SYNTHESIS OF ACTIVE METHYLENE AZO DISPERSE DYES BASED ON 4-AMINO-3-NITROBENZALDEHYDE AS DIAZO COMPONENT AND THEIR APPLICATION ON POLYESTER AND NYLON 6.6 FABRIC

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ABSTRACT

Active methylene azo disperse dyes were synthesized and characterized. A good percentage yield of each of the dyes were obtained in the range of 58-82 %. The dyes have well defined melting points in the range of 270 – 404 °C. The visible absorption spectra of the dyes showed that the dyes absorbed maximally within the visible region of the electromagnetic spectrum. The results of halochromism of the dyes showed that the dyes exhibited both negative and positive halochromism. The molar extinction coefficient of the dyes was generally high indicating high hue strength. On application of the dyes on fabric, a high percentage exhaustion of 73 and 69 percent was obtained on polyester and nylon 6.6 fabrics respectively. The assessment of fastness properties of the dyes showed that the dyes have ratings of 4-5 for wash fastness, fastness to pressing and perspiration on both fabrics.

Keywords: *Azo Dyes, Characterization, Molar Extinction coefficient and Fastness properties*

1.0 INTRODUCTION

Disperse dyes are characterized by the absence of solubilizing groups and low molecular weight. From a chemical point of view, more than 50 % of disperse dyes are simple azo compounds. About 25 % are anthraquinones and the rest are methine, nitro, and naphthoquinone dyes (Bello, 1995). Then most dominant group of these dyes are the azo disperse dyes which account for approximately 60–70 % of all disperse dyes manufactured (Abd-El-Aziz and Afifi, 2006; Marini, et al., 2010; Bello, 1995; Maradiya, and Patel, 2003). Disperse dyes are aromatic compounds that are soluble in organic solvents but sparingly soluble in water. They are used to dye hydrophobic fibres such as nylon, polyester, and acetate at high pressure and temperature. Structurally, the dyes are basically based on azo, anthraquinone or diphenylamine molecule with attached functional groups such as amine, nitro, cyano, etc (Choi *et al*., 2013; Salisu, 2015).

Disperse dyes based on 4-amino-3-nitrobenzaldehyde as diazo component and using arylamines as coupling components have been reported. The condensation of these dyes with indandion, 3-dicyanovinylindane and 1,3-bisdicyanovinylindane had not been reported (Salisu, 2015).

This research is aimed at synthesizing azo disperses by condensation of active methylene compound with arylamine dyes derived from 4-amino-3-nirtrobenzaldehyde. The objectives of the research are to characterize the dyes and apply them on polyester and nylon 6.6 fabrics. In addition, another objective is to study the dyes performance and their fastness properties.

2.0 MATERIALS AND METHODS

2.1 MATERIALS

All the chemicals used in the synthesis of the dyes and intermediates were of analytical grade and were used without purification. Melting points were determined using Gallenkamp melting point apparatus (Model: Sanyo MPD350.BM3.5). The visible absorption spectra were measured using UV-visible spectrophotometer (Model: JENWAY 3405). IR spectra were recorded on a FTIR SHIMADZU Machine (Model: FTIR-8400S) and the Mass spectra were determined on GC-MS SHIMADZU Machine (Model: GC-MS-QP2010).

2.2 METHODS

2.2.1 Synthesis of 4-acetylamino-3-nitrobenzaldehydediacetate

4-Acetylaminobenzaldehyde (50 g, 0.31 mol) was added to acetic anhydride (125 ml, 1.32 mol) and heated to 105 ^{0}C with vigorous stirring until dissolved. The solution was cooled rapidly with external ice water to 30 °C to give a fine precipitate. Nitric acid (20 ml, 0.48 mol) and acetic anhydride (50 ml, 1.32 mol) were carefully mixed and the mixture was added drop-wise to the stirred suspension of 4-acetylaminobenzaldehyde at such a rate that the temperature did not rise above 35 °C. After the addition of about one third of the acid, colourless crystals were deposited. Further drop-wise addition of the acid caused it to dissolve and towards the end of the addition the temperature was allowed to rise to 50 °C. The mixture was stirred at this temperature for a further 15 minutes and then poured into ice water (600 ml). The precipitated 4-acetylamino-3-nitrobenzaldehyde diacetate was filtered off, washed thoroughly with ethanol and then with water after which it was dried. Recrystallization from ethanol gave diacetate pale yellow leaflets.

