

Synthesis of various acid dyes from hydroquinone derivative

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Abstract:

Synthesis of 1,4-phenylene bis(3-aminobenzenesulfonate) was synthesized by reduction of condense product of hydroquinone and m-nitrobenzenesulfonyl chloride. The compound was used as a bifunctional middle component in the preparation of tetra azo acid dyes. This di amino compound was tetra azotized and coupled with naphthalene based acid coupling component to give various tetra azo acid dyes. The obtained dyes were characterized by spectroscopic technique (IR, NMR) and the dyeing assessment of all dyes was evaluated on wool, silk and nylon fabrics. These dyes gave brown, violet, yellow, orange and pink shades on each fibers with good to very good fastness properties. The percentage dye bath exhaustion, fixation have studied.

Key Word: Synthesis of 1,4-phenylene bis(3-aminobenzenesulfonate), Dyeing, Fastness properties, Tetra azo acid dyes.

Date of Submission: 01-11-2022

Date of Acceptance: 12-11-2022

I. Introduction

Acid dyes are water soluble anionic dyes that are applied to by direct printing on protein fibers and by the vigorous process; selected dyes may be printed on viscose from a paste containing area, other important uses includes the dyeing of leather, paper, jute, straw and anodized aluminum the coloring of food and drink, drugs, cosmetics, insecticides, fertilizers, wood, stains, varnishes, inks, plastics, resins and the manufacture of toners and pigments of the lake types¹. Traditionally, azo dyes are the most important class of commercial dyes, occupying more than half of the dye chemistry, which contain phenols as intermediates²⁻⁷. If they contain sodium salts of a sulphonic acid group in addition to a phenolic group, they are referred as an acid azo dye. All such dyes having phenolic and sulphonic acid moieties, contain hydroxyl (-OH) and sulphonic (-SO₃H) groups as auxochromic groups. The acid azo dyes are obtained and used exclusively as water- soluble sodium salts. In a weakly acid aqueous solution, they can dye supports with basic groups and form salts with them. The acid dyes are applied on nylon, wool and silk^{8,9}.

II. Material And Methods

All the chemicals and solvents used were of laboratory grade and solvents were purified. Completion of the reaction was monitored by TLC using silica gel GF₂₅₄ (E. Merck), The absorption spectra of all the dyes were recorded on a Shimadzu UV-1700 spectrophotometer at the wavelength of maximum absorption (λ_{max}) using water as solvent. IR (Infrared Spectrum) (KBr, cm⁻¹) were recorded on a Shimadzu-8400 FT-IR spectrometer, ¹H-NMR spectra on Bruker advance II 400 NMR spectrophotometer using TMS as internal standard and DMSO as solvent. The dyeing was done by using a Laboratory Rota Dyer instrument and exhaustion dyeing method and dyeing facilities was provided by ATUL Ltd. (India).

Procedure methodology

Synthesis of 1,4-phenylene bis(3-(substituted naphthalen-2-yl diazenyl)benzenesulfonate).

Step-1: Synthesis of 1,4-phenylene bis(3-nitrobenzenesulfonate) (2)^{10,11}

In a 250 ml round bottom flask, 3-nitrobenzene-1-sulfonyl chloride (31.9 g, 0.145 mol) was dissolved in dry methylene chloride (60 ml). Then Hydroquinone (8.0 g, 0.073mol) and triethyl amine (10.65 ml, 0.145 mol) were added drop wise to the solution. The reaction mixture was stirred for 4 h at room temperature. After completion of reaction, the solvent was evaporated and the residue obtained was dissolved in ethyl acetate. The solution was washed with 1N HCl, 1N NaOH, brine and dried over anhydrous Na₂SO₄, filtered and evaporated to dryness. Yield 78%; white crystal; M. F. C₁₈H₁₂N₂O₁₀S₂; mol. wt. 480.42; m. p. 139-145 °C; IR (KBr, cm⁻¹): 2974, 2880 (C-H), 1531 (N=O), 1360, 1193 (S=O).

Step-2: Synthesis of 1,4-phenylene bis(3-aminobenzenesulfonate) (3)^{12,13}

1,4-phenylenebis(3-nitrobenzenesulfonate) (34.56 g, 0.072 mol) was dissolved in a mixture of methanol and water (100 ml + 20 ml). Powdered iron (20 g, 0.36 mol) and hydrochloric acid (12 M, 30 ml) were added to it. The mixture was refluxed for 7 h. After mixture cooling at room temperature, mixture was filtered to remove the iron residue, the solvent was evaporated. HCl (1 N, 200 ml) was added and the mixture was extracted with ethyl acetate (3 x 100 ml). The organic solution was washed with brine, water, dried over anhydrous Na₂SO₄ and evaporated to dryness. Yield 46%; white solid; M. F. C₁₈H₁₆N₂O₆S₂; mol. wt. 420.45; m. p. 201-212 °C; IR (KBr, cm⁻¹): 3479, 3383 (N-H), 2970, 2883 (C-H), 1363, 1186 (S=O).

