

Synthesis and performance studies of novel bisazo reactive dyes on various fibres

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(Received: July 25, 2009; Accepted: August 21, 2009)

ABSTRACT

A demand for novel reactive dyes with improved properties have led to synthesis of cold brand reactive dyes by coupling tetrazotised 4,4'-methylene bis-2,5-dimethoxy aniline with various cyanurated coupling components such as H-acid, Chicago acid, K-acid, J-acid, N-methyl J-acid, N-phenyl J-acid, Gamma acid, N-methyl Gamma acid, Peri acid, N-phenyl peri acid, Tobias acid, Sulpho tobias acid, Laurent acid, Bronner's acid, Koch acid and their dyeing performance as reactive dyes has been assessed on cotton, wool and silk fibres. The purity of dyes was checked by Thin Layer Chromatography. The IR spectra showed all characteristic bands and ¹H NMR spectra of representative dye showed all the expected signals. The percentage dye bath exhaustion on different fibres was good. The dyed fibres showed moderate to very good fastness to light, washing and rubbing.

Key words: 4,4'-methylene bis-2,5-dimethoxy aniline, Bisazo reactive dyes, Dyeing, Cotton, Wool and Silk.

INTRODUCTION

Dyeing using reactive dyes have recently led to increased demands on the quality of the dyeing and the profitability of the dyeing process. There is consequently still a demand for novel reactive dyes which have improved properties, especially in respect of application. Reactive dyes which have an adequate substantivity and at the same time a good ease of washing out of the non fixed portions are required for dyeing. They should furthermore have a good tinctorial yield and high reactivity and dyeing having high degrees of fixing in particular should be produced¹. Major categories of dyes used in the coloration are Direct dyes, Vat dyes, Sulfur dyes, Azoic dyes and Reactive dyes; among them Reactive dyes represent an important class of cellulosic textile. The major advantages of

using reactive dyes are high wet fastness levels and bright shades. According to a survey² carried out in 1996, over 80% of the dyes used for dyeing were reactive dyes. Most of the reactive dyes used in India are azo dyes. It is reported³ that unmetallised azo reactive dyes yellow, orange and red shades. Violet, brown and black shades from azo and metallised azo reactive dyes are generally anthraquinone or phthalocyanine based. These dyes are used on higher value clothes which are normally mercerized⁴. The dyes with two reactive groups give a higher fixation than dyes with one reactive group^{5, 6}. Therefore, it was though interesting to synthesize the disazo reactive dyes based on 4,4'-methylene bis-2,5-dimethoxy aniline. The synthesized reactive dyes have been characterized and applied on the silk, wool and cotton.

EXPERIMENTAL

Materials and Methods

The purity of all the dyes has been checked by TLC⁷. The IR Spectra⁸ were recorded on a Perkin Elmer Model - 881 spectrophotometer and ¹H NMR spectra⁹ on a Varian 300 MHz instrument using TMS as internal standard and CDCl₃ as solvent. Absorption spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analysis of C, H, N was carried on Carlo Erba 1108 instrument. The light fastness was assessed in accordance with BS: 1006-1978¹⁰. The rubbing fastness test was carried out with a Crockmeter (Atlas) in accordance with AATCC-1961¹¹ and the wash fastness test in accordance with IS: 765-1979¹².

Synthesis of 4,4'-methylene bis-2,5-dimethoxy aniline

2,5-dimethoxy aniline¹³ (1.53g, 0.01 mole) was dissolved in water (125ml) and 36.5% hydrochloric acid (25ml) at 70°C. The reaction mixture was then reacted with 3% aqueous formaldehyde (25ml) solution at 40°C with stirring for an hour and neutralized with 10% sodium hydroxide, brownish precipitates obtained were filtered off, washed with hot water, dried and recrystallised from acetic acid. Yield 87 %, m. p. 173 - 174°C

Elemental analysis

Found C, 64.13; H, 6.89; N, 8.76% (C₁₇H₂₂O₄N₂ requires C, 64.15; H, 6.92; N, 8.80%)

Tetrazotisation of 4,4'-methylene bis-2,5-dimethoxy aniline (A)

4,4'-methylene bis-2,5-dimethoxy aniline (1.59g, 0.005 mole) was suspended in H₂O (60ml). Hydrochloric acid (0.36g) was added dropwise to this well stirred suspension. The mixture was heated gradually, till clear solution was obtained. The solution was cooled at 0-5°C in an ice bath. A solution of NaNO₂ (0.6g) in water (4ml) previously cooled to 0°C, was then added over a period of five minutes with stirring. The stirring was continued for an hour, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After just destroying excess of nitrous acid with required amount of a solution of sulphamic acid the clear tetrazo solution-A at 0-5°C thus obtained was

used for subsequent coupling reaction.

