



RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND DYEING ASSESSMENT OF ACID AZO DYES BASED ON 3-(2-AMINO-THIAZOL-4-YL) COUMARIN ON WOOLEN FABRIC

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ABSTRACT

A series of acid azo dyes were synthesized by the coupling of various Naphthoic acids with the diazonium salt solution of 3-(2-amino-thiazol-4-yl) coumarin. The resulting dyes were characterized by spectral techniques, *i.e.*, elemental analysis, UV, IR and ¹H-NMR spectroscopy. The dyeing performances of all the dyes were evaluated on woolen fabric. Dyeing of woolen fabric resulted in reddish pink to violet shades with good depth and levelness. The dyed fabrics showed moderate to very good washing and perspiration fastness.

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INTRODUCTION

Coumarins are attractive and versatile molecules that find applications in various fields like medicine, perfumery, dyes, pigments, optical brighteners, lasers, optical data storage devices, solar cells, etc (Luo *et al.*, 2001). Coumarin is not fluorescent, but the introduction of an electron withdrawing group such as a diazotized aromatic amine or an acetyl group makes it highly fluorescent. Coumarins are generally very convenient compounds for chemical modification due to the ease of synthesis (Takadate *et al.*, 1997). Chromen-2-one establishes a family of dyes that are applicable in different fields of science and technology (Murata *et al.*, 1994; Suppan, 1983; Nad *et al.*, 2003). Coumarin and their derivatives have been a subject of considerable interest in numerous fields (Kawski, 1991; Giri and Bajaj, 1992; Samanth, 2000). They exhibit strong fluorescence in the UV–VIS region that makes them suitable to use as colorants, dye laser media and nonlinear optical chromophore. Acid or anionic dyes are dyes with water solubilizing ionic substituent.

These dyes are completely ionized in the acidic condition used in the dyeing process (Christie, 2001). Acid dyes are usually applied to nitrogenous fibers like wool, silk and nylon (De Giorgi *et al.*, 1997; Abeta, 1992).

Acid dyes are attached to the wool fabric not only by electrostatic attraction but also by its affinity toward the fiber. Acid dyes are classified based on affinity, dyeing properties and chemical constitution of the dyes. There are many acid dyes reported in literature such as anthraquinone based acid dyes (Foris, 1977; Venkataraman, 1952), acid nitro dyes (Szadowski and Rzybylski, 1984), triphenylmethane acid dyes (McLellan, 2009) and acid azo dyes (Gaspar *et al.*, 1948; Bornengo *et al.*, 1980; Stohr *et al.*, 1985). Out of these, acid nitro dyes have good light fastness but low color strength (Szadowski, 1984). Triphenylmethane acid dyes are suffering from poor light fastness properties (Clark, 2011) and replacement of anthraquinone dyes with equivalent azo dyes has great importance (Annen *et al.*, 1987). The class of azo dyes plays an important role due to their wide range of color, brightness, simplicity and ease of manufacturing and dyeing performance (Venkataraman, 1970; Zhang *et al.*, 1997; Hallas *et al.*, 1997; Faustino *et al.*, 2008).

