Asian Journal of Chemistry Vol. 13, No. 2 (2001), 449–454

Studies on Synthesis of Some Acid Dyes and Their Application on Various Fibres

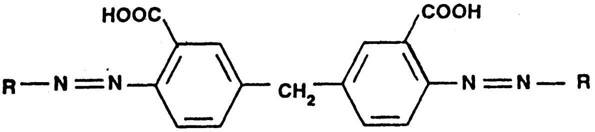
R.B. PATEL, NILESH PATEL, S.K. PATEL and K.C. PATEL*
Department of Chemistry, South Gujarat University, Surat-395 007, India

Various acid dyes have been prepared by coupling diazotised 4,4′-methylene-bis-anthranilic acid with various coupling components and their dyeing performance on viscose rayon, wool and silk fibres has been assessed. All the dyes gave a wide range of red to violet shades with very good depth and levelness on each fibre. The purity of all dyes has been checked by thin layer chromatography. The IR spectra showed all characteristic bands and a representative dye PMR spectra showed all the signals. The percentage dye-bath exhaustion and fixation on different fibres was reasonably good and acceptable. The dyed fibres showed fair to excellent fastness to light, washing and rubbing.

INTRODUCTION

Acid dyes are water-soluble anionic dyes that are applied to nitrogenous fibres such as wool, silk, nylon and modified acrylic fibres from acid or neutral baths[1, 2]. The acid dyes were probably originally so named because of the presence in their molecules of one or more sulphonic acid or other acidic groups[3, 4]. Attachment to the fibre is attributed at least partly to salt formation between anionic groups in the dyes and cationic groups in the fibre. The term applies to an application class rather than a chemical class, however, and since acidic groups are also present in many mordant, direct and reactive dyes, their presence is not a distinguishing feature. A number of monoazo dyes and bisazo dyes[5, 8] have been reported to give good dyeing and fastness properties.

The purpose of the present investigation was to obtain acid dyes with a higher degree of activity; we report here the synthesis and study of the dyeing properties of the acid dyes based on 4,4′-methylene-bis-anthranilic acid. The acid dyes of the following structure were prepared.



where, R = Coupling components such as H-acid, J-acid, K-acid, tobias acid, N-phenyl-J-acid, N-methyl-J-acid, gamma acid, laurent acid, chicago acid, peri acid, sulpho tobias acid, koch's acid, bronner's acid, schaffer's acid, G-acid, R-acid and bon acid.

EXPERIMENTAL

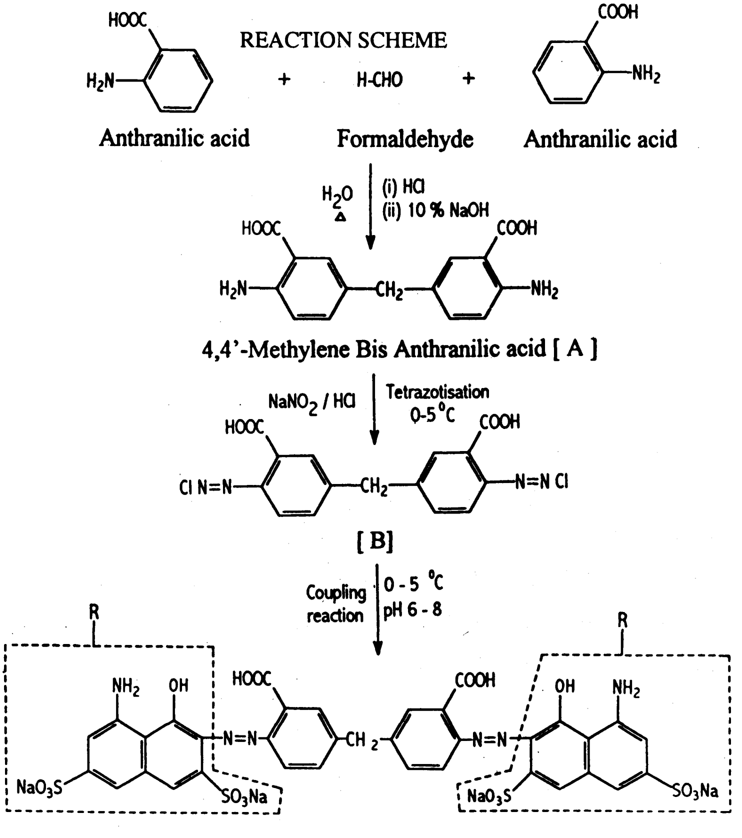
Synthesis of 4,4′-methylene-bis-anthranilic acid (A)

