Application of Acid Dyes on Silk Fabric and Fastness Properties Part II

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Summary: Synthesis of acid dyes was carried out by reacting diazotized substituted aryl amines and substituted naphthalene sulfonic acid as coupling component. Structural properties were studied by UV-visible spectroscopy, IR spectroscopy, ^{1}H-NMR spectroscopy, MALDI-TOF mass spectrometric analysis and elemental analysis. Application of dyes was carried out on silk fabric and their fastness to light, washing, perspiration, and crocking was determined. The results revealed that the synthesized dyes are efficient for dyeing silk fabric which is evident from their excellent fixation, binding stability and fastness properties.

Keywords: Acid dyes, Synthesis, Color fastness, Silk, Dyeing.

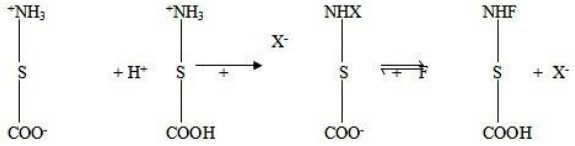
Introduction

Acid dyes are a large class of dyes which comprises various categories. Most important acid dyes are sulfonic acid derivatives of azoic dyes [1]. The practical uses of these dyes are characterized by their capacity to dye protein and polyamide fibers. Similar to direct dyes, they are anionic in nature with a general formula RSO_3Na, however, unlike direct dyes they give poor results on cellulosic fiber [1, 2]. Acid dyes are water soluble, bright in colors and have reasonably good washing fastness properties. They contain a chromophoric group and an acidic group, usually – SO_3H, in the form of sodium salt that impart water solubility [3].

FIBER–$NH_2 \cdot HSO_3$–DYE	FIBER–$NH_3^+ \cdot SO_3^-$–DYE
(Fiber with basic amino group)	(Dyed fiber with salt linkage
(Dye with acidic sulfonic group)	between dye and fiber)

Scheme 1

It is well known that Wool, Silk and Nylon fibers contain amino groups in their structure which, being basic in nature, can bond easily with acid dyes through salt linkage (Scheme-1) [3]. The term "acid dyes" derives from the dyeing process which is often carried out in an aqueous acid solution (pH~2-6) [4-7]. Protein fibers contain amino and carboxyl groups which are ionized mostly to NH_3^+ and COO^- [8]. In the acidic dye bath, the carboxyl ions of the fiber molecule main chain are converted to undissociated carboxyl groups due to addition of acid (HX) which makes silk fiber positively charged (^+H_3N-S-COOH) to take up an equivalent amount of acid anions X^-, as shown in Scheme-2 [9].



Scheme-2

The aim of the current investigation is the synthesis, characterization, application and evaluation of dyeing performance of novel acid dyes derivatives. Using substituted aryl amines as diazo component and substituted amino hydroxy sulfonic acid as coupling component, nine derivatives of sulfonic acid dyes were synthesized. After purification, the synthesized dyes were characterized by analytical methods and applied on silk fabric. The dyeing performance was explored using standard ISO procedures which revealed that the synthesized novel dyes exhibit high fixation, binding stability and excellent fastness properties (such as washing fastness, rubbing fastness, light fastness, color fastness to perspiration).

Experimental

Materials and Characterization

All reagent and solvents were of technical grade. Thin layer chromatography (TLC) was taken on silica gel PF 254 (Merck) plates. UV-visible spectra were measured in in de-ionized water using a Spectromiczo Baush and Lomb spectrophotometer. IR spectra were recorded on a Jasco A-30 spectrometer in KBr pellets. 1H-NMR spectra were recorded on a

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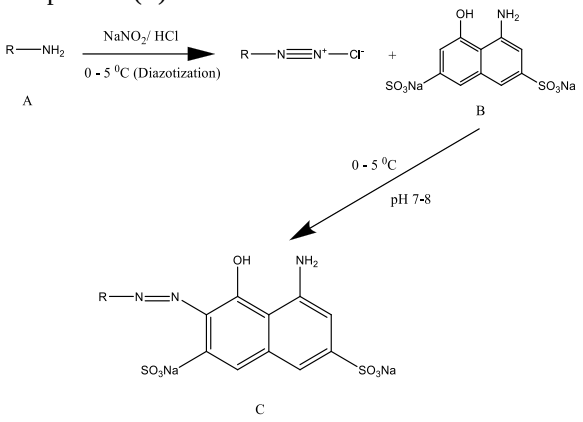
Bruker AM 300 spectrophotometer in deuterated DMSO. Dyeing was carried out using an I.R. dyeing machine (Roaches International Ltd., UK). The CIE color coordinates L*, a*, b* were recorded on a Datacolor Spectroflash SF-600 spectrophotometer (Datacolor, USA) using D65 illuminant and 10^o standard observer.

