Application of Sulfonated Arylamines Dichlorotriazine Based Reactive Dyes on Cotton Fabric and Study of Various Parameters to Define Color and Fastness Properties

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Summary: By following well-known methods, sulfonated arylamines dichlorotriazine based reactive dyes were synthesized, isolated and applied on knitted pure cotton fabric by exhaust process. Various parameters to define color and fastness properties were measured. Desire hue and properties can be obtained by changing the coupling reagent, sulfonated arylamine during the synthesis of sulfonated arylamines dichlorotriazine based reactive dyes. Orange, red and purple hue were obtained by using 1-naphthol-3-sulfonic acid, 6 amino, 1-naphthol-3-sulfonic acid, 7 amino and 1-naphthol-3,6-disulfonic acid, 8 amino respectively, while 1-naphthol-3,5-disulfonic acid, 8 amino and 1,5-disulfonic acid, 7 amino provided peach puff hue. The prepared dyes delivered a change in color equivalent to gray scale step 4/5 to 5 for wash fastness, gray scale step 3 to 4 for spotting with hydrochloric acid, gray scale step 3/4 to 5 for spotting with acetic acid, gray scale step 3 to 4/5 for steeping with sodium carbonate and gray scale step 1 to 3/4 for spotting with calcium hydroxide. Chromatographic, visible and infrared spectroscopic studies of synthesized dyes were also performed.

Introduction

Dyeing of yarn of fabric is a fundamental step to process raw textile stuffs to value added product. In pre-Industrial times, plant dyes were used to dye textiles. Nowadays, synthetic dyes are used almost exclusively [1-2]. The chromophoric groups present in the dye molecule contribute the color, solubility and point of attachments with substrate that enhance dyeing efficiency and various fastness properties. Share of reactive dyes to dye cotton in the world textile dye market is greater than all other dyestuff [3-4]. It is an only class of dyes that actually from covalent bond with the substrate and provides excellent wash fastness properties. In the various part of the world, work is still in progress to grow new reactive dyestuffs for dyeing various substrates [5-14]. With a view towards these considerations, five different types of sulfonated arylamines (a-e) were coupled with cyanuric chloride and diazotized sulphanilic acid to obtain arylamines dichlorotriazine based reactive dyes of different hue and to evaluate various properties. We are particularly interested to investigate those types of formulation that would be stable on substrate to acid as well as alkaline condition because mostly reactive dyes have a tendency to hydrolyze under basic condition. On initial step of study, we are declaring that formulated dye I (orange) that was synthesized using 1-naphthol-3-sulfonic acid, 6 amino as a coupler provided comparatively good result of fastness to alkalis as compare than other prepared dyes (II-V). All prepared dyes can be successfully used for dyeing cellulose fibers.

Results and Discussion

The dyes (I-V) were prepared by following literature procedures, Fig. 1 [15]. In each case, the reaction yields were found more than 100 %, indicating the presence of salt that was removed dissolving the dye in DMF and brought out with chloroform. The purity of isolated dyes was checked by TLC using iso-propyle, 1- butanol and distilled water (4: 4: 3) as mobile phase solvents. When dyes adsorbed onto silica gel chromatography plates, they produced one or two

