

Studies on Synthesis of Bifunctional Reactive Dyes and Their Application on Silk, Wool and Cotton Fibres

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Various bifunctional reactive dyes have been prepared by diazotised acid components such as Bronner acid, K-acid, Sulphotobias acid, Metanilic acid, J-acid, Peri acid, Laurent acid, Tobias acid, Chicago acid and 4-amino toluene 8-sulphonic acid and coupling with 4,4'-methylene bis-*o*-anisidine cyanurated H-acid and their dyeing performance on silk, wool and cotton fibres has been assessed.

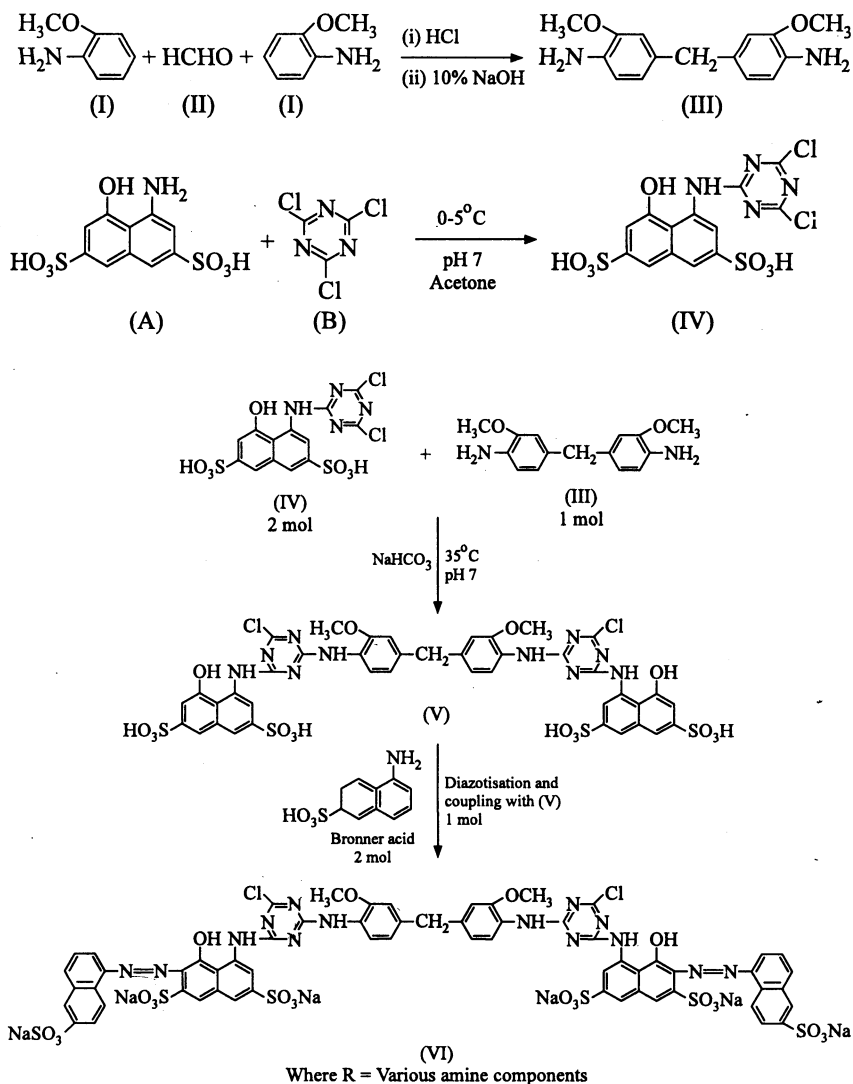
INTRODUCTION

The bifunctional reactive dyes carry two reactive groups. The term was used to describe dyes of the sumifix supra range, which carry two dissimilar reactive groups, *i.e.*, mixed bifunctional dyes. The concept of dyes with two reactive groups of the same type, *e.g.*, bisulphato ethylsulphonyl and bistriazinyl types¹. Sheng *et al.*² prepared bifunctional reactive dyes containing a vinyl sulphonyl group and a monochloro triazine group are widely used, and it is known that the two reactive groups have different reactivity. Monochloro-S-triazine has also been used extensively in conjunction with sulphatoethyl sulphones (which increase the stability and solubility of dye) to give the first mixed bifunctional reactive dyes³. Patel *et al.*⁴ have synthesized reactive dyes based on 4,4'-methylene bis *o*-toluidine for viscose rayon, wool and silk.