Cyanuration of H-acid

Cyanuric chloride (1.85g, 0.01mole) was stirred in acetone (25ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19g, 0.01 mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about an hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further 4 hours then clear solution was obtained. The cyanurated H-acid solution was used for subsequent coupling reaction.

Formation of Dyes (D₁ to D₁₅)

To an ice cold and well stirred solution of cyanurated coupling component (R), a freshly prepared solution of tetrazo-A solution as previously prepared was added dropwise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 during addition. Stirring was continued for 4 hours, maintaining the temperature below 5°C. Sodium chloride (12g) was then added and the mixture was stirred for 1 hour. The solid dye separated out was filtered washed with minimum amount of acetone and dried at room temperature.

The same procedure was used to prepare other dyes using different cyanurated coupling components.

Dyeing of fibres

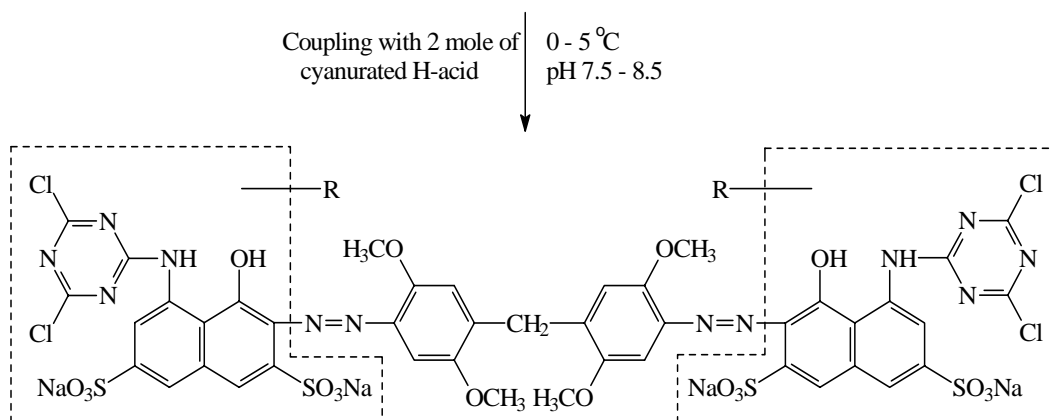
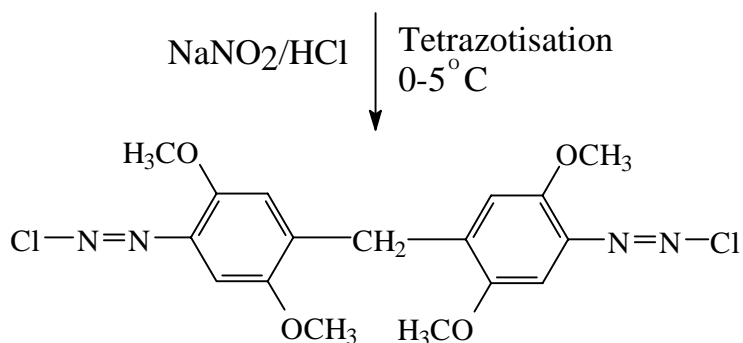
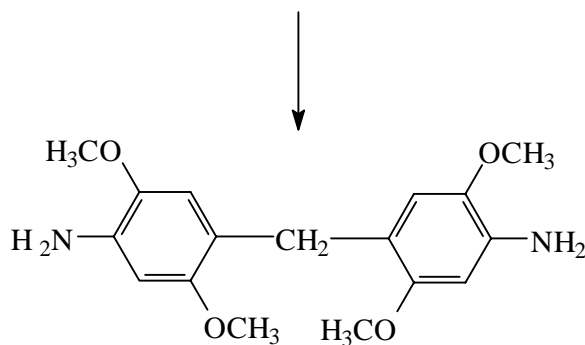
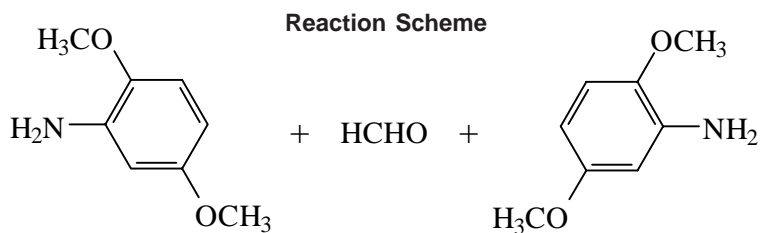
All the dyes D₁ to D₁₅ were applied on cotton, wool and silk by using different reported procedure¹⁴ having the dye bath material given in Table 1.

