

Synthesis, Characterization And Dyeing Properties Of Acid Dyes On Wool, Silk And Nylon Fibers

Hiren S. Patel¹ and Navin B. Patel²

Organic Research Laboratory, Department of Chemistry, Veer Narmad South Gujarat University, Udhana-Magdalla Road, Surat-395 007, Gujarat, India.

Abstract:

Some new azo acid dyes were prepared by coupling various diazotized acid components such as J- acid, H- acid, G- acid, N-methyl J-acid acid, Chromotropic acid, Gamma acid, C-acid, Bronner acid, Tobias acid, Koch acid, Naphthanoic acid, Sulphotobias acid with Ethane-1,1-diybis(4,1-phenylene)bis(3-nitrobenzenesulfonate). The dyes were characterized by elemental, IR and TLC analyses. Their dyeing performance as acid dyes has been assessed on Wool, silk and nylon fibres.

Keywords: Acid azo dyes, Dyeing performance, IR

Date of Submission: 26-10-2023

Date of Acceptance: 06-11-2023

I. Introduction

The acid dyes were probably originally so named because of the presence in their molecules of one or more sulphonic acid or other acidic group. 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.

Acid dyes are anionic, soluble in water and are essentially applied from acidic bath. These dyes possess acidic groups, such as SO₃H and COOH and are applied on wool, silk and nylon when ionic bond is established between protonated -NH₂ group of fibre and acid group of dye. Overall wash fastness is poor although lightfastness is quite good. As dye and fibre contain opposite electrical nature, strike rate and uptake of acid dye on these fibres is faster; electrolyte at higher concentration is added to retard dye uptake and to form levelled shades. Acid generates cation on fibre and temperature helps to substitute negative part of acid with anionic dye molecules.[1] An acid dye is a dye that is typically applied to a textile at low pH. They are mainly used to dye wool, not cotton fabrics.[2] Some acid dyes are used as food colorants[3-4] and some can also be used to stain organelles in the medical field.

Acid dyes are generally divided into three classes according to their fastness requirements, migration ability, and dyeing pH.[5] Acid dyes affix to fibers by hydrogen bonding, Van der Waals forces[6] and ionic bonding. While some acid dyes work in water, many choose to activate dyes in acid dye-baths instead. According to the Brønsted-Lowry acid-base theory, an acid is a molecule or ion capable of donating a proton, and this is determined by the acid dissociation constant. Compared to most acids, water has a much higher pKa value, meaning that it dissociates to give H⁺ with more difficulty. In this context, if an acid is used instead of water, then the hydrogen ion (H⁺) is more easily able to dissociate in order to react with the aniline dye anion, allowing the dye to dissolve.

Chemically the acid dyes consist of azo, anthraquinone, triphenylmethane, azine, xanthene, ketonimine, nitro and nitroso compounds [7]. Azo dyes may be applied as preformed 1:1 or 1:2 metal complexes. A complete range of hues can be obtained, many of them being very bright and the fastness properties vary from poor to very good.

Acid dyes are thought to be attached to fibers by ionic bonds, hydrogen bonds and Vander Waals forces. Acid dyes themselves are not generally acid (dye -SO₃H), but rather sulphonate salts (dye -SO₃Na) of the strong sulphonic acid group. These dyes are usually compound with group that can easily be protonated, e.g. amino. Thus +H₃N-Dye-SO₃- would show acidic properties but they are not ascribed to a sulphonic acid group (-SO₃H) in the alternate formulation H₃N-Dye-SO₃, although the letter is often used to ease nomenclature. The designation "sulpho" appears to be used without specifying a sulphonate or an ionized salt (-SO₃Na+) or a protonated ionized form (-SO₃-H+).

Acid dyes are obtained from naphthalene intermediates. Due to the presence of a number of water soluble groups in an acid dye molecule, there is every possibility that the dye may come out on repeatedly washing with water. To increase the wash fastness and to have better dye fiber interaction, the number of solubilising groups are restricted and the molecular weight of the dye is adjusted in such a way that the ratio of

the solubilising groups to the molecular weight of the dye falls between one to three hundred or four hundred approximately. Certain bulky groups are attached either to the diazo component or to the coupling component for increasing the molecular weight of the dye molecule.

In the laboratory, home, or art studio, the acid used in the dye-bath is often vinegar (acetic acid) or citric acid. The uptake rate of the dye is controlled with the use of sodium chloride. In textiles, acid dyes are effective on protein fibers, i.e. animal hair fibers like wool, alpaca, and mohair. They are also effective on silk.[8] They are effective in dyeing the synthetic fiber nylon, but of minimum interest in dyeing any other synthetic fibers.

Acid dyes can also be used as food colouring, helping to increase the attractiveness of certain foods, and thus becoming more appealing to customers. Some examples include erythrosine, tartrazine, sunset yellow and allura red, to name a few, many of which are azo dyes.[9] These dyes can be used in frosting, cookies, bread, condiments or drinks. In order to prevent health hazards, a dye must be approved for consumption before it can be marked as edible. Some separation methods that can be used to identify unapproved dyes include the solid phase extraction process, the overpressured thin layer chromatography process, and the use of reversed-phase plates.[10]

II. Materials and Methods

Synthesis of Ethane-1,1-diybis(4,1-phenylene)bis(3-aminobenzenesulfonate) based acid dye.