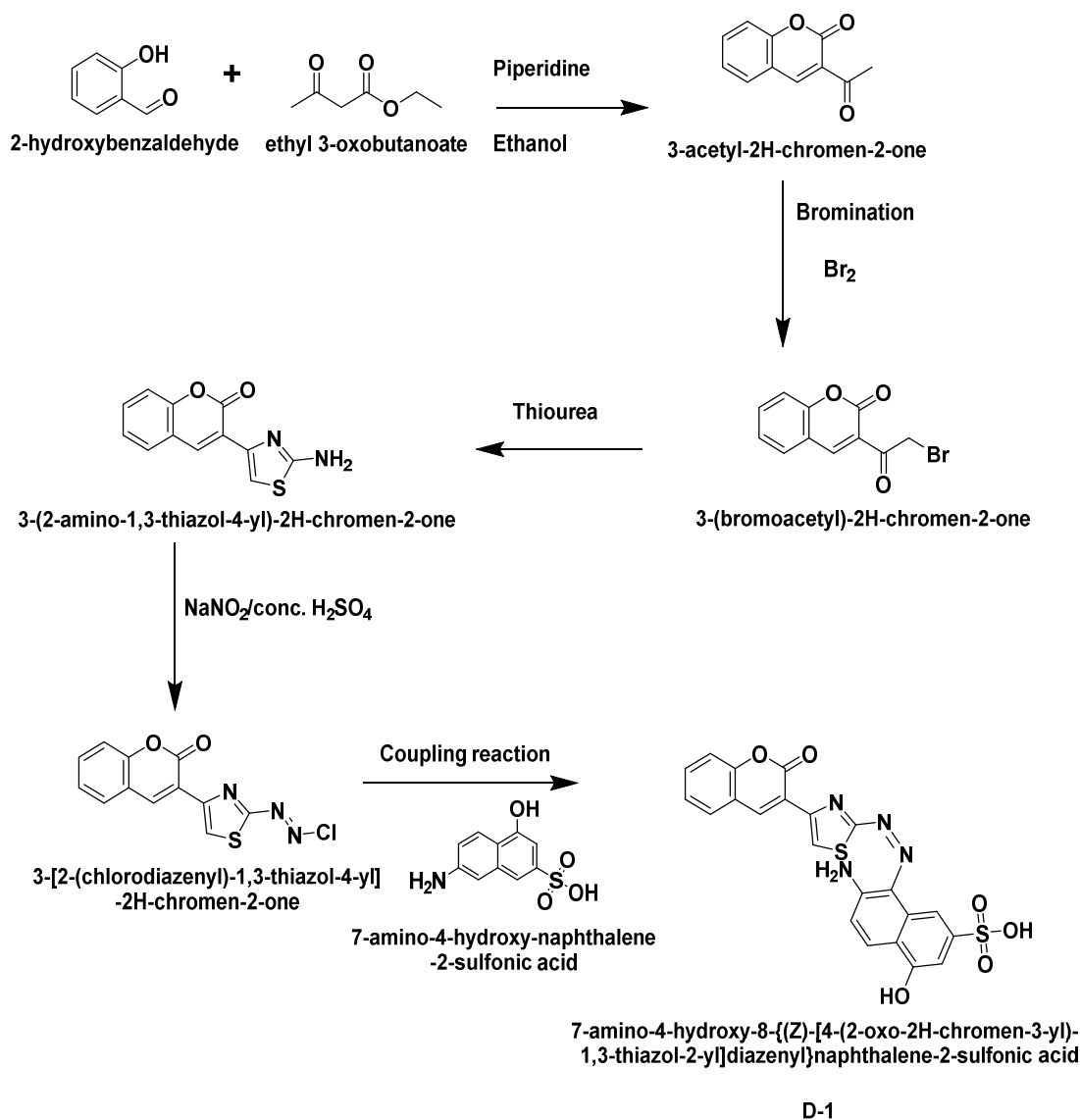
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They are used in dyeing textiles, leather, paper, food, cosmetic products (Zhi-Gang *et al.*, 2009). They are also used in high tech applications such as lasers and non-linear optical systems (Sternberg *et al.*, 1990), photodynamic therapy (Gregory, 1994), dye sensitized solar cells (Mekkawi *et al.*, 2005), metallochromic indicators (Marchevsky *et al.*, 1985), thermal transfer printing and fuel cells (Gregory, 1993). Acid azo dyes containing aromatic heterocyclic moiety have been investigated due to their wide applications. Heterocyclic azo dyes have been periodically reviewed (Elgmeie *et al.*, 1994; Shuttleworth *et al.*, 1990; Weaver *et al.*, 1982). Use of heterocyclic diazo or coupling component has made the production of colorants having brilliant color and chromophoric strength (Towns, 1999).

MATERIALS AND METHODS

All the employed chemicals were of analytical reagent grade. The naphthoic acids shown in Table II were used for diazotization. Woolen fabrics were gifted by Atul Ltd., Valsad, Gujarat. Melting points were determined by the open capillary method and are uncorrected. The infrared spectra were recorded in KBr pellets on a Perkin-Elmer Spectro 400 (SAIF, CHANDIGARH). The ¹H-NMR spectra were recorded on BRUKER AVANCE II 400 NMR Spectrometer (SAIF, CHANDIGARH). An Infra Colour Dyeing Machine (ROTA DYER) was used for dyeing of woolen fabrics.