Color fastness properties were all evaluated in accordance with the standard ISO procedures using SDC laboratory consumables. Wash Fastness test was performed according to test method ISO CO3 Society of dyes and colorist test method (Fifth edition 1990.PP-C04-1). The dyed sample with multifibre strip is subjected to the following solution. Soap 5g/l, sodium carbonate anhydrous 2g/l at 60 °C for 30 min in liquor ratio 1:50, rinse and dry, evaluate the change in shade and staining. Rating system of grey scale is used 1 represent poor, 5 report excellent. The Light fastness test was using ISO-105-B02 method. The dyed fabric was exposed to artificial light (MBTF lamp) 100 hrs with ISO blue wool the light fastness rating corresponds to the number of blue wool reference showing contrast equal to test sample in which 1 is poor and 5 is excellent. The Perspiration fastness test was performed using ISO-105/E04 method. Samples were exposed to L-histidine monohydrochloride monohydrate disodium orthophosphate (pH-alkaline 8.0) at 37 °C for 4 hrs. Color fastness to rubbing was performed using ISO-105-X12 (AATCC-08) test method. Applied force of 9N was used and rotation was10 times, with a crocking distance of 13.5 cm.

Synthesis of Dyes

Substituted aryl amines (10 mmol), as reported in Scheme 3 and marked as "A" component (Table-1), was dissolved in 2-5 ml of conc. hydrochloric acid. Sodium nitrite (10 mmol) was separately dissolved in 20 ml water and the solutions were cooled in an ice bath at 0-5 °C. Sodium nitrite solution was then added drop wise, under constant stirring, to the amine hydrochloride. Test of nitrous acid was performed using a starch iodide paper. Excess of sodium nitrite was removed by sulfamic acid coupling component (B) as mentioned in Scheme 3. Naphthalene sulfonic acids (10 mmol) was dissolved in 300 ml water and the pH was adjusted to 5-6 by the addition of 10 % sodium carbonate solution. To this solution, diazotized solution of aryl amines (A) was then added drop wise at around 0-5 °C under constant stirring and the pH was continuously monitored and maintained at 7- 8 by adding 10% aqueous Na_2CO_3 solution at a temperature of around 0- 5 °C. The completion of reaction was checked by β- naphthol solution spot test on a filter paper. The aqueous dye solution was stirred for 3-4 h. TLC was checked using a mixed mobile phase (MeOH: Hexane: H_2O=9:1:1). The dye was then separated by salting out with a 10% sodium chloride solution followed by filtration. The product was dried under vacuum at 60 °C and purified by dimethyl formamide. A general synthesis procedure is shown in Scheme 2 and the corresponding diazo (A) and coupling components (B) are all listed in Table-1.



Scheme-3: Dye Formation Reaction.

Application and evaluation of acid dyes on silk fabric

Scoured and bleached silk fabric was dyed with 1% of synthesized dyes, based on the weight of fabric (o.w.f.). The liquor-to-fabric ratio was maintained at 20:1 during dyeing. The pH of the dyeing bath was continuously monitored and maintained at 2.5 to 3.5. The temperature of dye bath was raised to 60 °C at the rate of 2 °C/min for 30 min. The Glauber's salt was then added to the dye bath and process was continued further for 30 min. The dyed fabric was then removed and rinsed thoroughly with cold water followed by another wash with a nonionic detergent at 50 °C. The fabric was then air dried at room temperature before any further characterization was performed.

Table-1: Diazo and coupling components.

Dyes Code	A	A Diazo Component	B	B Coupling Component
C1	A1	2- Methoxyaniline -5- sulfonic acid	B1	1-Amino-8-naphthol-3,6-disulfonic acid (H-acid)
C2	A2	4- Amino-acetophenone	B2	1- Amino-8-naphthol-3,6- disulfonic (H-acid)
C3	A3	3- Amino acetophenone	B3	1- Amino-8-naphthol-3-, 6- disulfonic acid (H-acid)
C4	A4	3- Amino sulfonic acid	B4	1- Amino -8- naphthol-3, 6- disulfonic acid (H-acid)
C5	A5	4- Amino sulfonic acid	B5	1- Amino-8-naphthol-3,6- disulfonic acid (H-acid)
C6	A6	4- Amino sulfonic acid	B6	1- Aminoacetye-8-naphthol-3,6- sulfonic acid (N-Acetyl H-acid)
C7	A7	3-Amino sulfonic acid	B7	1-Aminoacetye-8-naphthol-3,6- disulfonic acid (N-Acetyl H-acid)
C8	A8	4-Aminoacetophenone	B8	1-Aminoacetye-8-naphthol-3,6- disulfonic acid (N-Acetyl H-acid)
C9	A9	3-Aminoacetophenone	B9	1-Aminoacetye-8-naphthol-3,6- disulfonic acid (N-Acetyl H-acid)