2.2.2 Synthesis of 4-amino-3-nitrobenzaldehyde

4-Acetylamino-3-nitrobenzaldehyde diacetate (30 g, 0.107 mol) was added to concentrated hydrochloric acid (100 ml) and heated on a water-bath for 15 minutes. After cooling, water (150 ml) was added and the precipitated 4-amino-3-nitrobenzaldehyde was filtered off, washed with water and dried. It was purified by re-crystallization from water to give orange needles.

2.2.3 Diazotization of 4-amino-3-nitrobenzaldehyde

4-Amino-3-nitrobenzaldehyde (3.2 g, 0.02 mol) was added to a mixture of acetic acid (24 ml) and water (6 ml), and then cooled by stirring to 12 °C. Sodium nitrite (1.5 g, 0.02 mol) dissolved in water (10 ml) was added in one portion and then concentrated hydrochloric acid (10 ml) was added immediately. The mixture was maintained at 15-20 °C for 15 minutes, and then excess nitrous acid was destroyed by addition of small amount of urea. The solution was diluted with ice water (200 ml) to give a clear solution of the diazonium salt.

2.2.4 Procedure for preparing coupling components

The coupling components used were: N,N-dimethylaniline, N,N-diethylaniline and N,N-dipropyl aniline. Each arylamine (0.02 mol) was dissolved in a mixture of concentrated hydrochloric acid (5 ml) and ice-water (200 ml) in order to generate the coupling sites. The solution mixture was cooled in an ice bath to 0-5 °C.

2.2.5 Coupling of diazotized 4-amino-3-nitrobenzaldehyde

Solid sodium acetate (20 g, 0.24 mol) was added to the already prepared coupling component to give a pH of ca 4. The diazonium solution formed was added drop-wise over 30 minutes with rigorous stirring to the coupling component prepared at 0-5 °C. Further sodium acetate was added as required to maintain the pH at ca 4. The solution was stirred for 2 hours. The resultant dye was then filtered off, washed thoroughly with water until washings were neutral and then dried.

2.2.6 Procedure for condensing aldehyde dyes with active methylene compound (AMC)

The aldehyde dyes (6 mmol) and the AMC (6 mmol) were dissolved with warming in absolute ethanol (150 ml). One drop of piperidine was added as catalyst and the solution was heated under reflux for 2 hours. On cooling the product re-crystallized out and was filtered off. The crude product was re-crystallized from toluene and then characterized.

2.2.7 Dyeing of polyester fabric

Carrier method of dyeing polyester was employed. In this method, polyester fabrics were cut into 1.0 g samples. Each sample was dyed in a dye bath made of the following recipe: 10 ml of 50 g/l phenol, 20 ml of 17 g/l anionic detergent, and 70 ml of water. The liquor to goods ratio being 50:1 while the depth of shade was 1.4 %. The fabric was wetted and thoroughly squeezed to remove excess water. It was immersed into the bath at 50 °C and allowed to reach the boil within 15 minutes. Dyeing was carried out for one hour at a temperature of 98 °C with agitation. At the end of the dyeing, the substrate was removed, squeezed and rinsed thoroughly under running tap water and then allowed to dry at room temperature. The dyed material was treated in a bath containing 1g/l dispersing agent, 2 g/l caustic soda and 2 g/l sodium dithionite at 60 °C for 30 minutes. This was aimed at removing unfixed dyes and carrier residues that may be left on the fabric after dyeing.

2.2.8 Dyeing of nylon 6.6 fabrics

Without the using carrier, the same recipe employed for dyeing polyester was also used for dyeing nylon 6.6.

2.2.9 Determination of dye exhaustion

The extent of the dye exhaustion on polyester and nylon 6.6 fabrics were determined spectrophotometer (Masoud, 2005).

2.2.10 Determination of fastness properties of synthesized dyes

The dyed fabrics were assessed for wash fastness using ISO 3 standard procedure (Nkeonye, 1992). The dyed samples were further assessed for change in shade and staining of the adjacent fabrics in accordance with BS 1006, AO3 1990. The fabrics also were assessed for light fastness using British Standard for determination of Daylight B01, Fastness to pressing and perspiration were also assessed using standard methods in literature (Saville, 2002).

3.0 RESULTS

3.1 Physical Characteristics of the Synthesized Dyes

The solvent used in recrystallization, colour of crystals, melting point and percentage yield of the synthesized dyes are presented in Table 1.