This compound was prepared by the following method: anthranilic acid (13.7

g, 0.1 mole) was dissolved in water (125 mL) and 36.5% hydrochloric acid (25 mL) at 50°C. The reaction mixture was then treated with 3% aqueous formaldehyde (35 mL) solution at 60°C with stirring for 1 h and neutralised with 10% sodium hydroxide; yellow precipitate obtained was filtered, washed with hot water, dried and recrystallized from acetic acid. Yield: 87%. m.p.: 233–235°C. Analysis, $C_{15}H_{14}O_4N_2$: Found: N, 9.70%, Required: N, 9.79%.

Tetrazotisation of 4,4′-methylene-bis-anthranilic acid (B)

This compound was prepared by the method reported in our previous paper[8]. 4,4^1-Methylene bis anthranilic acid (A) (2.86 g, 0.01 mole) was suspended in H_2O (60 mL); hydrochloric acid (10 mL) was added dropwise to 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 $NaNO_2$ (1.2 g, 0.02 mol) in H_2O (8 mL) 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 (B) at 0–5°C was used for subsequent coupling reaction.



D-1

Coupling of tetrazo solution (B) with coupling components (R): Formation of Dyes (D_1)

H-acid (6.38 g, 0.02 mole) was suspended in water (20 mL) and dissolved to neutral pH with sodium carbonate (10% w/v) to obtain a clear solution. The solution was cooled below 5°C in an ice-bath. To this well stirred solution, the above mentioned solution of tetrazo (B) was added drop-wise over a period of 10–15 min, maintaining the pH by simultaneous addition of sodium carbonate solution (10% w/v). The stirring was continued for 3 h keeping the temperature at 0–5°C. The reaction mixture was heated up to 60°C and sodium chloride added until the colouring material was precipitated. It was stirred for 1 h, filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80–90°C and extracted with dimethyl formamide. The dye was purified by using dimethyl formamide-chloroform and dried at 60°C. Yield 84%, m.p. 285°C (d). Analysis: $C_{35}H_{22}O_{18}N_6S_4Na_4$, Found: N, 8.49%, Required: N, 8.52%.

The same procedure was used for the preparation of dyes D_2–D_{17} (Table-1).

Dyeing of fibres

All the dyes were applied on viscose rayon, wool and silk by using the standard procedure[9].

Fastness test

Fastness to light was assessed in accordance with BS:1006-1978. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961, and the wash fastness test in accordance with IS:765-1979.

RESULTS AND DISCUSSION

All the dyes were red to violet in colour and obtained in excellent yield (73 to 90%). The purity of all dyes has been checked by thin-layer chromatography[10]. The absorption spectra of all the dyes were recorded on Beckman DB-GT grafting spectrophotometer. The characterisation data of dyes are given in Table-1.

Infrared spectra

The IR spectra of dyes D_1 to D_{17} were recorded on Perkin-Elmer spectrophotometer (Model 377) using KBr pellets. All the dyes in general showed S=O stretching vibrations at 1270–1260 and 1200–1120 cm^{-1}, N=N stretching vibration at 1390–1380 cm^{-1}, C=O stretching vibration at 1600–1570 cm^{-1}, C—H stretching vibration at 2900–2890 cm^{-1} [11], O—H stretching vibration at 3410–3400.

PMR Spectra

The dye D_1 showed signals at 2.51 (2H, —CH_2—), 7.27–7.92 (12H, ArH), 9.87 (4H, Ar—NH_2), 10.2 (2H, —COOH).

Fastness properties

The percentage exhaustion, fixation and fastness properties of dyes D_1 to D_{17} are given in Table-2. All the dyes D_1 to D_{17} showed good affinity for viscose rayon, wool and silk and gave fair to very good light, washing and rubbing fastness and very good to excellent exhaustion [Table-2].