RESULTS AND DISCUSSION

A series of reactive dyes were prepared in order to evaluate their stability for dyeing cotton, wool and silk fabrics.

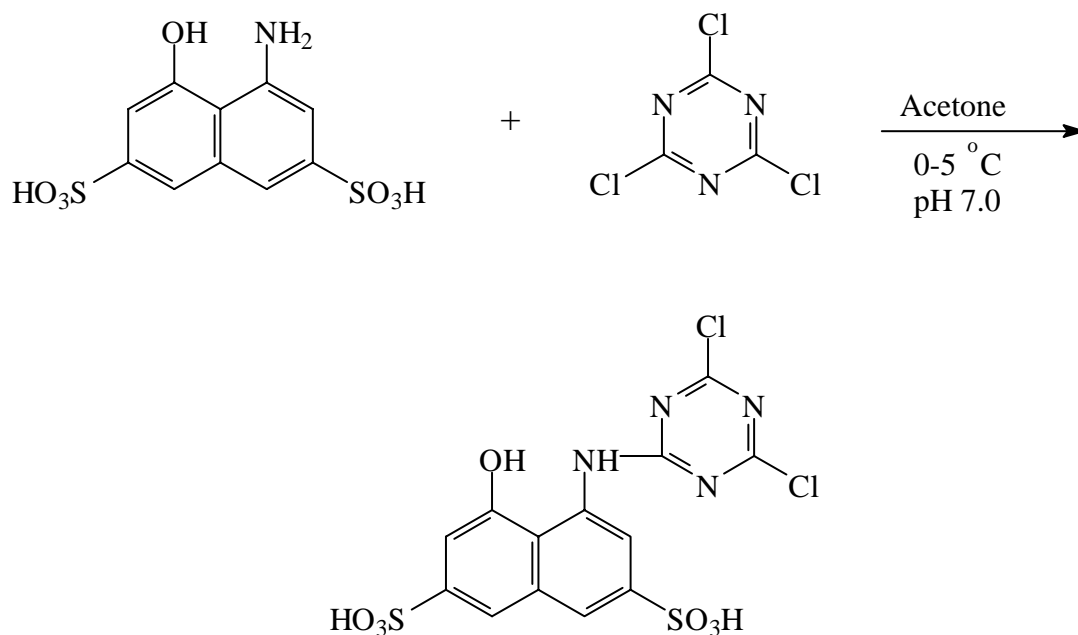
The yield of the dyes ranges from 76 to 86%. The structures are postulated and established based on the analytical and spectral evidences.

Reactive dyes D₁ and D₅ distinguish by the >N-CH₃ group. IR spectra of D₅ shows C-H



Where R = Various cyanurated coupling components for the formation of D₁ to D₁₅ (Table - 2)

Preparation of cyanurated H-acid (R)



stretching at 2820 cm^{-1} and C-H bending at 1438 cm^{-1} indicates the existence of $>\text{N}-\text{CH}_3$ group. D_7 and D_{15} distinguish by the -OH group. IR spectra of D_7 shows O-H bending (C-O stretching) at 1330 cm^{-1} indicates the existence of -OH group.