Table 1: Percentage Yield and Characterization Data of Synthesized Dyes

Dye No	Yield (%)	MW. (g/mol)	M.Pt. (^{0}C)	Recrystallization Solvent	Colour of Crystals
Dye 1	82	426.424	270-273	Acetone	Dark crystals
Dye 2	77	474.470	400-404	Toluene	Dark needles
Dye 3	78	522.516	360-364	Acetone	Dark crystals
Dye 4	58	454.477	250-255	Acetone	Dark green
Dye 5	66	490.513	265-279	Toluene	Dark green
Dye 6	59	550.570	382-384	Acetone	Dark powder

3.2 Visible Absorption Spectra of Synthesized Dyes

Table 2: Visible Absorption data of Dyes in Acetone (a^*), DMF (b^*), Diethylenetriamine(c^*), Toluene (d^*), Pyridine (e^*), and Xylene (f^*)

Dye No.	**Wavelength of maximum absorption 'λ_{max}' (nm)**					
	a^*	**b^***	**c^***	**d^***	**e^***	**f^***
Dye 1	510	510	510	510	_	515
Dye 2	475	490	505	535	_	515
Dye 3	530	625	540	_	585	_
Dye 4	515	585	515	515	_	520
Dye 5	620	490	495	535	_	520
Dye 6	520	510	515	_	555	_

3.3 Solvatochromism

Table 3: Solvatochromic Data of Dyes in Acetone (a^*), DMF (b^*), Diethylenetriamine(c^*)

Dye No.	**Wavelength of maximum absorption 'λ_{max}' (nm)**			**Difference in wave length '$\Delta\lambda$' (nm)**		
	a^*	**b^***	**c^***	**a^*-b^***	**a^*-c^***	**b^*-c^***
Dye 1	510	510	510	0	0	0
Dye 2	475	490	505	-15	-30	-15
Dye 3	530	625	540	-95	+10	+85
Dye 4	515	585	515	-70	0	+70
Dye 5	620	490	495	+130	+125	0
Dye 6	520	510	515	+10	+5	0

3.4 Halochromsim

Table 4: Halochromic Data of Synthesized Dyes

Dye No.	**Wave length of maximum absorption, λ_{max} (nm)**				**Difference in λ_{max} (nm)**	
	a^*	**g^***	**b^***	**h^***	**$g^* - a^*$**	**$h^* - b^*$**
Dye 1	510	350	510	515	−160	+5
Dye 2	475	550	490	515	−75	+25
Dye 3	530	530	625	545	0	−80
Dye 4	515	385	585	515	−130	−70
Dye 5	620	385	490	660	−235	+170
Dye 6	520	520	510	515	0	+5

a^*(acetone), g^* (a^*+ HCl); b^*(DMF), h^*(DMF + HCl)

3.5 Molar Extinction Coefficient and Exhaustion

Table 5**:** Molar Extinction Coefficient and Percentage Dye Exhaustion of Synthesized Dyes

Dye No	**$\varepsilon\times10^4$ (LMol^{-1}cm^{-1})**				**% Exhaustion**	
	Acteone	**DMF**	**Acetone**	**DMF**	**Polyester**	**Nylon 6.6**
Dye 1	510	510	5.3561	1.0456	73	60
Dye 2	475	490	8.4219	4.8393	71	67
Dye 3	530	625	1.2995	3.0881	29	64
Dye 4	515	585	1.1498	8,7320	74	72
Dye 5	620	490	6.9750	6.6750	52	73
Dye 6	520	510	1.4034	1.4034	71	76

3.6 Fastness Properties of the Synthesized Dyes

The result of wash fastness and light fastness are presented in Table 6. Result of fastness to pressing on polyester and Nylon 6.6 and perspiration are presented in Table 7, 8 and 9, respectively.

Table 6**:** Result of Wash (ISO 3) and Light (BOl: 1994) Fastness on Nylon 6.6 and Polyester

Sample	**Wash fastness**				**Light fastness**	
	Poyester		**Nylon 6.6**		**Polyester**	**Nylon 6.6**
	Colour change	**Staining**	**Colour change**	**Staining**	**Shade**	**Shade**
Dye 1	4	4	4 – 5	4 – 5	3	3
Dye 2	4 – 5	4 – 5	4	4 – 5	3	3
Dye 3	4	4	3 – 4	4	3	3
Dye 4	4 – 5	4 – 5	4	4	3	3
Dye 5	4 – 5	4 – 5	4 – 5	4 – 5	3	3
Dye 6	4	4 – 5	4 – 5	4 – 5	3	3