EXPERIMENTAL

Synthesis of 4,4'-methylene-bis-*o*-anisidine (III): *o*-anisidine (I) (11.26 mL, 0.1 mol) was dissolved in water (125 mL) and 36.5% HCl (25 mL) at 50°C. The reaction mixture was then treated with 3% aqueous formaldehyde (II) (35 mL) solution at 60°C with stirring for 1 h and neutralized with 10% sodium hydroxide. The white product was filtered, washed with hot water, dried and recrystallized from acetic acid. Yield 88%, m.p. 128°C, m.f. C₁₅H₁₈O₂N₂. Analysis (%): found, N = 10.85; required, N = 12.39.

Synthesis of cyanurated H-acid (IV): Cyanuric chloride (B) (3.69 g, 0.02 mol) was stirred in acetone (25 mL) at a temperature below 5°C for a period of 1 h. A neutral solution of H-acid (A) (6.39 g, 0.02 mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about 1 h. 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 h; then a clear solution was obtained. The cyanurated H-acid solution was used for preparation of 4,4'-methylene bis-*o*-anisidine cyanurated H-acid.

Synthesis of 4,4'-methylene bis-*o*-anisidine cyanurated H-acid (V): The temperature of ice-cooled and well stirred solution of cyanurated H-acid (IV) (4.67 g, 0.01 mol) was gradually raised to 45°C for 1/2 h. To this cyanurated H-acid the 4,4'-methylene bis-*o*-anisidine (III) (2.58 g, 0.01 mol) was added dropwise during a period of 1/2 h, maintaining the pH neutral by simultaneous addition of sodium bicarbonate solution (1% w/v). After the addition was

completed stirring was continued for further 3 h, to obtain 4,4'-methylene bis-*o*-anisidine cyanurated H-acid.

Diazotisation of various acid components such as Bronner acid (R): Bronner acid (4.46 g, 0.02 mol) was suspended in water; hydrochloric acid was added dropwise into this well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution was obtained. The solution was cooled to 0–5°C in an ice-bath. A solution of NaNO₂ in water, previously cooled to 0°C, was then added over a period of 5 min with stirring. The stirring was continued for 1 h, 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 at 0–5°C was used for subsequent coupling reaction.

Synthesis of 4,4'-methylene bis-*o*-anisidine cyanurated H-acid dyes (VI): A solution of diazotised Bronner acid (0.02 mol) was added to well stirred solution of compound (V) (0.01 mol) in water at pH 7–8. The pH was maintained throughout the reaction. The dye formed was stirred for further 2–3 h and then salted out by the addition of sodium chloride solution. It was filtered, dried and crystallized from DMF-acetone; yield 83%, m.p. 310°C (d).

All other dyes were prepared in a similar manner.

RESULTS AND DISCUSSION

All the dyes were yellow to red in colour obtained in excellent yield (70 to 88%). The purity of all dyes has been checked by thin-layer chromatography⁵. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting Spectrophotometer. The characterization data of dyes are given in Table-1.

Dyeing of fibres: All the dyes (A₁–A₁₀) were applied on silk, wool and cotton fibres using the reported procedure⁶.

The IR spectra of the dyes A₁ to A₁₀ were recorded on Perkin-Elmer spectrophotometer (Model 377) using KBr pellets. Dyes A₁ to A₁₀ showed characteristic band at 2890–2790 v(—CH₂—), 860–790 v(S-triazine), 630–590 v(C—Cl), 1680–1590 v(—NH—), 1385–1375 v(—N=N—) and 3450–3400 cm⁻¹ due to v(O—H).

The PMR spectra (300 MHz, CDCl₃) of a representative dye (A₁₀) showed signals at 1.18–1.22 (6H, —CH₃), 2.71–3.61 (2H, —CH₂—), 6.40–8.21 (aromatic proton), 8.4 (4H, —NH—) and 2.29 (6H, —OCH₃).