Step-3: Tetrazotisation of 1,4-phenylene bis(3-aminobenzenesulfonate) (4)^{14,15}

1,4-phenylene bis(3-aminobenzenesulfonate) (1.0 g, 0.002 mol) was suspended in hydrochloric acid (5 ml). The mixture was gradually heated up to 70 °C till solution become clear, it was cooled at 0-5°C in ice-bath. A solution of sodium nitrite (0.35 g, 0.005 mol) in distil water (4 ml) previously cooled to 0-5°C was added over a period of 5 minutes with stirring and the temperature was maintained at 0-5°C. The stirring was continued maintaining the same temperature for an hour, with positive test for nitrous acid on starch iodide paper, excess of nitrous acid was removed by adding required amount of sulfamic acid solution (10 %). This clear diazonium salt (4) solution was used immediately for coupling reaction.

Step-4: Synthesis of tetra azo acid dyes A₁.

J-acid (0.96 g, 0.004 mol) was suspended in water (20 ml) and dissolved at neutral pH with sodium carbonate (10 % w/v) to obtain a clear solution. The solution was cooled to below 0-5 °C in an ice bath. To this well stirred solution, above mentioned diazonium salt solution (4) was added drop wise over a period of 15-20 minutes. Maintaining the pH 7.0-8.0 by simultaneous addition of sodium carbonate solution (10 % w/v). The reaction was further stirred for 3 h at 0-5 °C. The resulting dye solution was salted out using sodium chloride at 50-60 °C. The precipitated dye was filtered, washed with sodium chloride solution (5 % w/v) and dried in an oven at 50 °C to give A₁.

Same procedure was followed to synthesize other tetra azo acid dyes A₂ to A₁₂ using various naphthalene based acid coupling components such as J-acid, H-acid, Laurent-acid, Tobias acid, Amino G-acid, Bronner acid, C- acid, Phenyle-J-acid, Mix cleav acid, Gamma acid, , Napthanoic acid, G-acid and Characterizations of all the dyes are recorded in **Table-1**



Fig.1 Experimental scheme for tetraazoacid dye

Table-1: Characterization of acid dyes (A₁₋₁₂)

Dye no.	Coupling comp. (R)	Colour observed	λ_{max} (nm)	Molecular formula	Mol. Wt. (g/mol)	Yield (%)	m. p. (°C)	R _f Value
A ₁	J-acid	Light brown	477	C ₃₈ H ₂₆ O ₁₄ N ₆ S ₄ Na ₂	964.87	81	>300 °C	0.42
A ₂	H-acid	Dull cream	544	C ₃₈ H ₂₄ O ₂₀ N ₆ S ₆ Na ₄	1168.95	79	>300 °C	0.40
A ₃	Laurent-acid	Mauve	466	C ₃₈ H ₂₆ O ₁₂ N ₆ S ₄ Na ₂	932.88	82	>300 °C	0.41
A ₄	Tobias acid	Light yellow	474	C ₃₈ H ₂₆ O ₁₂ N ₆ S ₄ Na ₂	1587.68	78	>300 °C	0.43
A ₅	Amino G-acid	Light Orange	482	C ₃₈ H ₂₄ O ₁₈ N ₆ S ₆ Na ₄	1136.95	80	>300 °C	0.40
A ₆	Bronner acid	Dark orange	483	C ₃₈ H ₂₆ O ₁₂ N ₆ S ₄ Na ₂	932.88	80	>300 °C	0.42
A ₇	C-acid	Cream	422	C ₃₈ H ₂₄ O ₁₈ N ₆ S ₆ Na ₄	1136.95	77	>300 °C	0.36
A ₈	Phenyl J acid	Dark brown	480	C ₄₇ H ₃₆ O ₁₂ N ₆ S ₄ Na ₂	1051.06	72	>300 °C	0.35
A ₉	Mix cleave acid	Light pink	469	C ₃₈ H ₂₆ O ₁₂ N ₆ S ₄ Na ₂	932.88	78	>300 °C	0.36
A ₁₀	Gamma acid	Dark Maroon	502	C ₃₈ H ₂₆ O ₁₄ N ₆ S ₄ Na ₂	964.87	72	>300 °C	0.40
A ₁₁	Napthanoic acid	purple red	486	C ₃₈ H ₂₆ O ₁₂ N ₆ S ₄ Na ₂	932.88	83	>300 °C	0.42
A ₁₂	G-acid	Brown pink	502	C ₃₈ H ₂₂ O ₂₀ N ₆ S ₆ Na ₄	1138.92	70	>300 °C	0.45

Table 2. IR and ¹H NMR Data of tetrazo acid dye (A₁₋₁₂).