Scheme 1. Proposed synthetic route for the 3-(2-amino-thiazol-4-yl) coumarin based dyes (D-1 to D-15)

MATERIALS AND METHODS

We wish to describe a simple and efficient protocol for the rapid preparation of various Acid dyes from the diazotization of 3-(2-amino-thiazol-4-yl) coumarin with various Naphthoic acids.

SCHEME

STEP I: PREPARATION OF 3-Acetyl-coumarin

To a solution of salicylaldehyde (0.025 mol, 3.44g) and acetoacetic ester (0.025 mol, 3.1g) in absolute ethanol (15 ml) 2-3 drops of piperidine was added and shaken gently.

Table 1. Dye Bath Materials Used

Dye Bath Materials	
Materials	Wool
Fibre (g)	5 g
Amount of dye (g)	0.1 g
Glauber's salt (20%)	2.5-3.0 ml
Formic acid solution	1.5-2.0 ml
pH	4.0
MLR	1:50
Dyeing time (min)	60 min
Dyeing temp. (°C)	100° C
Total volume	100 ml

After 30 min needle shaped crystals of 3-acetyl coumarin were separated out which were filtered dried and recrystallised from ethanol (Czerney, 1983). m.p. 124°, yield: 3.18g (68%)

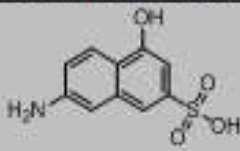
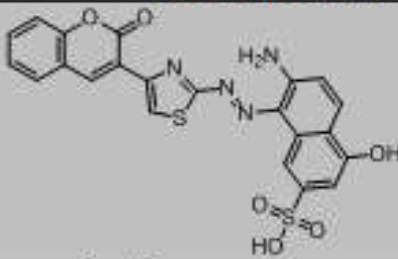
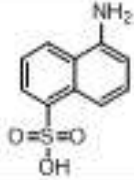
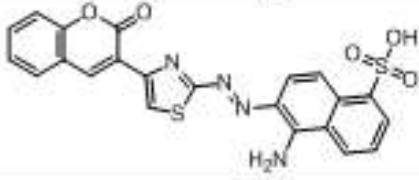
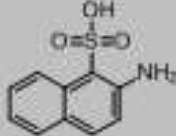
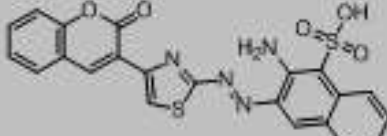
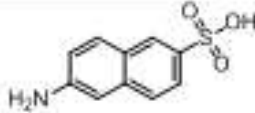
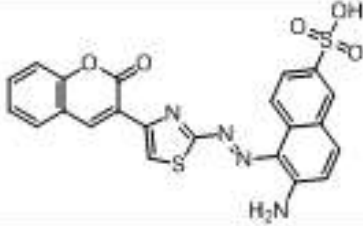
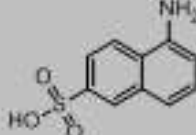
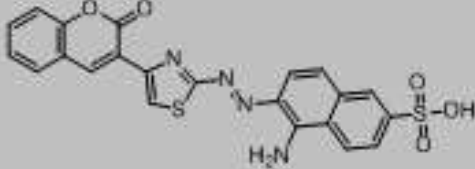
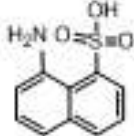
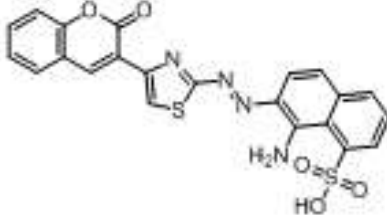
STEP II: PREPARATION OF 3-Bromo acetyl coumarin

To a solution of 3-acetyl coumarin (0.01 mol, 2g) in CHCl_3 (15 ml), bromine (1.7g) in 6 ml CHCl_3 was added with intermittent shaking and warming. The mixture was heated for 15 min on a water bath to expel most of the HBr. It was then cooled filtered and washed with ether and recrystallised from acetic acid.³⁷ m.p. 162°, yield: 1.97g, (70%)

STEP III: PREPARATION OF 2-Amino-4-(coumarinyl-3) thiazole

A solution of 3-Bromo acetyl coumarin (0.005mol, 1.35g) in hot ethanol was treated with thiourea (0.01mol, 0.8g) so that clear solution was obtained which soon deposited some crystals.