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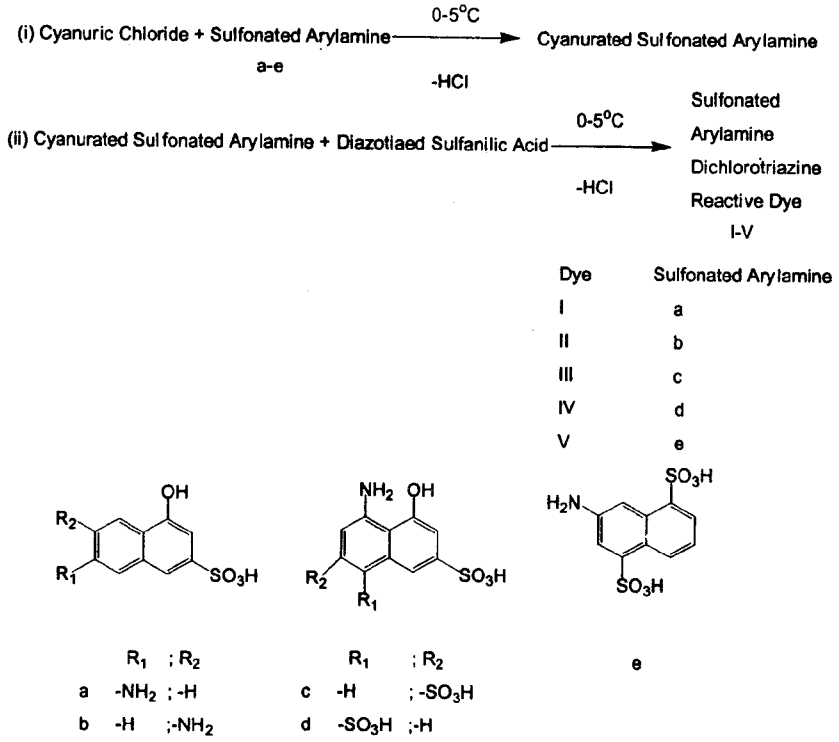

Fig. 1: Synthesis of Sulfonated Arylamine Dichlorotriazine Reactive Dyes.

Table- 1: Chromatographic and spectroscopic studies.

Entry	Dye	Rf of the major product	IR (cm^{-1})	Color of 0.03 % aqueous solution of dye	λ_{max} in nm (Absorbance of 0.03% aqueous solution of dye)
1	I	0.510	3432 (OH), 3370 (NH), 1584 (C=N),1167 (C-N), 1030 (Aryl Chloride)	Yellowish red	540 (3.426)
2	II	0.660	3420 (OH), 3360 (NH), 1588 (C=N),1178 (C-N), 1032 (Aryl Chloride)	Blood red	523 (3.325)
3	III	0.472	3400 (OH), 3382 (NH), 1569 (C=N),1179 (C-N), 1032 (Aryl Chloride)	Purple	536 (3.451)
4	IV	0.392	3406 (OH), 3394 (NH), 1597 (C=N),1179 (C-N), 1038 (Aryl Chloride)	Golden yellow	400 (0.339)
5	V	0.493	3364 (NH), 1581 (C=N),1170 (C-N), 1032 (Aryl Chloride)	Golden yellow	400 (0.389)

Table- 2: Data recorded on a Color Measuring System by observing the reflectance of dyed fabric (1 % Shade) of knitted cotton under a calibrated daylight illuminant lamp.

Entry	Dye's code	Color's name	Y	X	Z	L	A	b	ΔE (H)	Munsell HV / C
1	None	Gray	66.61	65.17	75.64	81.61	-0.29	2.18	0.00	4.71Y 8.40 / 0.27
2	I	Orange	25.41	37.30	4.90	50.40	43.86	29.52	60.59	0.74YR 5.57/13.46
3	II	Red	34.86	43.12	33.02	59.04	27.03	8.17	35.95	2.06R 6.39/6.97
4	III	Purple	21.37	27.58	30.93	46.22	25.59	-7.31	44.86	2.71RP 5.17/7.02
5	IV	Peach puff	49.71	52.87	41.29	70.50	10.46	14.63	19.85	3.59YR 7.43/3.79
6	V	Peach puff	52.25	55.72	41.36	72.28	11.09	16.67	20.66	4.08YR 7.59/4.18

Table- 3: Study of fastness properties.

Entry	Dye's code	Colorfastness grade after washing	Colorfastness grade after spotting with HCl	Colorfastness grade after spotting with CH_3CHOOH	Colorfastness grade after steeping with Na_2CO_3	Colorfastness grade after spotting with $Ca(OH)_2$
1	I	5	4	5	3/4	3/4
2	II	4/5	3/4	4/5	4/5	1/2
3	III	5	4	4/5	3/4	1
4	IV	5	3	3/4	3	1
5	V	4/5	3	4	3/4	2/3

minor spots with a major spot. The Rf values of the major products, important infrared bands, color and absorbance of 0.03 % aqueous solution of each dye and observed values of wavelength for absorption maximum (λ_{max}) are tabulated in Table- 1.