Dye no.	IR data((KBr) ν cm ⁻¹)	¹ H NMR data (DMSO) (chemical shift in δ ppm)
A ₁	3525 (O-H & N-H), 1590 (-N=N-), 1344, 1160 (-S=O asym., sym.), 1188, 1011 (-S=O asym., sym.).	9.80 (s, 2H, -OH), 6.90-7.84 (m, 20H, Ar-H), 5.80 (s, 4H, -NH ₂).
A ₂	3529 (O-H & N-H), 1594 (-N=N-), 1348, 1164 (-S=O asym., sym.), 1192, 1015 (-S=O asym., sym.).	9.84 (s, 2H, -OH), 6.94-7.88 (m, 18H, Ar-H), 5.84 (s, 4H, -NH ₂).
A ₃	3530 (N-H), 1595 (-N=N-), 1349, 1165 (-S=O asym., sym.), 1193, 1016 (-S=O asym., sym.).	6.99-7.94 (m, 22H, Ar-H), 5.82 (s, 4H, -NH ₂).
A ₄	3522 (N-H), 1587 (-N=N-), 1340, 1157 (-S=O asym., sym.), 1185, 1013 (-S=O asym., sym.).	6.88-7.80 (m, 22H, Ar-H), 5.78 (s, 4H, -NH ₂).
A ₅	3528 (N-H), 1598 (-N=N-), 1342, 1163 (-S=O asym., sym.), 1183, 1010 (-S=O asym., sym.).	6.92-7.86 (m, 20H, Ar-H), 5.83 (s, 4H, -NH ₂).
A ₆	3527 (N-H), 1591 (-N=N-), 1343, 1158 (-S=O asym., sym.), 1180, 1009 (-S=O asym., sym.).	6.91-7.89 (m, 22H, Ar-H), 5.79 (s, 4H, -NH ₂).
A ₇	3520 (N-H), 1592 (-N=N-), 1339, 1156 (-S=O asym., sym.), 1191, 1019 (-S=O asym., sym.).	6.93-7.82 (m, 20H, Ar-H), 5.81 (s, 4H, -NH ₂).
A ₈	3522 (O-H & N-H), 1588 (-N=N-), 1338, 1156 (-S=O asym., sym.), 1182, 1014 (-S=O asym., sym.).	9.89 (s, 2H, -OH), 6.94-7.87 (m, 30H, Ar-H), 5.84 (s, 2H, -NH).
A ₉	3529 (N-H), 1594 (-N=N-), 1343, 1163 (-S=O asym., sym.), 1190, 1011 (-S=O asym., sym.).	6.91-7.89 (m, 22H, Ar-H), 5.83 (s, 4H, -NH ₂).
A ₁₀	3530 (O-H & N-H), 1600 (-N=N-), 1350, 1164 (-S=O asym., sym.), 1180, 1005 (-S=O asym., sym.).	9.90 (s, 2H, -OH), 6.88-7.80 (m, 20H, Ar-H), 5.86 (s, 4H, -NH ₂).
A ₁₁	3521 (N-H), 1585 (-N=N-), 1348, 1166(-S=O asym., sym.), 1181, 1008 (-S=O asym., sym.).	6.90-7.84 (m, 22H, Ar-H), 5.81 (s, 4H, -NH ₂).
A ₁₂	3520 (O-H), 1586 (-N=N-), 1346, 1168(-S=O asym., sym.), 1184, 1012 (-S=O asym., sym.).	9.91 (s, 2H, -OH), 6.87-7.83 (m, 20H, Ar-H).

Table 3. Results of Exhaustion and Fixation study of A₁₋₁₂ on wool, silk and nylon.