Table 2. Structure of the coupling components and corresponding acid azo dyes

Dye	Coupling Component	Acid azo dye structure
D ₁		
D ₂		
D ₃		
D ₄		
D ₅		
D ₆		

Continue.....

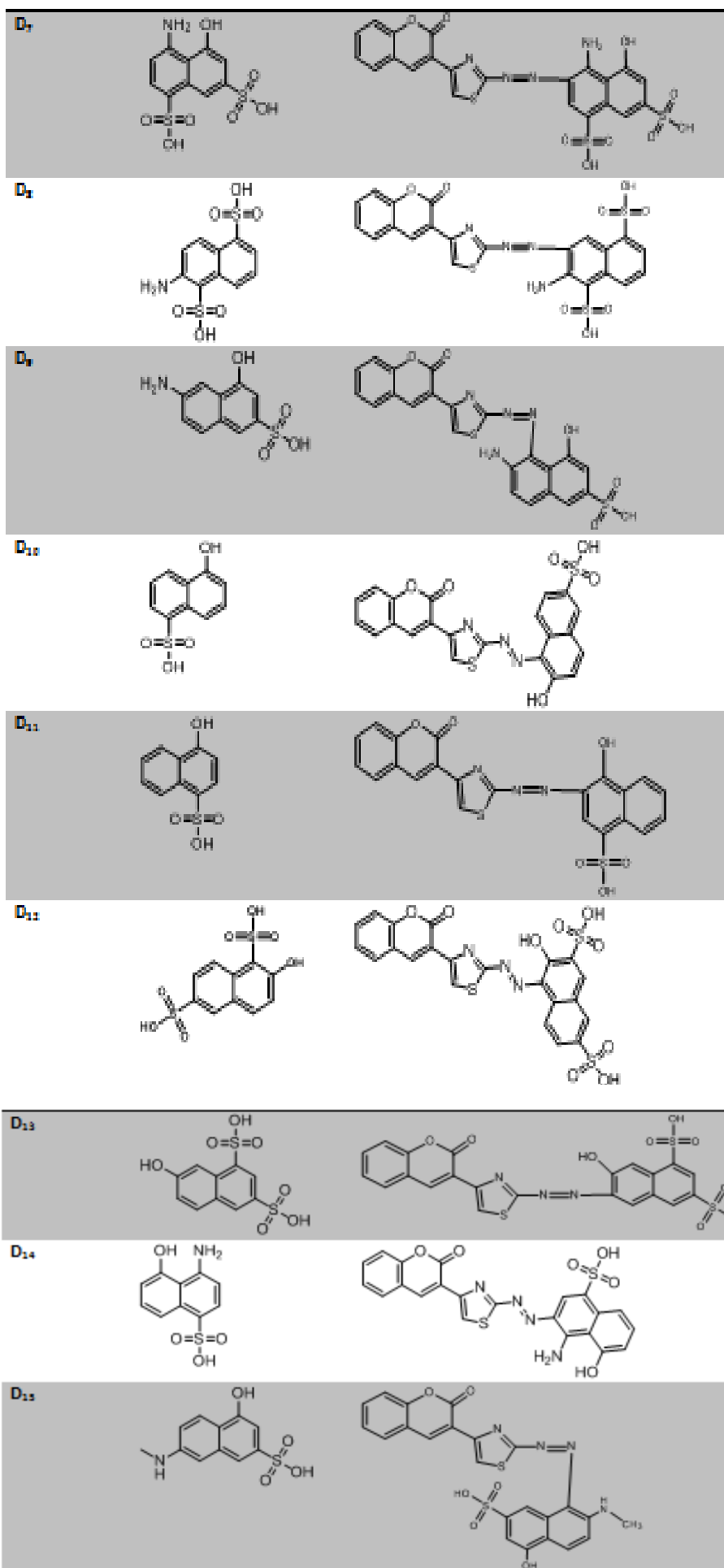


Table 3. IR DATA OF SELECTED COMPOUNDS FROM D-1 TO D-15

Sr. No.	Dye	IR (KBr, ν cm^{-1})
1.	D-1	3420, -OH stretching, phenol 1709, -C=O stretching 1045, -C-O stretching 1606, -C=C stretching, Aromatic ring 1570, -N=N stretching, Azo group 944, -C-S stretching 1671, -C=N stretching 1163, -S=O stretching, sulphonic acid
2.	D-4	3316-3383, -N-H stretching, Primary amine 1695, -C=O stretching 1095, -C-O stretching 1534, -C=C stretching, Aromatic ring 1603, -N=N stretching, Azo group 924, -C-S stretching 1177, -S=O stretching, sulphonic group
3.	D-5	3320-3384, -N-H stretching, Primary amine 1697, -C=O stretching 1095, -C-O stretching 1537, -C=C stretching, Aromatic ring 1605, -N=N stretching, Azo group 925, -C-S stretching 1178, -S=O stretching, sulphonic group 1665, -C=N stretching
4.	D-6	3320-3383, -N-H stretching, Primary amine 1698, -C=O stretching 1095, -C-O stretching 1537, -C=C stretching, Aromatic ring 1605, -N=N stretching, Azo group 925, -C-S stretching 1177, -S=O stretching, sulphonic group 1666, -C=N stretching