The absorption maximum of the dyes depends on hue that was developed changing the sulfonated arylamines (a-e) during the synthesis of dyes, A desire hue (orange, purple, peach puff and red) can be easily achieved by just changing sulfonated arylamine. Melting point of all dyes was found more than 300 °C. The remarkable degree of levelness and brightness after washing is indicative good penetration and the excellent affinity of these dyes for cellulosic fibers. All Recorded data for color measurement is tabulated in Table- 2.

Formulated dyes provided satisfactory results of fastness to wash (entries from number 1 to 5 in Table- 3). The dyed specimens were evaluated for resistance to simulated action of acids and alkalies. In all cases (entries from number 2 to 5 in Table- 3) colorfastness grade to sodium carbonate were found better than calcium hydroxide except one case (entry number 1 in Table- 3) where it was found equal to fastness grade to sodium carbonate. Colorfastness rates to hydrochloric acid and acetic acid were found better than colorfastness to alkalis. It is hinted at on the study basis that during cotton finishing process avoid the use of alkaline sizes and alkaline cleaning agents when apply these dyes. Soaping at the boil must be carried out in a neutral or weakly acidic liquor to prevent cleavage of the dye-fiber bond. Study revealed that synthesized dyes are superior in terms of preparation and application on cotton.

Experimental

General

Chemical Materials were obtained from the Aldrich, Sinochem and Clariant Textile Chemical Companies. Melting point of dyes was determined on a melting point apparatus, Griffen, MPA 350, UK and IR spectra were recorded as

Table- 4: Exhaustion (% E), fixation (% F), and total fixation efficiency (% T) of the dyes on cotton fabric (1 % owf).

Entry	Dye's code	$(K/S)_{after\ soaping}$	$(K/S)_{before\ soaping}$	% E	% F	% T
1	I	25.94	28.20	83	92	76
2	II	21.85	23.00	86	95	82
3	III	01.94	02.23	80	87	70
4	IV	02.09	02.65	59	79	47
5	V	04.51	05.50	61	82	50

KBr disics using a Hitachi 270-30 spectophotometer. Heλios Spectronic Unicam Spectrophotometer was used to record visible spectra. Thin layer chromatography (TLC) was conducted using silica gel, GF_{254} (coated on 20 x 20 cm glass plates). The fabric samples were dyed and tested for wash fastness in *ROCHES* machine. The reflectance of dyed material was measured on Z-Σ80 II Color measuring system, Nippon Denshoku Kogyo Co. Ltd. Tokyo, Japan. The change in color was assessed in a color assessment cabinet, Verivide G210, under the illuminant D_{65}. Tested fabrics were rated by using Gray Scale for assessing change in color, BSI, 3 York Street Manchester M2 2AT. Thickness of cotton's fabric was measured by using Digital thickness gauge, DGTM001B, Masdan lab, Italy.

Synthesis of dyes (I-V)

A literature method was followed to obtain and monitor the formation of dichlorotriazine based reactive dyes (I-V) [15]. Reactions were planed to obtain 0.5 mole of each dye. To obtain arylamines dichlorotriazine based reactive dyes (I-V) five different types of sulfonated arylamines 1-naphthol-3-sulfonic acid, 6 amino; 1-naphthol-3-sulfonic acid, 7 amino; 1-naphthol-3,6-disulfonic acid, 8 amino; 1-naphthol-3,5-disulfonic acid, 8 amino and 1,5-disulfonic acid, 7 amino were coupled with cyanuric chloride and diazotized sulphanilic acid.

Specification of cotton's fabric:

Knitted textile fabric was purchased from a local market and qualitatively investigated

according to AATCC test method 20-2002 for the determination of brand. It was found pure cotton. Thickness and density were measured using Digital thickness gauge under pressure of 20 Kpa according to a test procedure EN 12625-3:2005. Bulking thickness and apparent bulking density of cotton's fabric by installing 2 Kpa weight were found 735.7 μm and 0.292 g/cm^3 respectively.