Dye no.	% Exhaustion = Y x 100/50	% Fixation = Z x 100/Y	% Exhaustion = Y x 100/50	% Fixation = Z x 100/Y	% Exhaustion = Y x 100/50	% Fixation = Z x 100/Y
A ₁	75.20	79.33	72.30	94.05	72.30	89.90
A ₂	76.33	83.42	73.24	91.48	75.50	90.06
A ₃	72.15	90.97	75.65	82.84	72.25	86.51
A ₄	75.10	82.55	75.88	87.63	74.13	89.06
A ₅	78.46	90.49	79.50	89.30	75.21	88.43
A ₆	77.23	90.65	72.40	89.08	71.40	81.23
A ₇	74.30	90.84	80.22	82.15	75.45	80.85
A ₈	73.60	77.44	73.00	78.53	68.03	91.04
A ₉	80.10	81.77	78.11	88.98	81.09	83.86
A ₁₀	72.23	88.61	71.92	86.20	71.05	86.57
A ₁₁	76.05	85.48	80.70	89.83	77.70	86.22
A ₁₂	73.50	91.10	74.25	88.22	75.60	83.11

Table-4: Fastness properties of acid dyes on wool, silk and nylon fabrics (A₁₋₁₂).

Dye No.	Fastness to Light			Fastness to washing			Fastness to perspiration						Fastness to rubbing					
							Acidic			Alkaline			Dry			Wet		
	W	S	N	W	S	N	W	S	N	W	S	N	W	S	N	W	S	N
A ₁	3	3	5	4-5	4	4	4-5	2	4	4-5	4	4	2-3	2	4-5	2	3-4	4
A ₂	3	3-4	4	4	3	3-4	4-5	2-3	4	3-4	3	4	3-4	2-3	4	2-3	4	3-4
A ₃	4-5	2	4-5	3	3-4	4	3	3-4	4	4	2-3	4	2	4	4	2	3	4
A ₄	4-5	3	5	3-4	3	4-5	4	4	4-5	3	3-4	4-5	3	3	4-5	3	2-3	4
A ₅	3	3-4	4	3	4	3-4	4-5	4	3-4	3-4	3	3-4	4	3-4	3-4	2-3	3-4	3-4
A ₆	4	2-3	4-5	3-4	3-4	4	3-4	3	4	3-4	4	4	2-3	4	4	3-4	4	4
A ₇	5	3	4-5	4-5	4	4	4-5	3	4-5	4-5	3-4	4-5	3-4	3	4-5	2	3-4	4
A ₈	3-4	4	4	3-4	3	4	3	4	4	3	3	4	2-3	2-3	4	2-3	4	4
A ₉	3	5	4	4	2-3	3-4	3	2-3	3-4	3	3	3-4	3-4	3	3-4	2-3	3	3-4
A ₁₀	4-5	3-4	3-4	4-5	3	3-4	3-4	4	3-4	4-5	2-4	3-4	2	4	3-4	2	4	3-4
A ₁₁	4	2-3	4	3	3	3	4	3	3-4	3	3	3-4	2-3	3	3-4	3	4	3-4
A ₁₂	4	4	3-4	4	3-4	3	4	3-4	3	3	4	3	2	3-4	3-4	2	3	3

III. Result

Exhaustion and Fixation Study

The result of acid azo dyes (A₁₋₁₂) showed the percentage exhaustion values for wool ranges from 72% to 80%, in which dye A₁₂ shows maximum exhaustion value 80.10% while dye A₁₂ shows minimum exhaustion value 72.15%; for silk ranges from 71% to 80%, in which dye A₁₁ shows maximum exhaustion value 80.70% while dye A₁₀ shows minimum exhaustion value 71.92%; and for nylon ranges from 68% to 81%, in which dye A₉ shows maximum exhaustion value 80.70% while dye A₈ shows minimum exhaustion value 68.03 %.

The percentage fixation values of dyes (A₁₋₁₂) for wool varied from 77% to 91%, in which dye A₇ shows maximum fixation value 90.84% while dye A₈ shows minimum fixation value 77.44%; for silk varied from 78% to 94%, in which dye A₁ shows maximum fixation value 94.05% while dye A₈ shows minimum fixation value 78.53%; and for nylon varied from 80% to 90%, in which dye A₈ shows maximum fixation value 91.04% while dye A₇ shows minimum fixation value 80.85%.

Fastness Properties

The acid azo dyes of (A₁₋₁₂) show fair to good light fastness property and good to very good washing, perspiration, rubbing fastness properties on wool, silk, nylon fibers. Out of this A₃ A₅, A₇, A₁₀ showed good light fastness and very good washing, perspiration, rubbing fastness properties.

Acknowledgements

I would like to thank Head of Department of Chemistry, Veer Narmad South Gujarat University surat for providing me necessary facilities. I wish to thank S.A.I.F., Chandigarh for Spectral analysis. I wish to thank Atul Limited, Atul for providing dyeing, library facilities and recording fastness properties.

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