Results and discussion

Nine derivatives of sulfonic acid dyes were synthesized using substituted aryl amines as diazo component and substituted amino hydroxyl sulfonic acid as coupling component. The dyes were purified, and their structures were confirmed by UV-visible spectra, IR spectra, ^{1}H-NMR, MALDI-TOF spectra in negative ion mode for mass. These dyes were then applied on silk fabric by an exhaust dyeing process, and the colors of the dyes were characterized using the maximum absorption wavelengths (λ_{max}, nm) in the UV-visible absorption spectra, ranging from red to blue red color.

The color parameters of dyed silk fabric before and after washing, light exposure, and alkaline perspiration were determined by the SF600 spectrophotometer and the resulting values are listed in Table-2, 3 and 4. The Color Parameters obtained for fabrics dyed using the synthesized dyes (C1 to C9), before and after washing with nonionic detergent at 50 ºC are listed in Table 2 which indicated that the dyeing resulted in the shades of moderate depth. The hue angles for the dyes C1 to C5 indicates that the silk fabric dyed using these dyes exhibit lighter color. The positive a* values are obtained for all the samples indicating red [10]. In contrast, for the fabric dyed using the synthesized dyes C1 to C5, negative b* values are obtained indication the blueness of the shades. Similar trends were obtained in the color parameters obtained after light exposure, and alkaline perspiration (Table 3 and 4). These results indicated the satisfactory performance of all the synthesized dyes on silk fabric [10, 11].

Washing, light, perspiration and rubbing fastness measurements of the dyed silk fabrics were all carried out using the standard ISO procedures [13-18]. The results obtained for these measurements are listed in Table 5. The change in shade ratings were assigned by comparing with a change in color grey scale. The ratings on the grey scale for change in color were in the range from 1 to 5, where rating 1 representing the highest loss of color and rating 5 representing no color change. Similarly the degrees of staining were all assigned using a corresponding grey scale for staining which also start from 1 for maximum staining, to 5 for no staining. A multifibre fabric (SDC) composed of six different fiber types (wool, acrylic, polyester, nylon, cotton and acetate) was used as adjacent fabric in fastness tests. As mentioned in Table 5, for all the dyes used (C1 to C9), 5 and 4-5 ratings values were obtained. These values imply that the dyed samples have very good wash fastness properties on the basis of the change in color.

Table-2: Color Parameters of dyed silk fabric before and after washing with a nonionic detergent at 50 °C.

Sample Name	L*	a*	b*	C*	h*	X	Y	Z	x	y
C-1 Before Wash	22.45	23.31	-6.23	24.13	345.03	5.12	3.64	5.12	0.3691	0.2623
C-1 After Wash	26.83	34.44	-9.27	35.67	344.93	5.06	3.17	5.01	0.3821	0.2394
C-2 Before Wash	18.31	9.98	-7.89	12.72	321.67	2.98	2.59	4.04	0.3104	0.2692
C-2 After Wash	18.40	10.11	-5.69	11.66	318.6	2.70	2.41	3.95	0.2980	0.2660
C-3 Before Wash	17.12	10.00	-5.57	11.45	330.89	2.70	2.33	3.30	0.3245	0.2793
C-3 After Wash	16.98	9.75	-4.90	10.75	328.7	2.59	2.15	3.18	0.3270	0.2714
C-4 Before Wash	17.67	6.34	-8.70	10.77	306.06	2.63	2.44	3.99	0.2906	0.2696
C-4 After Wash	16.46	6.06	-8.08	10.16	306.00	2.17	2.38	3.79	0.2601	0.2853
C-5 Before Wash	17.08	7.13	-8.01	10.73	311.69	2.55	2.32	3.69	0.2975	0.2711
C-5 After Wash	17.64	7.05	-7.95	10.71	310.20	2.14	2.07	3.30	0.2849	0.2756
C-6 Before Wash	32.67	52.66	8.68	53.37	9.36	13.71	7.39	5.71	0.5114	0.2755
C-6 After Wash	31.62	52.28	7.70	52.90	9.26	13.14	7.17	5.40	0.5110	0.2788
C-7 Before Wash	35.01	50.33	5.91	50.68	6.69	14.96	8.50	7.41	0.4847	0.2754
C-7 After Wash	34.88	50.05	5.68	50.17	6.39	14.56	8.07	7.09	0.4899	0.2715
C-8 Before Wash	30.69	47.28	14.03	49.32	16.53	11.64	6.52	3.94	0.5268	0.2950
C-8 After Wash	30.16	46.21	14.00	48.88	16.01	11.56	6.31	3.17	0.5494	0.2999
C-9 Before Wash	40.65	51.74	16.40	54.28	17.59	19.65	11.65	7.20	0.5105	0.3025
C-9 After Wash	40.14	50.22	15.11	53.41	17.05	18.21	10.45	6.85	0.5128	0.2992