5.	D-8	3420, -N-H stretching, Primary amine 1718, -C=O stretching 1095, -C-O stretching 1537, -C=C stretching, Aromatic ring 1606, -N=N stretching, Azo group 925, -C-S stretching 1177, -S=O stretching, sulphonic group
6.	D-14	3347, -O-H stretching, Phenol 1716, -C=O stretching 1096, -C-O stretching 1605, -N=N stretching, Azo group 925, -C-S stretching 1177, -S=O stretching, sulphonic group 756, aromatic substitution, four adjacent hydrogen atoms

Table 4. ^1H NMR DATA OF SELECTED DYES FROM D-1 to D-15

Dye No.	Chemical Shifts (in ppm)	Multiplicities	Relative number of protons	Assignment
D-3	6.40 - 8.40	M	9	Aromatic protons
	3.82	S	1	-NH group
	8.86	S	1	-SO ₃ H group
D-4	7.20 - 7.76	M	9	Aromatic protons
	8.50	S	1	-SO ₃ H group
	3.67	S	1	-NH group
	2.57	S	1	-CH proton(cyclic ester ring)
	2.12	S	1	-SH proton (thiazole ring)
D-5	7.13-7.81	M	9	Aromatic protons
	3.84	S	1	-NH group
	8.49	S	1	-SO ₃ H group
	5.59	S	1	-CH proton(cyclic ester ring)
	1.89	S	1	-SH proton (thiazole ring)
D-14	7.00-8.50	M	8	Aromatic protons
	8.80	S	1	-OH group
	9.00	S	1	-SO ₃ H group
	1.94	S	1	-CH proton (cyclic ester ring)
	1.16	S	1	-SH proton (thiazole ring)
	3.45	S	1	-NH group