PMR spectra of reactive dyes D_1 and D_4 shows chemical shift at 6.55-8.30 ppm due to presence of aromatic protons; 2H due to methylene group shows singlet at 2.49 ppm; 12H due to $-\text{OCH}_3$ group shows singlet near 2.72 & 2.87 ppm; 2H due

to -OH group shows singlet near 3.30 ppm; 2H due to -NH group shows singlet near 4.20 ppm.

D_2 and D_3 shows O-H bending (C-O stretching) at 1340 cm^{-1} and N-H bending at 1520 cm^{-1} indicates the existence of -OH group and secondary amine. D_6 shows chemical shift at 3.37 ppm as singlet of 2H due to -OH group but there is no chemical shift of $>\text{NH}$ group which indicates that in the structure of D_6 H-atom of $>\text{NH}$ group is replaced by the phenyl group. D_7 shows chemical

Table 1: Materials and conditions for 2% shade

Materials	Cotton	Wool	Silk
Weight of the fabric	2.0 gm	2.0 gm	2.0 gm
Amount of the dye under study	40 mg	40 mg	40 mg
Glauber's salt solution (20% w/v)	1.0 ml	1.5 ml	1.0 ml
Soda ash solution (10% w/v)	1.0 ml	-	-
Formic acid solution (10% w/v)	-	1.5 ml	1.0 ml
Sodium chloride	0.5 g	-	-
MLR	1:40	1:40	1:40
Total volume of the solution in dye bath	80 ml	80 ml	80 ml
pH of the dye bath	8.0	3.0	3.0
Dyeing temperature	100°C	100°C	85°C
Time for dyeing	90 min	60 min	40 min

Table 2: Characterization of reactive dyes

Dye No.	Coupling components (R)	Molecular Formula	Yield(%)	R _f Value	Elemental Analysis: Found (Calcd.)		
					% C	% H	% N
D ₁	H-acid	C ₄₃ H ₂₈ O ₁₆ N ₁₂ Cl ₄ S ₄ Na ₄	85	0.43	38.75 (38.80)	2.08 (2.10)	12.60 (12.63)
D ₂	Chicago acid	C ₄₃ H ₂₈ O ₁₆ N ₁₂ Cl ₄ S ₄ Na ₄	80	0.36	38.78 (38.80)	2.06 (2.10)	12.59 (12.63)
D ₃	K-acid	C ₄₃ H ₂₈ O ₁₆ N ₁₂ Cl ₄ S ₄ Na ₄	76	0.42	38.76 (38.80)	2.07 (2.10)	12.61 (12.63)
D ₄	J-acid	C ₄₃ H ₃₀ O ₁₂ N ₁₂ Cl ₄ S ₂ Na ₂	81	0.38	44.53 (44.56)	2.55 (2.59)	14.49 (14.51)
D ₅	N-methyl J-acid	C ₄₅ H ₃₄ O ₁₂ N ₁₂ Cl ₄ S ₂ Na ₂	77	0.44	45.50 (45.53)	2.84 (2.86)	14.14 (14.16)
D ₆	N-phenyl J-acid	C ₅₅ H ₃₈ O ₁₂ N ₁₂ Cl ₄ S ₂ Na ₂	73	0.40	50.36 (50.38)	2.87 (2.90)	12.80 (12.82)
D ₇	Gamma acid	C ₄₃ H ₃₀ O ₁₂ N ₁₂ Cl ₄ S ₂ Na ₂	75	0.39	44.54 (44.56)	2.57 (2.59)	14.49 (14.51)
D ₈	N-methyl Gamma acid	C ₄₅ H ₃₄ O ₁₂ N ₁₂ Cl ₄ S ₂ Na ₂	81	0.37	45.49 (45.53)	2.83 (2.86)	14.13 (14.16)
D ₉	Peri acid	C ₄₃ H ₃₀ O ₁₀ N ₁₂ Cl ₄ S ₂ Na ₂	75	0.43	46.36 (46.40)	2.65 (2.69)	15.09 (15.11)
D ₁₀	N-phenyl peri acid	C ₅₅ H ₃₈ O ₁₀ N ₁₂ Cl ₄ S ₂ Na ₂	79	0.35	52.18 (52.21)	2.99 (3.01)	13.25 (13.29)
D ₁₁	Tobias acid	C ₄₃ H ₃₂ O ₄ N ₁₂ Cl ₄	74	0.41	55.94 (55.96)	3.45 (3.47)	18.20 (18.22)
D ₁₂	Sulpho tobias acid	C ₄₃ H ₃₀ O ₁₀ N ₁₂ Cl ₄ S ₂ Na ₂	83	0.45	46.37 (46.40)	2.64 (2.69)	15.06 (15.11)
D ₁₃	Laurent acid	C ₄₃ H ₃₀ O ₁₀ N ₁₂ Cl ₄ S ₂ Na ₂	78	0.36	46.35 (46.40)	2.66 (2.69)	15.08 (15.11)
D ₁₄	Bronner's acid	C ₄₃ H ₃₀ O ₁₀ N ₁₂ Cl ₄ S ₂ Na ₂	80	0.46	46.38 (46.40)	2.64 (2.69)	15.09 (15.11)
D ₁₅	Koch acid	C ₄₃ H ₂₆ O ₂₂ N ₁₂ Cl ₄ S ₆ Na ₆	74	0.38	33.61 (33.64)	1.67 (1.69)	10.93 (10.95)