Table 7: Fastness to Pressing on Polyester

Sample	**Dry**		**Damp**		**Wet**	
	Colour change	**Staining**	**Colour change**	**Staining**	**Colour change**	**Staining**
Dye 1	4	4 – 5	4 – 5	4– 5	4 – 5	4 – 5
Dye 2	4 – 5	4	4 – 5	4 – 5	4 – 5	4 – 5
Dye 3	4 – 5	4	4 – 5	4 – 2	4 – 5	4 – 5
Dye 4	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 6	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5

Table 8: Fastness to Pressing on Nylon 6.6

Sample	**Dry**		**Damp**		**Wet**	
	Colour change	**Staining**	**Colour change**	**Staining**	**Colour change**	**Staining**
Dye 1	4 – 5	4	4 – 5	4 – 5	4 – 5	4 – 5
Dye 2	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 3	4	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 4	4 – 5	3	4 – 5	4	4 – 5	4 – 5
Dye 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 6	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5

Table 9: Fastness to Perspiration on Polyester and Nylon 6.6

Samples	**Polyester**				**Nylon 6.6**			
	Alkaline		**Acidic**		**Alkaline**		**Acidic**	
	C. C.	**D. S.**	**C. C.**	**D. S.**	**C. C.**	**D. S.**	**C. C.**	**D. S.**
Dye 1	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 2	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 3	4	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 4	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5
Dye 6	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5	4 – 5

4. DISCUSION OF RESULTS

4.1 Synthesis of dyes and active methylene compounds

4-Amino-3-nitrobenzaldehyde was prepared by nitrating 4-acetylaminobenzaldehyde with nitric acid in acetic anhydride at 35-50 °C. The resultant 4-acetamido-3-nitrobenzylidene diacetate was hydrolysed in hot concentrated hydrochloric acid, and was fully characterized by melting point. The amine was diazotized smoothly in an aqueous mixture of hydrochloric and acetic acid at 12-20 °C on addition of sodium nitrite. The diazonium ion was coupled in good yield to N,N-dimethylaniline, N,N-diethylaniline and N,N-diproylaniline in dilute hydrochloric acid at 0-5 °C, with addition of sodium acetate. The relative low percentage yield for dyes 4 and 6 could be due to good solubility of the products in acetone during re-crystallization. The products obtained were further characterized by determining the melting points, and this corresponded with literature value for disperse dyes (Bello and Griffiths, 1989; El-Molla, et al., 2013). Active methylene compound (AMC), 3-dicyanovinylindan-1-one, was prepared by adding anhydrous sodium acetate to a stirred mixture of malononitrile and absolute ethanol at 22 °C. On addition of sodium acetate to the mixture red colouration occurred. After about 40 minutes the mixture was diluted with water and acidified to pH 1-2 by addition of hydrochloric acid. After 10 minutes stirring 3-dicyanovinylindane-1-one was precipitated and washed thoroughly in water. A good yield of 93 % of the product was obtained after re-crystallization in acetic acid. 1,3-Bisdicyanovinylindane was ontained in good yield (92 %).

4.2 Physical Characteristics of the Dyes

The physical characteristics of the dyes were shown in Table 1. Each of the different dyes synthesized possessed distinctive physical characteristics. The dyes exhibited well-defined melting points. This generally shows that the values were quite high and ranged between 270-570 °C. This range when compared to literature value for other different set of disperse dyes was found to differ. This could be due to difference in molecular structure of the dyes in literature compared to the synthesized dyes (Al-mousawi and Elapasery, 2013; Zadafiya et al., 2013). The condensed dyes gave much higher melting point of about 250-404 °C. The colour of the dye crystals varied from orange to dark green for all the dyes. The structures of the dyes were planer thus, can lie flat against the polymer molecules. Their planarity accounts for their good substantivity for hydrophobic fibres (Mosoud *et al.,* 2005).

4.3 Visible absorption spectra

The wavelength of maximum absorbance (λ_{max}) range of the synthesized dyes were 475-620 nm in acetone, 460-625 nm in DMF, and 455-555 nm in DETM, all within the visible region. Dyes 5 and 6 with dicyano groups recorded higher molar extinction coefficient in acetone. This might be due to the rod like nature of the cyano groups that interfere to a lesser extent. Furthermore, it is observed that all the dyes have λ_{max} value in the region of 475–625 nm, in all the solvents used. The variation of λ_{max} and high absorbance value of the dyes could be correlated in terms of substituent effect of the group present in azo disperse dyes (Ghoneim *et al*., 2008). Absorption maxima were not exactly dependent on the electron accepting power of para-substituents in the azo components. This effect was very difficult to explain as it was shown that when electron withdrawing groups were incorporated into the dyes small amounts of bathochromic effect were observed. This is in good agreement with the results of Richard, (1982) and Bello and Griffiths. (1989).