Table 5. Different coupling components to form various acid dyes at pH 4 & 8

NO. (Dyes)	R Coupling Components	M.F.	M.W (g/mol)	YIELD %	M.P. °C	% ANALYSIS (FOUND) CALC.		
						C	H	N
D-1	R ₁ , J-acid	C ₂₂ H ₁₄ O ₆ N ₄ S ₂	494	88	350	(53.46)	(2.85)	(11.30)
						53.49	2.86	11.34
D-2	R ₂ , Laurent acid	C ₂₂ H ₁₄ O ₅ N ₄ S ₂	478	77	310	(55.26)	(2.91)	(11.70)
						55.28	2.95	11.72
D-3	R ₃ , Tobias acid	C ₂₂ H ₁₄ O ₅ N ₄ S ₂	478	75	285	(53.25)	(2.93)	(11.71)
						55.28	2.95	11.72
D-4	R ₄ , Bronner's acid	C ₂₂ H ₁₄ O ₅ N ₄ S ₂	478	81	Chars at 242	(53.26)	(2.90)	(11.70)
						55.28	2.95	11.72
D-5	R ₅ , Cleve's acid	C ₂₂ H ₁₄ O ₅ N ₄ S ₂	478	82	252	(53.26)	(2.93)	(11.72)
						55.28	2.95	11.72
D-6	R ₆ , Peri acid	C ₂₂ H ₁₄ O ₅ N ₄ S ₂	478	85	286	(53.24)	(2.91)	(11.71)
						55.28	2.95	11.72
D-7	R ₇ , K-acid	C ₂₂ H ₁₄ O ₅ N ₄ S ₂	478	79	250	(46.00)	(2.43)	(9.73)
						46.03	2.46	9.76
D-8	R ₈ , Sulpho Tobias acid	C ₂₂ H ₁₄ O ₈ N ₄ S ₃	558	80	295	(47.32)	(2.52)	(10.01)
						47.35	2.53	10.04
D-9	R ₉ , Gamma acid	C ₂₂ H ₁₄ O ₆ N ₄ S ₂	494	82	290	(53.46)	(2.84)	(11.29)
						53.49	2.86	11.34
D-10	R ₁₀ , Schaffer's acid	C ₂₂ H ₁₄ O ₆ N ₄ S ₂	478	85	260	(53.46)	(2.85)	(11.30)
						53.49	2.86	11.34
D-11	R ₁₁ , N.W. acid	C ₂₂ H ₁₃ O ₆ N ₃ S ₂	479	79	291	(55.13)	(2.73)	(8.76)
						55.16	2.74	8.77
D-12	R ₁₂ , R-acid	C ₂₂ H ₁₃ O ₉ N ₃ S ₃	559	76	312	(47.23)	(2.30)	(7.51)
						47.27	2.34	7.52
D-13	R ₁₃ , G- acid	C ₂₂ H ₁₃ O ₉ N ₃ S ₃	559	83	300	(47.22)	(2.31)	(7.50)
						47.27	2.34	7.52
D-14	R ₁₄ , S- acid	C ₂₂ H ₁₄ O ₆ N ₄ S ₂	494	82	268	(53.45)	(2.81)	(11.33)
						53.49	2.86	11.34
D-15	R ₁₅ , N-methyl J acid	C ₂₂ H ₁₄ O ₆ N ₄ S ₂	508	84	256	(54.36)	(3.15)	(11.00)
						54.38	3.17	11.03

Table 6. Results of acid dyeing and wash fastness properties on wool fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Sr. No.	Dye	Colour shade on wool	Change in shade	Stain on Multifibre					
				Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
1.	D1	Dark pink	1	3	4-5	4	3	1-2	4
2.	D-5	Dark violet	2-3	2-3	4-5	4	2	1-2	3-4
3.	D-7	Carrot pink	1-2	3-4	4-5	4	3-4	4	4
4.	D-8	Carrot light pink	3-4	2-3	4-5	3-4	2	2	3
5.	D-11	Light brown	1	3-4	4-5	4	2-3	3	4
6.	D-13	Brown	2	3	4-5	4	2	2	3
7.	D-14	Grey	1	4	4-5	4-5	3-4	3	4

Table 7. Results of acid dyeing and perspiration (acidic) fastness properties on wool fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Sr. No.	Dye	Colour shade on wool	Change in shade	Stain on Multifibre					
				Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
1.	D-1	Dark pink	3	4-5	4-5	4-5	4	4	4-5
2.	D-5	Dark violet	4	4-5	4-5	4-5	4	4	4-5
3.	D-7	Carrot pink	4	4	4-5	4-5	4	4-5	4-5
4.	D-8	Carrot light pink	3-4	4	4-5	4-5	3-4	4-5	4-5
5.	D-11	Light brown	3	4-5	4-5	4-5	4-5	4-5	4-5
6.	D-13	Brown	3-4	3-4	4	4	2-3	3	3
7.	D-14	Grey	4	4-5	4-5	4-5	4	4-5	4-5

It was then boiled in water containing sodium acetate, which was then filtered dried and crystallized from ethanol. m.p. 225°, and yield: 0.792g (65%)

STEP IV: DIAZOTISATION OF 2-Amino-4-(coumarinyl-3) thiazole

Dry sodium nitrite (0.69 g, 0.01 mole) was added portionwise over a period of 30 minutes; to concentrated sulphuric acid

(2.0mL) under stirring below 65°C. The resulting solution was added into the mixture of acetic acid–propionic acid (17/3 v/v). The resulting nitrosyl sulphuric acid mixture was cooled to 0°C and the diazo component (1.77 g, 0.01 mole) was added portionwise and stirring was continued at this temperature for 2 hr. The excess of nitrous acid (gave a positive test on SI paper) was decomposed with the required amount of urea.