Table 3: ¹H NMR data of reactive dyes

Dye No.	¹ H NMR (ppm)
D ₁	2.49(2H,s,-CH ₂ -), 2.71(6H,s,-OCH ₃), 2.87(6H,s,-OCH ₃), 3.34(2H,s,-OH), 4.20(2H,s,>NH), 6.93-7.86(10H,m,Ar-H)
D ₂	2.51(2H,s,-CH ₂ -), 2.69(6H,s,-OCH ₃), 2.86(6H,s,-OCH ₃), 3.30(2H,s,-OH), 4.21(2H,s,>NH), 6.98-7.90(10H,m,Ar-H)
D ₃	2.48(2H,s,-CH ₂ -), 2.72(6H,s,-OCH ₃), 2.86(6H,s,-OCH ₃), 3.32(2H,s,-OH), 4.23(2H,s,>NH), 7.01-8.05(10H,m,Ar-H)
D ₄	2.49(2H,s,-CH ₂ -), 2.72(6H,s,-OCH ₃), 2.88(6H,s,-OCH ₃), 3.30(2H,s,-OH), 4.01(2H,s,>NH), 6.55-8.30(12H,m,Ar-H)
D ₅	2.45(2H,s,-CH ₂ -), 2.65(6H,s,-OCH ₃), 2.84(6H,s,-OCH ₃), 3.28(2H,s,-OH), 1.50(6H,s,-CH ₃), 6.70-7.93(12H,m,Ar-H)
D ₆	2.47(2H,s,-CH ₂ -), 2.70(6H,s,-OCH ₃), 2.85(6H,s,-OCH ₃), 3.37(2H,s,-OH), 6.81-7.99(22H,m,Ar-H)
D ₇	2.48(2H,s,-CH ₂ -), 2.71(6H,s,-OCH ₃), 2.89(6H,s,-OCH ₃), 3.33(2H,s,-OH), 4.18(2H,s,>NH), 6.90-7.95(12H,m,Ar-H)
D ₈	2.46(2H,s,-CH ₂ -), 2.67(6H,s,-OCH ₃), 2.86(6H,s,-OCH ₃), 3.31(2H,s,-OH), 1.55(6H,s,-CH ₃), 7.10-8.21(12H,m,Ar-H)
D ₉	2.50(2H,s,-CH ₂ -), 2.68(6H,s,-OCH ₃), 2.87(6H,s,-OCH ₃), 4.15(2H,s,>NH), 7.10-8.21(14H,m,Ar-H)
D ₁₀	2.53(2H,s,-CH ₂ -), 2.72(6H,s,-OCH ₃), 2.90(6H,s,-OCH ₃), 6.95-7.90(24H,m,Ar-H)
D ₁₁	2.50(2H,s,-CH ₂ -), 2.66(6H,s,-OCH ₃), 2.89(6H,s,-OCH ₃), 4.17(2H,s,>NH), 7.01-8.12(16H,m,Ar-H)
D ₁₂	2.47(2H,s,-CH ₂ -), 2.68(6H,s,-OCH ₃), 2.90(6H,s,-OCH ₃), 4.22(2H,s,>NH), 7.11-8.25(14H,m,Ar-H)
D ₁₃	2.45(2H,s,-CH ₂ -), 2.69(6H,s,-OCH ₃), 2.88(6H,s,-OCH ₃), 4.25(2H,s,>NH), 6.98-7.88(14H,m,Ar-H)
D ₁₄	2.49(2H,s,-CH ₂ -), 2.71(6H,s,-OCH ₃), 2.89(6H,s,-OCH ₃), 4.17(2H,s,>NH), 7.13-8.20(14H,m,Ar-H)
D ₁₅	2.48(2H,s,-CH ₂ -), 2.73(6H,s,-OCH ₃), 2.90(6H,s,-OCH ₃), 4.19(2H,s,>NH), 7.08-8.23(10H,m,Ar-H)