TABLE-1
CHARACTERISATION

Dye No.	Coupling component (R)	m.f. (yield %)	m.w.	m.p. (°C)	R_f value	Nitrogen (%) Found (Required)
D_1	H-acid	$C_{35}H_{22}N_6O_{18}S_4Na_4$ (84)	986	285	0.84	8.49 (8.52)
D_2	J-acid	$C_{35}H_{24}N_6O_{12}S_2Na_2$ (79)	806	292	0.78	10.40 (10.52)
D_3	K-acid	$C_{35}H_{22}N_6O_{18}S_4Na_4$ (82)	986	312	0.72	8.48 (8.52)
D_4	Tobias acid	$C_{35}H_{26}N_6O_4$ (76)	594	324	0.79	14.10 (14.14)
D_5	N-phenyl-J-acid	$C_{47}H_{32}N_6O_{12}S_2Na_2$ (74)	958	318	0.81	8.74 (8.77)
D_6	N-methyl-J-acid	$C_{37}H_{28}N_6O_{12}S_2Na_2$ (85)	834	296	0.85	10.03 (10.07)
D_7	Gamma acid	$C_{35}H_{24}N_6O_{12}S_2Na_2$ (87)	806	315	0.73	10.39 (10.42)
D_8	Laurent acid	$C_{35}H_{24}N_6O_{10}S_2Na_2$ (90)	774	295	0.86	10.81 (10.85)
D_9	Chicago acid	$C_{35}H_{22}N_6O_{18}S_4Na_4$ (78)	986	298	0.75	8.46 (8.52)
D_{10}	Peri acid	$C_{35}H_{24}N_6O_{10}S_2Na_2$ (84)	774	311	0.82	10.84 (10.85)
D_{11}	Sulfo tobias acid	$C_{35}H_{24}N_6O_{10}S_2Na_2$ (88)	774	317	0.87	10.82 (10.85)
D_{12}	Koch's acid	$C_{35}H_{20}N_6O_{22}S_6Na_6$ (77)	1134	297	0.77	7.38 (7.41)
D_{13}	Bronner's acid	$C_{35}H_{24}N_6O_{10}S_2Na_2$ (74)	774	292	0.81	10.81 (10.85)
D_{14}	Schaffer's acid	$C_{35}H_{22}N_4O_{12}S_2Na_2$ (86)	776	287	0.78	7.18 (7.22)
D_{15}	G-acid	$C_{35}H_{20}N_4O_{18}S_4Na_4$ (83)	956	315	0.83	5.81 (5.86)
D_{16}	R-acid	$C_{35}H_{20}N_4O_{18}S_4Na_4$ (79)	956	314	0.76	5.83 (5.86)
D_{17}	Bon-acid	$C_{37}H_{22}N_4O_{10}Na_2$ (73)	704	294	0.79	7.91 (7.95)

TABLE-2
SHADE, PERCENTAGE EXHAUSTION AND FIXATION OF ACID DYES ON WOOL, SILK AND VISCOSE RAYON

Dye No.	Shade on dyed fibre	% Exhaustion			% Fixation		
		V	S	W	V	S	W
D_1	Blue	49.0	68.5	67.5	62.0	87.0	79.0
D_2	Brown	52.5	65.0	78.0	59.0	79.5	81.0
D_3	Light yellow	54.0	72.5	65.0	60.5	79.0	78.5
D_4	Brown	51.0	74.0	80.0	58.0	82.0	80.5
D_5	Orange	55.0	69.0	66.5	61.5	84.5	82.0
D_6	Dark red	50.0	70.5	64.0	59.0	81.0	76.5
D_7	Yellow	53.5	75.0	74.0	71.0	78.0	75.0
D_8	Red	50.5	71.0	78.5	58.5	83.5	79.0
D_9	Brown	50.0	66.5	68.0	63.0	89.0	81.0
D_{10}	Light pink	52.0	68.0	66.0	59.5	85.0	78.0
D_{11}	Orange	54.5	72.5	72.0	58.5	82.5	77.0
D_{12}	Light orange	51.0	69.0	69.0	62.0	79.0	76.5
D_{13}	Orange	53.0	67.5	73.5	61.5	84.5	80.0
D_{14}	Orange	49.5	73.5	79.5	60.5	79.5	79.5
D_{15}	Reddish brown	54.5	74.0	75.5	58.0	83.0	81.5
D_{16}	Red	52.5	67.0	71.0	63.0	78.5	77.5
D_{17}	Light orange	51.5	72.0	77.5	62.5	84.0	76.0