TABLE-1
PHYSICO-CHEMICAL CHARACTERIZATION OF VARIOUS DYES

Dye No.	R	m.f. [Yield (%)]	m.w.	Nitrogen (%)	
				Found	R _f value
A ₁	Bronner acid	C ₆₁ H ₃₈ N ₁₄ O ₂₂ Cl ₂ S ₆ Na ₆ (83)	1719	11.38 (11.40)	0.46
A ₂	K-acid	C ₆₁ H ₃₆ N ₁₄ O ₃₀ Cl ₂ S ₈ Na ₈ (87)	1955	10.19 (10.22)	0.45
A ₃	Sulpho tobias acid	C ₆₁ H ₃₆ N ₁₄ O ₂₈ Cl ₂ S ₈ Na ₈ (88)	1923	10.18 (10.19)	0.38
A ₄	Metanilic acid	C ₅₃ H ₃₄ N ₁₄ O ₂₂ Cl ₂ S ₄ Na ₄ (70)	1619	12.08 (12.10)	0.39
A ₅	J-acid	C ₆₁ H ₃₈ N ₁₄ O ₂₄ Cl ₂ S ₆ Na ₆ (87)	1751	11.19 (11.20)	0.43
A ₆	Peri acid	C ₆₁ H ₃₈ N ₁₄ O ₂₂ Cl ₂ S ₆ Na ₆ (85)	1719	11.38 (11.40)	0.41
A ₇	Laurent acid	C ₆₁ H ₃₈ N ₁₄ O ₂₂ Cl ₂ S ₆ Na ₆ (80)	1719	11.39 (11.40)	0.48
A ₈	Tobias acid	C ₆₁ H ₃₈ N ₁₄ O ₂₂ Cl ₂ S ₆ Na ₆ (70)	1719	11.38 (11.40)	0.42
A ₉	Chicago acid	C ₆₁ H ₃₆ N ₁₄ O ₃₀ Cl ₂ S ₈ Na ₈ (79)	1955	10.00 (10.02)	0.49
A ₁₀	4-Amino toluene 8-sulphonic acid	C ₆₃ H ₄₂ N ₁₄ O ₂₂ Cl ₂ S ₆ Na ₆ (80)	1747	11.20 (11.21)	0.36

Fastness properties: The percentage exhaustion, fixation and fastness properties of dyes A₁ to A₁₀ are given in Tables 2 and 3. All the dyes showed good affinity for silk, wool and cotton and gave moderate to very good light, washing and rubbing fastness and good to very good exhaustion and fixation.

TABLE-2
SHADE, PERCENTAGE EXHAUSTION AND FIXATION OF REACTIVE DYES ON SILK, WOOL AND COTTON

Dye No	Shade on dyed fibre	λ _{max}	% Exhaustion			% Fixation		
			Silk	Wool	Cotton	Silk	Wool	Cotton
A ₁	Light orange	465	79.10	60.15	50.50	82.70	79.80	64.50
A ₂	Dark orange	485	67.50	65.50	50.65	94.35	78.70	61.00
A ₃	Orange	505	67.80	65.30	46.10	94.20	78.55	59.50
A ₄	Brown	495	77.00	61.70	48.90	83.80	77.80	62.00
A ₅	Brown	525	79.50	64.20	50.00	93.70	76.10	61.50
A ₆	Dark brown	490	73.20	63.85	46.55	89.70	80.25	65.00
A ₇	Dark violet	480	69.20	63.30	45.60	94.10	78.90	66.50
A ₈	Violet	470	69.50	63.70	44.50	92.15	75.30	61.50
A ₉	Gray	535	73.20	63.85	46.55	89.70	80.25	65.00
A ₁₀	Orange	510	67.50	65.50	50.65	94.35	78.70	61.00

TABLE-3
FASTNESS PROPERTIES OF REACTIVE DYES ON SILK, WOOL AND COTTON

Comp.	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
A ₁	4	4	4	5	4	4	4	5	5	4	5	5
A ₂	5	4	5	5	4	4	3-4	4-5	5	4	4-5	5
A ₃	3	4	4	4-5	5	4	4	4-5	5	5	4	4-5
A ₄	5	4	5	4	3-4	4-5	5	4	5	4	4	4
A ₅	4-5	5	4-5	4	5	4	4	5	4	4-5	5	5
A ₆	4	4	4	5	4	4	4-5	4	5	4	4	4
A ₇	3-4	5	5	4-5	4	4	3-4	5	3-4	5	5	4-5
A ₈	4	3-4	3-4	5	4	4-5	5	4	4-5	3-4	5	5
A ₉	5	4-5	4	3-4	4	5	4	5	4	4	5	5
A ₁₀	4	5	4-5	5	4	4	4	4-5	4	3-4	4-5	4

where S = Silk, W = Wool and C = Cotton

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