Table 4: Shade, Percentage exhaustion and fixation of reactive dyes on cotton, wool and silk

Dye No.	Shade on Dyed fibre	λ_{max}	Exhaustion (%)			Fixation (%)		
			Cotton	Wool	Silk	Cotton	Wool	Silk
D ₁	Violet	510	69.87	67.67	67.95	90.12	91.61	90.50
D ₂	Light violet	495	70.50	70.15	72.60	90.07	89.80	84.02
D ₃	Brown	475	72.55	75.50	72.10	89.59	89.40	81.14
D ₄	Violet	500	72.32	73.25	70.65	88.49	86.68	88.46
D ₅	Light violet	490	74.70	66.90	69.40	90.36	90.43	86.46
D ₆	Light violet	495	77.67	74.63	69.95	86.25	92.46	84.34
D ₇	Orange	470	71.80	67.00	73.05	87.05	84.32	87.61
D ₈	Pink	490	67.15	64.85	75.35	89.35	85.58	87.59
D ₉	Light yellow	470	75.10	74.00	66.25	91.21	89.18	90.56
D ₁₀	Pink	480	74.32	67.95	70.50	87.45	88.30	82.97
D ₁₁	Light brown	465	70.92	65.10	73.50	89.53	90.62	88.43
D ₁₂	Orange	485	67.12	76.10	76.70	87.89	85.41	89.30
D ₁₃	Pink	480	65.85	69.00	70.60	92.63	83.33	85.69
D ₁₄	Light pink	475	71.57	67.23	75.25	86.62	87.76	85.71
D ₁₅	Light yellow	470	69.00	72.00	67.00	88.40	88.88	82.08

Table 5: Fastness properties of reactive dyes

Dye No.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	Cotton	Wool	Silk	Cotton	Wool	Silk	Cotton	Wool	Silk	Cotton	Wool	Silk
D ₁	6	5	5-6	5	5	4	4	3-4	4	3	5	3-4
D ₂	5	4	4	3-4	3	4-5	3	4	3	4	4	3
D ₃	4	4	4-5	3	4	3	4	3	3-4	3	3	3
D ₄	4-5	5	4	4	4	4	3	3-4	4	3-4	3-4	4-5
D ₅	3-4	5	4-5	4	3	3	3-4	4	4	4	4	3
D ₆	4	4	4	4-5	3	3-4	4	5	3	3	3	3-4
D ₇	5	4-5	4-5	4	3-4	3	3	4	3	4	4	3
D ₈	3-4	4	4-5	3-4	4	4	4	3-4	3-4	3-4	3	3
D ₉	4	4-5	4	3	4	3	3-4	3	4	3	3-4	3
D ₁₀	5-6	4	4	4	3	4-5	3	4	3	3-4	3	3-4
D ₁₁	4	4	4-5	4-5	4	3-4	3	4	4-5	4	4	4
D ₁₂	4	3-4	3-4	4	3	3	3-4	3	3	4-5	4	3-4
D ₁₃	4-5	3	4	5	5	3	4	5	3-4	4	3	3
D ₁₄	4	5	4	5	3-4	3-4	4-5	4	4-5	5	3	3
D ₁₅	4-5	3	5	4	3	4	5	4	4	4-5	3-4	3