Table 8. Results of acid dyeing and perspiration (alkaline) fastness properties on wool fabrics; grading: 5 – excellent, 4 – very good, 3 – good, 2 – fair, 1 – poor

Sr. No.	Dye	Colour shade on wool	Change in shade	Stain on Multifibre					
				Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
1.	D-1	Dark pink	3	4	4-5	4-5	3-4	3-4	4
2.	D-5	Dark violet	3	3-4	4	4	3-4	3-4	4
3.	D-7	Carrot pink	4	3-4	4-5	4-5	3-4	3-4	4
4.	D-8	Carrot light pink	4	3-4	4-5	4	3	3-4	3-4
5.	D-11	Light brown	1-2	4	4-5	4-5	3-4	3-4	4
6.	D-13	Brown	4	4	4-5	4-5	3	4	4-5
7.	D-14	Grey	2-3	4	4-5	4	4	4-5	4-5

Thus obtained clear diazonium salt solution was used for the subsequent coupling reaction.

STEP V: COUPLING OF 2-Amino-4-(coumarinyl-3) thiazole with various Naphthoic acids

J-acid (2.39 g, 0.01 mole) was suspended in water (20 mL) and acetic acid (10 mL); and cooled to 0°C. The freshly prepared diazonium salt solution was added dropwise to this well-stirred solution over a period of 2 hrs. Under vigorous stirring, keeping the temperature below 5°C. The reaction mixture was stirred for 45 min at 0-3°C, maintaining pH at 4.0-5.0 with a help of a 10% sodium acetate solution. The reaction mass was then diluted with 100 mL water, filtered, washed with water and dried in oven at 50°C. Dye was recrystallized from acetone.

PROCESS OF DYEING

0.2 g weighed sample of the dye is taken in a 100 ml beaker. Then, dissolving it in 50-60 ml of hot distilled water and adding it in hot pot and diluting upto 100 ml. 1-2 ml of soda ash is added to increase pH if the dye remains undissolved. Addition of 2.5-3.0 mol of glaubar's salt i.e. (20% w/v) and 1.5-2.0 mol of formic acid to the hot pot. Then dipping of the woolen cloth of weight 4 g in the hot pot and closing it. The hot pot is then fixed in Infra color instrument and maintaining temperature 100°C for 1 hour. Initially, temperature is 31.5°C. It increases slowly at the rate of 2.5°C/min to attain temperature constant upto 100°C.

RESULTS AND DISCUSSION

Physical properties of dyes

A series of azo dyes were prepared by the diazotization and coupling reaction. The synthesized dyes were then dried in oven at temperature of 50°C. These dyes were then recrystallised from Acetone and DMF solvents and obtained as crystalline powders. These dyes gave a wide range of colors ranging from violet to dark pink and red to dark brown.

Analytical and spectral data of the dyes

The IR & ¹H NMR data of the synthesized dyes are given below in table III, IV and V.

FTIR DATA OF SELECTED DYES FROM D-1 to D-15

Dyeing properties of dyes

The acid mono azo dyes were applied at a 2 % depth on wool fabric. Their dyeing properties are shown in Tables VI–VIII.

These dyes gave a wide range of colors varying from reddish pink to violet shades with good levelness, brightness and depth on the fabrics. The variation in the shades of the dye fabric results from both the nature and position of the substituent present on the coupling compound. The dyeing showed medium fastness to wash, with good to very good washing, perspiration (acidic and alkaline) fastnesses.

Determination of the percentage exhaustion and fixation

The percentage exhaustion and fixation of the dyed fabrics were determined according to the reported methods (Shishtawy *et al.*, 2007). The percentage exhaustion was observed for each dye in the range 75-85% and the fixation for all the dyes is about 70-90%.

Fastness property

Wash fastness of the selected dyes were carried out according to the ISO 105 CO3 method. Perspiration (acidic and alkaline) fastness of the selected dyes were carried out according to the ISO 105 EO4 method. (Standard Methods for the determination of the Color Fastness of Textiles & Leather, SDC, UK, AATCC Technical Manual, AATCC, USA, MARKS & SPENCER Test Methods, M & S, UK)

Conclusion

All newly synthesized acid mono azo dyes exhibited moderate to good fastness to wash, acidic and alkaline perspiration. The remarkable degree of levelness after dyeing indicates good penetration into, and affinity of these dyes for the fabric matrix. They give deep and bright hues with leveling dyeing. The nature of the substituent in the coupling component has little influence on the shade of the dyeing.

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