Table-3: Color parameters of dyed silk fabric before and after light exposure.

Sample Name	L*	a*	b*	C*	h*	X	Y	Z	x	y
C-1 Untreated	22.45	23.31	-6.23	24.13	345.03	5.12	3.64	5.12	0.3691	0.2623
C-1 Treated	22.00	23.95	-6.12	23.95	344.89	4.78	3.59	5.00	0.3575	0.2722
C-2 Untreated	18.31	9.98	-7.89	12.72	321.67	2.98	2.59	4.04	0.3104	0.2692
C-2 Treated	17.23	10.49	-8.35	13.78	323.14	2.74	2.51	4.37	0.2848	0.2609
C-3 Untreated	17.12	10.00	-5.57	11.45	330.89	2.70	2.33	3.30	0.3245	0.2793
C-3 Treated	16.96	10.14	-5.25	11.42	332.63	2.68	2.29	3.21	0.3253	0.2759
C-4 Untreated	17.67	6.34	-8.70	10.77	306.06	2.63	2.44	3.99	0.2906	0.2696
C-4 Treated	17.23	6.46	-6.81	10.85	307.04	2.59	2.39	3.75	0.2966	0.2737
C-5 Untreated	17.08	7.13	-8.01	10.73	311.69	2.55	2.32	3.69	0.2975	0.2711
C-5 Treated	17.87	7.38	-8.21	11.77	312.48	3.15	3.50	2.37	0.3492	0.3880
C-6 Untreated	32.67	52.66	8.68	53.37	9.36	13.71	7.39	5.71	0.5114	0.2755
C-6 Treated	31.13	53.17	9.77	54.71	10.23	14.68	8.03	6.14	0.5088	0.2783
C-7 Untreated	35.01	50.33	5.91	50.68	6.69	14.96	8.50	7.41	0.4847	0.2754
C-7 Treated	33.16	49.57	4.89	48.25	5.11	12.36	7.76	6.44	0.4653	0.2921
C-8 Untreated	30.69	47.28	14.03	49.32	16.53	11.64	6.52	3.94	0.5268	0.2950
C-8 Treated	28.15	45.34	13.29	48.79	14.19	10.07	5.19	2.90	0.5545	0.2857
C-9 Untreated	40.65	51.74	16.40	54.28	17.59	19.65	11.65	7.20	0.5105	0.3025
C-9 Treated	41.01	52.76	17.56	55.91	18.47	20.21	12.48	6.29	0.5184	0.3201

Table-4: Color parameters of dyed silk fabric subjected to alkaline perspiration.