4.4 Solvatochromism

This describes the influence of solvent polarity on the absorption maximum of the dyes (Yakubu, 1992). Solvent effects on organic reactivity and on absorption spectra have been studied for more than a century. It is well known that the photo-physical behaviour of a dissolved dye depends on the nature of its environment. The intensity, shape, and maximum absorption wavelength of the absorption band of the dye in solution depends strongly on the solvent-solute interactions and solvent nature (Peter, 2011). This effect is closely related to the nature and degree of dye–solvent interactions. The solvent dependent spectral shifts can arise from either non-specific (dielectric enrichment) or specific (e.g. hydrogen-bonding) solute–solvent interactions (Zakerhamdi *et al.,* 2012). Solvatochromic effects may give an indication of the magnitude expected for nonlinear optical properties since it reflects the polarizability of a chromophore (Asiri and Al-amodi, 2009). Moreover, the presence of donor and acceptor moieties in azo dyes is interested in the study of solvatochromism (Mosoud *et al.,* 2005).

It is however evident from literature that, the bathochromic effect of the active methylene compound incorporated into the acceptor half of the chromogen follows a similar pattern irrespective of the electron donating groups in the donor half of the chromogen. This order was generally observed for dye 5 which was more bathochromic than 3, and finally dye 4 was also more bathochromic than dyes 1, 2 and 6. Quantitatively, bathochromic shift is determined by two opposing factors at the acceptor ring. These are the electron withdrawing strength of the acceptor group and steric influence of the atom attached to the ring. It has been shown that dyes derived from 2,2-indene-1,3-diyledene bispropanedinitrile might suffer from steric hinderance due to the positioning of two cyano groups at one carbon atom but is not much affected adversely because cyano groups are rod-like in shape. Whatever this steric interference might incur on the λ_{max} is much counterbalanced by the strength of electron withdrawing cyano group being strongly attached. A strong group attached to the acceptor ring in a situation like this is believed to lead to increased conjugation thus lowering the ionization potential across the molecules and therefore bringing about a bathochromic shift or red shift (Bello and Yakubu, 1997). The results indicate that the λ_{max} is highly dependent upon solvent polarity. It was observed that wavelength shifted towards shorter wavelengths as the solvent was changed from polar to nonpolar.

4.5 Halochromism

Halochromism can be explained as reversible colour change due to a change in pH of a solution. Changes in pH cause change in the ratio of ionised and non-ionised states, and, since these two states have different colours, the colour of the solution changes. Halochromism in the aminoazo dyes is due to protonation of the azo group at the nitrogen atom and is usually accompanied by a large bathochromic shift (positive halochromism) (Bello and Griffiths, 1989).

This colour change can be used in acid-base titrations where the colour change of the halochrome corresponds to the end-point of the reaction. The halochromism of the azo disperse dyes synthesized were studied in acetone and DMF as solvent. The shift of absorption maxima on acidification with hydrochloric acid were summarized and tabulated in Table 4. In all cases, the acid solutions were neutralized carefully with weak alkali (sodium bicarbonate) to verify that the original spectra were completely resorted, showing that decomposition of the dyes had not occurred during protonation (Yakubu, 1992; Alnajjar *et al.,* 2013).

The results also showed that the dyes exhibited negative and positive halochromisms on addition of one drop of hydrochloric acid to the solution of the dyes in acetone and DMF. It's common with azo disperse dyes to show marked colour changes in solution on addition of acid (Asiri and Al-amodi, 2009). It is well known that the red shift increases as the electron-withdrawing nature of the acceptor ring decreases, and conversely, the positive halochromism decreases if the electron withdrawing groups are attached to the acceptor ring.

This dye shows a marked change in absorption maximum from 520 – 515 nm, indicating negative halochromism of – 5 nm. The decrease could be attributed to the flow of electrons from trialkylamino nitrogen towards the azo group as a result of the component aromatic system on absorption of light. However, the situation changes when using DMF as solvent. Unlike in acetone, majority of the dyes showed negative halochromism in DMF, most of the dyes showed both negative and positive halochromism on addition of a drop of HCl.