shift at 3.33 ppm as singlet of 2H due to -OH group & 4.18 ppm as singlet of 2H due to >NH group. D₈ shows C-H stretching at 2830 cm⁻¹ and C-H bending at 1445 cm⁻¹ indicates the existence of >N-CH₃ group. D₉ shows chemical shift at 4.15 ppm as singlet of 2H due to >NH group but in D₁₀ there is no chemical shift of >NH group which indicates that in the structure of D₁₀ H-atom of >NH group is replaced by the phenyl group. D₁₂ shows S=O stretching at 1155 cm⁻¹ and 1055 cm⁻¹ indicates the existence of -SO₃H group but there is no peak of S=O stretching in D₁₁. D₁₃ & D₁₄ shows chemical shift at 4.25 ppm and 4.17 ppm as singlet of 2H due to >NH group. D₁₅ shows N-H bending at 1530 cm⁻¹ indicates the existence of secondary amine.

All the dyes gave excellent uniformity of colouration on cotton, wool and silk. A remarkable degree of levelness indicates good penetration and affinity of these dyes to the fabric. The shade varies from light yellow to violet. The difference in the colour of newly synthesized dyes depends upon the substituents present and / or the position of the substituents on the rings. The dyes with H-acid give violet colour and K-acid gives light yellow colour.

The results of the exhaustion study reveal that exhaustion on silk and wool are comparatively

better than cotton. On cotton ranges from 65 to 77%, for wool fabric ranges from 64 to 76% and for silk ranges from 66 to 76%. The results of the fixation study reveal that fixation on silk and cotton are comparatively better than wool. On cotton ranges from 86 to 92%, for wool fabric ranges from 83 to 92% and for silk ranges from 81 to 90%. Excellent behavior is shown in the fastness to washing. Most of the dyes have good to excellent rubbing fastness (dry and wet) and this may be attributed to appropriate diffusion of the dye molecules into the fabric. All the dyes show generally moderate to very good light fastness properties. The washing fastness properties ranges from good to excellent fastness on cotton, wool and silk. (Light fastness: 1-poor, 2-slight, 3-moderate, 4-fair, 5-good & 6-very good; Wash & Rubbing fastness: 1-poor, 2-fair, 3-good, 4-very good, 5-excellent)

ACKNOWLEDGMENTS

The authors express their gratitude to Head of the Department of Chemistry, Veer Narmad South Gujarat University, Surat for providing necessary research facilities, CDRI Lucknow for ¹H NMR spectra and Atul Ltd. for providing dyeing and analytical facilities.

REFERENCES

- Herbert Klier, Bernhard Muller, Edmond Ruhlmann and Athanassios Tzikas, *United State Patent*, 5, 552, 532 (1996).
- ATIRA (Ahmedabad) Survey of process houses by Chem. Tech. Div., (1996).
- Shore J., *Colorants and Auxiliaries, Soc. Dyes and Col.* **1**: (1990).
- Shah K. M., *Handbook of Synthetic Dyes and Pigments*, Multi-Tech Publishing Co., **1**: 229 (1998).
- Patel R. S., Patel P. S., Patel K. C. and Patel S. K., *Asian J. of Chem.*, **14**(1), 420-426 (2002); C. A., **136**, 311202_a (2002).
- J. R. Mehta, R. R. Shah, S. K. Patel and K. C. Patel; *Acta Ciencia Indica, Chem.*, **XXX C**(1): 9 (2004).
- Fried B. and Sherma J., *Thin Layer Chromatography Techniques and Applications*, Marcel Dekker, Inc. New York and Basel (1982).
- Colthup N. B., Daly L. H. and Wiberley S. E., *Introduction of Infra red and Raman Spectroscopy*, (1964).
- Bovey F. A., *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, New York (1969).
- Standard Test Method*. BS 1006.1978 (UK): ISO 105, 1994 (India).
- AATCC Test Method 8*, (1961).
- Indian Standard*. ISO: 765 (1979).
- Kurt Habig, *Konrad Baessler, Ger.* **2**, 354, 288 (1975); C. A., **83**, 113952u (1975).
- Shenai V. A., *Chemistry of Dyes and Principles of Dyeing*, Sevak Publication, Bombay (1973).