Sample Name	L*	a*	b*	C*	h*	X	Y	Z	x	y
C-1 Untreated	22.45	23.31	-6.23	24.13	345.03	5.12	3.64	5.12	0.3691	0.2623
C-1 Treated Alkaline	20.98	23.01	-6.06	23.77	344.29	5.05	3.31	5.00	0.3779	0.2477
C-2 Untreated	18.31	9.98	-7.89	12.72	321.67	2.98	2.59	4.04	0.3104	0.2692
C-2 Treated Alkaline	17.81	9.32	-6.87	12.26	320.87	2.11	2.28	3.67	0.2617	0.2828
C-3 Untreated	17.12	10.00	-5.57	11.45	330.89	2.70	2.33	3.30	0.3245	0.2793
C-3 Treated Alkaline	16.41	9.34	-5.15	10.98	329.24	2.19	2.21	3.10	0.2920	0.2946
C-4 Untreated	17.67	6.34	-8.70	10.77	306.06	2.63	2.44	3.99	0.2906	0.2696
C-4 Treated Alkaline	16.59	5.67	-7.95	10.17	305.00	2.14	2.22	3.48	0.2729	0.2831
C-5 Untreated	17.08	7.13	-8.01	10.73	311.69	2.55	2.32	3.69	0.2975	0.2711
C-5 Treated Alkaline	16.48	6.89	-7.47	9.88	310.11	2.17	2.12	3.50	0.2785	0.2721
C-6 Untreated	32.67	52.66	8.68	53.37	9.36	13.71	7.39	5.71	0.5114	0.2755
C-6 Treated Alkaline	31.34	51.55	8.30	52.14	8.88	12.89	6.79	4.60	0.5308	0.2796
C-7 Untreated	35.01	50.33	5.91	50.68	6.69	14.96	8.50	7.41	0.4847	0.2754
C-7 Treated Alkaline	34.66	50.55	5.35	49.07	6.10	13.68	7.98	7.21	0.4788	0.2764
C-8 Untreated	30.69	47.28	14.03	49.32	16.53	11.64	6.52	3.94	0.5268	0.2950
C-8 Treated Alkaline	29.81	46.14	13.80	48.12	15.05	10.66	5.52	2.79	0.5619	0.2909
C-9 Untreated	40.65	51.74	16.40	54.28	17.59	19.65	11.65	7.20	0.5105	0.3025
C-9 Treated Alkaline	39.71	50.64	15.10	53.22	16.61	18.21	10.29	6.80	0.5158	0.2915

Table-5: Washing, crocking, and light fastness of dyed silk fabric.

Dye Code	Change in Shade	Staining on multifibre*						Crocking		Light Fastness
		CA	CO	PA	PES	PAC	WO	Dry	Wet	
C-1	4-5	5	4	5	5	5	5	5	5	4
C-2	4	4-5	3	4	4-5	4-5	3-4	4-5	4-5	4
C-3	4-5	5	4	5	5	5	5	4-5	4-5	4-5
C-4	4-5	5	3-4	4	5	5	5	5	5	4-5
C-5	4	5	3-4	4	5	4-5	5	5	5	4-5
C-6	4-5	5	3	5	4-5	5	5	5	4-5	4-5
C-7	4-5	4-5	3-4	4	5	5	5	5	4-5	4
C-8	4-5	5	3-4	4-5	5	5	5	5	4-5	4-5
C-9	4-5	5	4	4-5	5	4-5	5	5	3-4	4-5

* Description of multi-fiber fabric: CA, cellulose acetate; CO, cotton; PA, polyamide; PES, polyester; PAC, polyacrylic; WO, wool.

Table-6: Results of various fastness properties of dyes on silk fabric on multi-fiber.

		Fastness To							
Dye Code	Light hours	Wash		Perspiration alkaline		Rubbing		% Dye Fixation by K/S Values	% Exhaustion
	100	y	s	y	s	dry	wet		
C-1	4	4-5	4	4-5	4	5	5	76.34	79.76
C-2	4	4	3	4	3-4	4-5	4-5	74.03	78.73
C-3	4-5	4-5	4	3-4	3	4-5	4-5	71.69	80.06
C-4	4-5	4-5	3-4	4-5	4-5	5	5	83.17	57.95
C-5	4-5	4.0	3-4	4-5	4-5	5	5	67.60	78.48
C-6	4-5	4-5	3	4-5	3-4	5	4-5	74.20	73.32
C-7	4	4-5	3-4	4	3-4	5	4-5	85.71	64.00
C-8	4-5	4-5	3-4	4-5	3-4	5	4-5	66.35	63.79
C-9	4-5	4-5	4	4	4	5	3-4	90.69	57.89

y = Wash fastness test was performed before washing the dyed fabric using nonionic detergent at 50 ºC. **s** = Wash fastness test was performed after washing the dyed fabric using nonionic detergent at 50 ºC.

The percentage of dye bath exhaustion was determined by absorbance measurement at λ max using of the dyebath, before and after the dyeing process using UV-visible spectroscopy. These values are listed in Table 6 and reveals that the dye exhaustion was the best for C1, C2, C3 and C5. For the other dyes, moderate values were obtained which are likely due to lower solubilities of these dyes compared to the one mentioned above. Dye exhaustion can be improved by adding electrolytes.

Conclusion

Synthesized sulfonic acid dyes impart red and dark red color to silk fabric. Wash, light, rubbing, perspiration fastness studies show that all the fastness is overall good. Dye exhaustion values are in the range of 57-80% which indicate good dyeing properties.

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