4.6 Molar Extinction Coefficient and Percentage Dye Exhaustion of Synthesized Dyes

The data reported in Table 5 show the high values of extinction coefficient (ε) for all of the dyes in acetone and DMF, indicating that the dyes have high colour strength. It can be observed from Table 4 and 5 that to a large extent, the exhaustion of the dye onto the polyester fabric was not inversely proportional to the molecular weight of the dyes in series 1, likewise the percentage exhaustion for series 2 was not directly proportional to the molar mass of the dye. The result was contrary to the 3,5-dibromoaminobenzaldehyde dyes reported by Bello *et al.,* (2013). It can also be observed that the percentage exhaustion of the dyes condensed with indandione as electron withdrawing group proved to have higher substantivity than their 3-dicyanovinylindane counterpart and in some cases even better than the aldehyde dyes and those based on other AMC. This can be explained by the fact that both indandione and 3-dicyanivinylindane are having at least an oxygen atom in their structure which can participate in hydrogen bond formation inside the fibre structure, while 1,3-bisdicyanovinylindane does not carry any oxygen atom or hydrogen-bonding heteroatoms in its structure. Another possible explanation is that, oxygen is more spherical than cyano group and therefore less substantive, this was shown in the literature cited by Yakubu (1992).

4.7 Wash fastness properties

The wash fastnesses of the dyed fabrics were tested according to ISO 3 standard procedure (Nkeonye, 1987). It was clearly shown that all the synthesized dyes gave a very good wash fastness on both polyester and nylon 6.6 fabrics. Most of the dyes on both polyester and nylon 6.6 had a rating of 4 – 5 for change in colour and 4 – 5 for staining on adjacent fabric.

4.8 Light fastness properties

The light fastness of each of the dyes was measured by employing the standard method for determination of colour fastness of textiles. Light fastness assessment was carried out using daylight according to ISO BO1: 1994 standard procedure. The result for the light fastness was presented in Table 6. Several reports suggested that, fading of azo dyes is mainly a consequence of decomposition of the –N=N– moiety by oxidation, reduction or photolysis. The rates of these processes should depend on the chemical structure of the dye, the type of substrate and treatment conditions. Since the dyed substrates employed in this study were polyester and nylon 6.6 fabrics, the fading process likely occurs by oxidation. The ease of oxidation of azo linkages should be a function of electron density (Khosravi *et al.,* 2005). The effect of electron-withdrawing substituents in the diazo residue or when incorporated into the terminal amino group can be explained in terms of their reduction of the electron density at the amino nitrogen atom. Similarly, the low light fastness values for the azo dyes can be accounted for by the increased electron density at the terminal nitrogen atom (Otutu and Osabohein, 2009).

4.9 Fastness to pressing

Pressing fastness can be an important property of disperse-dye on polyester, because of the use of heat treatments in the finishing of the fabric. Disperse dyes are not chemically combined with the fibre/fabric, but are mechanically held in solid solution. Thus, when they undergo the influence of heat they are free to vaporize out of the fibre with little or no decomposition (Hauser, 2011). Table 7 shows the results of fastness to pressing on polyester and nylon 6.6 fabrics respectively. The results depicted that all the synthesized dyes had good to very good fastness to pressing. The result in the table shows that the synthesized dyes had an average pressing fastness rating of 4 – 5.

4.10 Fastness to perspiration

Perspiration fastness test was determined according to ISO, 105- E04 1994 standard method. Both alkaline and acid perspiration tests were evaluated. The results of the perspiration fastness test (Table 9) shows that both alkaline and acidic perspiration fastness on polyester and nylon 6.6 were very good. Almost all the dyes gave a rating of 4 – 5 for change of colour and staining of adjacent fabric. The high perspiration fastness of the dyes may be due to the state of the dyes in the fabrics, being in form of insoluble particles to the attack of most chemicals in aqueous solution.

5.0 Conclusion

Active methylene based azo disperse dyes were synthesized. The characterization of the dyes showed that they have well defined melting point range of 270 - 384 °C and most of them gave a good percentage yield of over 58 %. The results of visible absorption spectra show that the dyes absorbed maximally within the visible region. Solvathochromic data show that Dye 5 had the highest bathochromic shift of 130 nm and 125 nm in acetone and DMF. The dyes exibited negative and positive halochromism. Dye 5 was found to be the most negative and positive with value of -235 nm and +170 nm respectively. The dyes have high molar extinction coefficient and high percentage exhaustion on both polyester and nylon 6.6 fabrics. The result of wash fastness, fastness to pressing and fastness to perspiration were very good with an average rating of 4-5. In the case of light fastness, a low average rating of 3 was obtained.

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