Application of dyes on Knitted cotton's fabric:

Dyeing of knitted cotton fabric (with synthesized dyes I-V) was carried out according to the procedures reported in the literature [16-18]. The fabric was washed in an aqueous solution anionic-non ionic detergent, Sundopan DTC, rinse several times in water and dried at room temperature. The dyeing of fabric was performed with liquor ratio of 1: 15 in an exhaust process. A dye bath containing calculated amount of dye for dyeing fabric with 1 % shade, 65 g of Gluaber's salt and 7 g of sodium carbonate per dm^3 of the dye bath. Sodium carbonate was added only after the dye has been absorbed on the fiber. Fabric was wetted out in cold water before dyeing. The dyeing was continued for 45 minutes longer at 40 °C. The dyed sample was squeezed and cut down into two equal portions. Half portion of the fabric was treated with 1 % aqueous solution of cationic fixing agent (Sandofix FFN) at the liquor ratio of 1: 15 for half an hour. Finally, both parts of dyed fabric washed at 40 °C with anionic-non ionic detergent (Sundopan DTC, 5 g/ L) at the ratio of 1: 50 for 10 minutes, kept under running water for 5 min (at room temperature), rinsed with the various portions of warmed water (60 °C) at the ratio of 1: 50 for 10 minutes so that the final water was colorless and dried at room temperature. The fabrics that were not treated with cationic fixing agent and dyed with dyes I, II, III, IV and V delivered a change in color equivalent to gray scale step 3, 2/3, 3, 3 and 2/3 respectively for wash fastness test [19].

The percentage degree of exhaustion (%E, percentage of the dye absorbed or chemically bounded to the fabric) was measured by sampling the dyebath before and after the dyeing process. The absorbance value of a dye-liquor sample was measured at its wavelength of maximum absorbance using UV/Visible spectrophotometer (Heλios Spectronic Unicam) and the exhaustion value was calculated using equitation 1 [20].

$$\% E = [1 - (A_2/A_1)] \times 100 \quad (1)$$

Where A_1 and A_2 are the absorbance values of the diluted dye solution before and after the dyeing processes, respectively.

In order to determine the percentage fixation of each dye (the percentage of dye chemically bounded to the fabric), the half part of the dyed sample was retained and not processed for the soaping and rinsing. The colour strength values (K/S) of the dyed samples before and after soaping were determined on a calibrated color measuring system (Datacolor Spectraflash SF650X, USA) using CIE supplement 10° observer and illuminant D_{65}. Finally, the fixation of each dye on fabric in percentage was calculated (Table 4) using the Kubelka-Munk equitation 2 [21].

$$\% F = [(K/S)_{\text{after soaping}} / (K/S)_{\text{before soaping}}] \times 100 \quad (2)$$

The overall fixation efficiency (% T, the amount of dye originally applied which is covalently fixed) was calculated using equitation 3 [20].

$$\% T = (\% F \times \% E)/100 \quad (3)$$

Color Measurements:

Color of the dyed fabrics was specified on Munsell system using reflectance method, that is mainly used for quantify color sensationally and comparison of color difference in the field of textiles [22]. The Munsell color notation of dyed fabrics were determined from its daylight reflectance Y and chromaticity coordinate x and y, in CIE system *(Z- ∑80 II Color measuring system)* by using sample bed and pipe of 10 Ø. Before recording the data for samples, the color measuring system was calibrated with a standard plate (having XYZ coordinates 94.28, 92.31 and 110.83, respectively) as per instruction stated in the operational manual of the color measuring system. The recorded values of Y X Z and L a b for each fabric, are the mean valve of four readings that were taken by rotating the dyed fabric by 90, 180, 270 and 360 degree angle from a fixed point. Computer program of the day light illuminating system converted CIE data to Munsell color notation. Color difference was calculated using the formula given as under by comparing the dyed fabric with the mean L a b value of target fabric, that was un-dyed knitted cotton [23].

$$\Delta E\,(H) = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

Fastness Test:

Wash fastness test was performed according to CO1, BS 1006:1990 and the colorfastness to acids and alkalis was determined according to *AATCC Test Method 6-2001* after drying the test fabrics.

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