TABLE-3
FASTNESS PROPERTIES OF ACID DYES ON WOOL, SILK AND VISCOSE RAYON

Dye No.	Light-fastness			Wash-fastness			Rubbing-fastness					
							Dry			Wet		
	V	S	W	V	S	W	V	S	W	V	S	W
D_1	4	5	6	4–5	4–5	5	5	5	4	5	5	4–5
D_2	4–5	5–6	5	4	5	4–5	4–5	5	5	5	5	4
D_3	4–5	6	6	4	5	5	5	5	5	4	4	5
D_4	4	5	5	4	4	4	4	4–5	4	4–5	4	5
D_5	4–5	6	5–6	4–5	5	5	4–5	4	4–5	4	4–5	4
D_6	5–6	5–6	5	4–5	4	4–5	4	4	4	4–5	4	4
D_7	5	6	5–6	5	5	5	5	5	4	4	4–5	5
D_8	5	5	6	4	4–5	4	5	5	4–5	5	5	5
D_9	5–6	6	6	5	5	5	4–5	4	5	5	5	4–5
D_{10}	4–5	4–5	5	4	4	4–5	4	4	4	4–5	5	5
D_{11}	5	6	6	4	4	5	4–5	5	4	4–5	4	4
D_{12}	4–5	6	5–6	4–5	5	4	5	4–5	5	5	5	4
D_{13}	5	5–6	5	4	4	4	4–5	5	4	5	5	5
D_{14}	4–5	4–5	6	4	4	5	4	4	4	4–5	4–5	4
D_{15}	5	5	5	4–5	5	4	5	5	4–5	4	4	5
D_{16}	5	6	5	5	5	4	4–5	5	5	4	5	5
D_{17}	5–6	5	6	4–5	4–5	5	5	4	5	4–5	4	4

where W = Wool, S = Silk and V = Viscose rayon

REFERENCES

1. K. Peter, P. Jarmila and M. Jiri, Czech. CS 269, 613, Appl., 88/8, 254 (1991); *Chem. Abstr.*, **116**, 237353u (1992).
2. De Giorgi and M. Rita, *J. Soc. Dyers Colours*, **109**, 405 (1993); *Chem. Abstr.*, **121**, 233050y (1994).
3. Takashi Omura, Yutaka Kayane, Sho Takahashi, Tetsyya Miyamoto, Atiru Takeshita, Naoki Harada and Kalsumasa Otake, *Jpn Kokai Tokyo Koho Jp.*, 60,173,060 (1985); *Chem. Abstr.*, **104**, 90463 c (1986).
4. FIAT Final Report No. 1313, Vol. III, p. 351 (1948).
5. Y.C. Chao and C.W. Yeh, *Dyes Pigm.*, **24**, 285 (1993;, *Chem. Abstr.*, **120**, 137080s (1994).
6. Ion Sebe and Mucus Clopotar, *Rev. Roum. Chim.*, **38**, 1083 (1993); *Chem. Abstr.*, **121**, 257905g (1994).
7. Pual Wight, PCT Int. Appl. Wo 9913,008 (CI CO9B 21/08) (1999); *Chem. Abstr.*, **130**, 253667u (1999).
8. M.S., Patel, S.K. Patel and K.C. Patel, *Orient. J. Chem.*, **13**, 261 (1997); *Chem. Abstr.*, **128**, 155466s (1997).
9. V.A. Shenai, Chemistry of Dyes and Principles of Dyeing, Sevak Publications, Bombay (1973).
10. Fried Berbard and Sherma Joseph, Thin Layer Chromatography Techniques and Applications, Marcell-Dekker, Inc., New York and Basel (1982).
11. N.B. Colthup, L.H. Daly and E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York-San Francisco-London (1975)

(*Received*: 25 August 2000; *Accepted*: 25 November 2000) AJC-2201