupling component of choice while stirring. The synthesized dye was filtered, recrystallized from ethanol and washed thoroughly with water before being dried in an oven operated at 42°C.

Dyeing of Polyester Fabric

Polyester fabric was dyed via the HTHP dyeing method by using a 1% dye stock solution. This was prepared by dissolving 1g of the particular dye of interest in 100 g of dimethylformamide (DMF). A material: Liquor ratio of 1: 50 was maintained all through the dyeing process. The temperature of the dye bath was increased to 50°C and the polyester fabric was introduced into it. Thereafter, the temperature was steadily increased to 130°C and dyeing continued for an additional 60 minutes. The pH of the dye bath was kept fairly constant at 4.5- 5.5 by adding few drops of glacial acetic acid. After dyeing, the dyed polyester fabric was introduced into a solution containing 2gpl sodium hydroxide and 2gpl sodium hydrosulphite at 70°C for 25 minutes. Thereafter, the fabric was rinsed in water and air dried (Obi & Onuh, 2022; Pawar et al., 2018).

Wash Fastness Evaluation

The dyed sample was immersed in a detergent solution containing 0.50g of detergent in 30cm^3 of distilled water. The sample was stirred gently for 30 minutes and then removed and rinsed thoroughly with water. Thereafter, the sample 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 (Pawar et al., 2018).

Light Fastness Evaluation

The dyed sample was firmly attached to a white card board 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 (Obi et al., 2022).

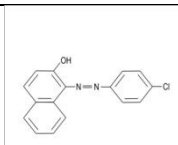
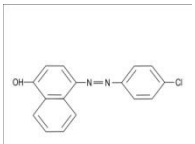
Heat Fastness Evaluation

The dyed sample was placed on a white background and ironed for 30 seconds using a pressing iron set at 60°C. The ironed sample was compared with the control sample to see if any colour change had occurred. The changes in colour shades were related to the standard gray scale rating (grade 1- 5) where 1 is poor and 5 are excellent (Obi & Onuh, 2022).

3. RESULTS AND DISCUSSION

The possible structures of the synthesized dyes are listed on table 1, while table 2 shows some physical properties of the synthesized dyes. All the dyes were recrystallized from ethanol solvent and their purities were monitored by Thin Layer Chromatography (TLC). Their melting points were determined by using Sanyo Gallen kamp MPD 350 variable heater instrument and are uncorrected.

Table 1 Possible Chemical Structures and Formula of the Synthesized Dyes

Dye no	Possible chemical structure	Chemical formula
1A		$C_{16}H_{11}N_2OCl$
1B		$C_{16}H_{11}N_2OCl$

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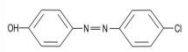
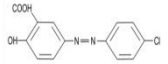
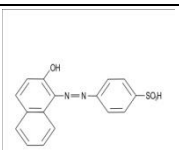
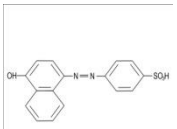
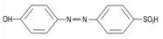
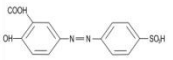
1C		$C_{12}H_9N_2OCl$
1D		$C_{13}H_9N_2O_3Cl$
2A		$C_{16}H_{12}N_2O_4S$
2B		$C_{16}H_{12}N_2O_4S$
2C		$C_{12}H_{10}N_2O_4S$
2D		$C_{13}H_{10}N_2O_6S$

Table 2 Physical Properties of the Synthesized Dyes

Dye no	Colour	Texture	Melting Point [°C]	Percentage Yield [%]
1A	Paprika	Powdered	159	95.4
1B	Victor red	Powdered	144	63.6
1C	Cadmium yellow	Jelly	125	47.2
1D	Unbleached titanium	Powdered	156	65.1
2A	French yellow	Crystal	158	98.2
2B	Italian brown	Powdered	118	30.5
2C	Deep cadmium yellow	Jelly	143	55.8
2D	Lead yellow	Powdered	135	83.9

All the dyes had high percentage yields except dyes 1C and 2B. No reason was identified for their low yields as compared with the other dyes. More so, dyes synthesized from phenols were generally found to be jelly in nature. Again, no reason was identified for this.

The functional groups in the synthesized dyes were identified by using an IR spectrometer (Bulk Scientific Infra-red Spec M530) as seen on table 3 and showed the presence of vibrational OH, C-H, C=C, N=N, C-Cl, C-Br, NO_2, and Ar-H bonds (Emmmanuel et al., 2022; Joseph et al., 2020; Lata et al., 2017; Agho et al., 2017; Nandiyanto et al., 2019).

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Table 3 IR Spectra of the Synthesized Dyes

IR Peaks [cm^{-1}]							
V_{O-H}	V_{C-H}	V_{Ar-H}	V_{C-C}	$V_{N=N}$	V_{COOH}	V_{C-Cl}	V_{C-SO3H}
3649-3640	3067-3060	1617-1579	1600-1560	1496-1400	1725- 1700	800- 730	1365- 1340

As on table 4, the various solvents used (methanol, ethanol and ethyl acetate) had a marked effect on the maximum wavelength (λ_{max}) of the dyes. Solvents with higher polarity favoured more $\pi \rightarrow \pi^*$ transitions, thereby causing a bathochromic shift when compared with the solvents of lower polarity. They do this by lowering the energy of transition and causing more transitions from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). Hence, the dyes had the highest and lowest λ_{max} values in methanol and ethyl acetate solvents respectively. This is called a solvatochromic effect.

Table 4 Maximum Wavelength (λ_{max}) of the Synthesized Dyes

Dye no	λ_{max}in Methanol [nm]	λ_{max}in Ethanol [nm]	λ_{max}in Ethyl acetate [nm]
1A	448	446	443
1B	443	438	432
1C	440	432	429
1D	436	431	427
2A	432	428	422
2B	428	421	418
2C	423	419	413
2D	417	409	401

The presence of the electron withdrawing groups (SO_3H, COOH, Cl) which also acted as auxochromes had a remarkable effect on the values of λ_{max} of the dyes. Comparing the members of dye 1 and 2 series, it can be seen that dyes 1D and 2D had the least maxii absorption wavelength (λ_{max}) values in their respective series. This could be because of the presence of the extra electron withdrawing group (-COOH) in addition to the existing -Cl group (in 1D) and -SO_3H group (in 2D). This additional presence of -COOH further deactivated the compound thereby causing a lesser $\pi \rightarrow \pi^*$ transition and thus, a hypsochromic shift was observed. This lesser transition occurred because the energy between the HOMO and LUMO is increased, and this increment leads to the stabilization of the HOMO.

More so, dye 2 series were generally found to have lower λ_{max} values than dye 1 series. Again, this could be attributed to the lower electron withdrawing effect of -Cl found in dye 1 series as compared with -SO_3H found in dye 2 series. A stronger electron withdrawing group will deactivate the compound more than a weaker one. This led to a bathochromic shift (increase in wavelength) in dye 1 series when compared with dye 2 series.

Dyes synthesized from 2-naphthol (1A and 2A) were found to have a higher λ_{max} value than dyes synthesized from 1-naphthol (1B and 2B) as seen on table 4. This observation is in line with that reported in Emmanuel et al [14], and could be traced to the fact that the hydroxyl (-OH) group is at an ortho position to the azo (-N=N-) group in dyes 1A and 2A as opposed to being in a para position to the azo group in dyes 1B and 2B. This closer position of the -OH group to the azo group in dyes 1A and 2A, suggested that there could have been hydrogen bonding existing between the hydroxyl and azo groups, which in turn had led to an increase in the wavelengths of the dyes, thus, a bathochromic shift occured.

As seen on table 4, dyes 1C and 2C had lower λ_{max} values than dyes 1B and 2B respectively. This is because in dyes 1C and 2C, the coupling component is a phenol, which has just one ring whereas in dyes 1B and 2B, the coupling component is a naphthol. Naphthol has two rings and thus experienced an extended conjugation of pii bonds. This extended conjugation of pii bonds causes an increase in the amount of transitions. This consequently led to a decrease in the energy of transition from the HOMO to the LUMO, thereby causing a bathochromic shift, which resulted in an increased λ_{max}value.

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Table 5 Fastness Ratings of the Synthesized Dyes on Polyester Fabric

Dye No	Light Fastness	Wash Fastness	Heat Fastness
1A	4-5	4	4-5
1B	4-5	4	4-5
1C	4-5	4	4
1D	4	4	4
2A	4-5	4-5	4-5
2B	4-5	4	4-5
2C	4	4	4
2D	4	4	4-5

Key: 1= extremely poor; 1-2= very poor; 2= poor; 2-3= fair; 3= moderate; 3-4= moderately good; 4=good; 4-5= very good; 5= excellent.

The dyeing of the polyester fabric was carried out using the synthesized dyes. All the fabrics had uniform dyeing. Light fastness is the resistance to the fading of the colour of a dyed or coloured fabric by the action of light. Heat fastness is the resistance to the fading of the colour of a dyed fabric by the action of heat, while wash fastness is the resistance to the fading of the colour of a dyed fabric when being washed. Various factors affect wash, light or heat fastness. However, the crystallinity of the fabric being dyed and the size of the dye used, are two important factors which affect fastness properties. Polyester fabric is known to be highly crystalline, thus, the pores in a polyester fibre are well structured and highly layered. Fastness ratings of the synthesized dyes on polyester fabric as shown on table 5 revealed that all the dyes had amazing light, heat and wash fastness properties with dyes 1A, 1B, 2A and 2B being remarkably outstanding.

The outstanding fastness properties of the dyes on polyester fabric could be linked to the highly crystalline structure of the polyester fabric as dyes which migrated into the fabric structure during the dyeing process found it difficult to easily migrate out during the fastness tests (Obi et al., 2022; Obi & Onuh, 2022; Emmmanuel et al., 2022). The fastness ratings can also be linked to the sizes of the dyes synthesized. Dyes 1A, 1B, 2A and 2B have bigger sizes than the rest of the dyes. These larger sized dyes will take more time to diffuse into the polyester fabric during the dyeing process. Once in, they will hardly migrate out of the dye during the fastness tests. This explains the higher resistance to colour-fading of the polyester fabrics dyed with dyes 1A, 1B, 2A and 2B.

4. CONCLUSION

These studies have revealed that apart from the amazing colouristic properties of these synthesized dyes, they also had an amazing fastness property on polyester fabric. It is worthy to note that these dyes were easily applied without a mordant, hence can be readily and massively used in large scale polyester textile fabric dyeing. More so, the auxochromes in the dye structure which in this case are electron withdrawing group caused a remarkable shift in the λ_{max} of the synthesized dyes.

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Author's Contribution

All the authors contributed equally to the conceptualization, writing and editing of this work.

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Ethical approval

Not applicable.

Informed consent

Not applicable.

Conflicts of interests

The authors declare that there are no conflicts of interests.

Data and materials availability

All data associated with this study are present in the paper.

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