Step – 1: Synthesis of Ethane-1,1-diybis(4,1-phenylene)bis(3-nitrobenzenesulfonate)[11,12]

In a 250 ml round bottom flask, 3-nitrobenzene-1-sulfonyl chloride (0.02 mol) was dissolved in dry methylene chloride (30 ml). Then bisphenol E (0.01 mol) and triethyl amine (0.02 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.

Step – 2: Synthesis of Ethane-1,1-diybis(4,1-phenylene)bis(3-aminobenzenesulfonate) [13,14]

Ethane-1,1-diybis(4,1-phenylene)bis(3-nitrobenzenesulfonate) (0.01 mol) was dissolved in a mixture of methanol and water (50 ml + 5 ml). Powdered iron (0.05 mol) and hydrochloric acid (12 M, 10 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, 100 ml) was added and the mixture was extracted with ethyl acetate (2 x 100 ml). The organic solution was washed with brine, water, dried over anhydrous Na₂SO₄ and evaporated to dryness.

Step – 3: Tetrazotisation of Ethane-1,1-diybis(4,1-phenylene)bis(3-aminobenzenesulfonate) [15,16]

Ethane-1,1-diybis(4,1-phenylene)bis(3-aminobenzenesulfonate) (0.002 mol) was suspended in mixture of sulphuric acid and glacial acetic acid (3 ml + 2 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 (0.005 mol) in distilled 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 solution was used immediately for coupling reaction.

Step – 4: Synthesis of tetra azo acid dyes H₁.

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 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 H₁.

Same procedure was followed to synthesize other tetra azo acid dyes H₂ to H₁₂ using various naphthalene based acid coupling components such as H-acid, G-acid, N-methyl-J-acid, Chromotropic acid, Gamma acid, C-acid, Bronner acid, Tobias acid, Koch acid, Napthanoic acid, Sulpho Tobias acid.

SCHEME

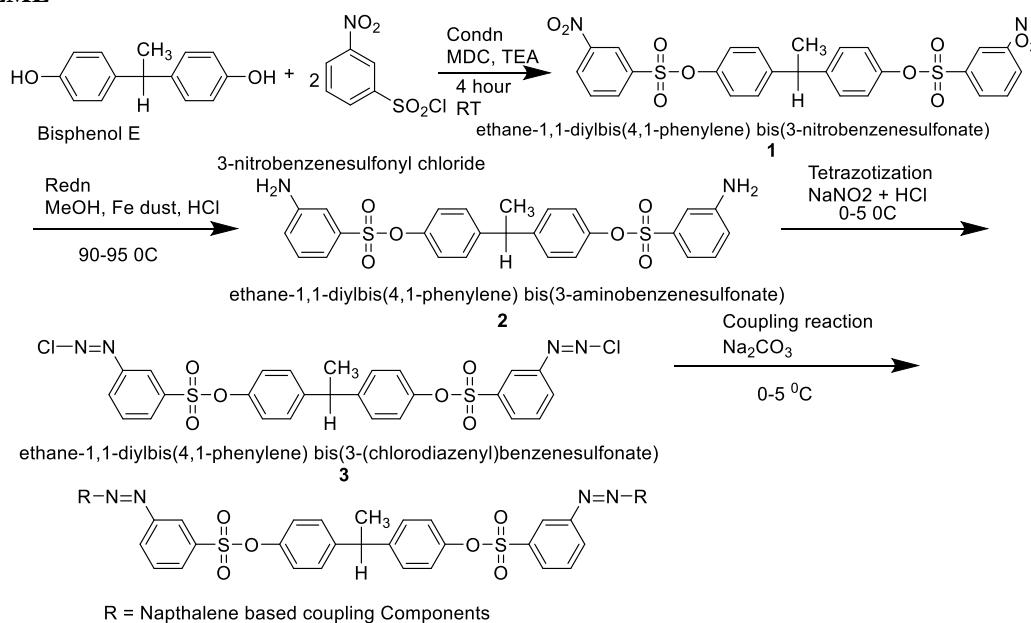

Fig.1 Experimental scheme for tetrazo acid dyes.

Table 1. IR and ^1H NMR Data of tetrazo acid dye (H_{1-12}).

Dye no.	IR data((KBr) ν cm^{-1})	^1H NMR data (DMSO) (chemical shift in δ ppm)
H ₁	3521 (O-H & N-H), 1593 (-N=N-), 1340, 1159 (-S=O asym., sym.), 1190, 1012 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H) 4.62 (s, 4H, -NH ₂), 6.78-8.47 (m, 24H, Ar-H), 9.01 (s, 2H, -OH).
H ₂	3527 (O-H & N-H), 1591 (-N=N-), 1346, 1163 (-S=O asym., sym.), 1191, 1013 (-S=O asym., sym.).	1.62(s, 3H, -CH ₃), 4.16 (s, 1H), 5.79 (s, 4H, -NH ₂), 6.80-8.47 (m, 22H, Ar-H), 9.01 (s, 2H, -OH)
H ₃	3533 (N-H), 1593 (-N=N-), 1351, 1163 (-S=O asym., sym.), 1193, 1016 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 6.80-8.68 (m, 24H, Ar-H), 9.86 (s, 2H, -OH).
H ₄	3520 (N-H), 1585 (-N=N-), 1338, 1158 (-S=O asym., sym.), 1185, 1013 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 2.68, (s, 6H, -CH ₃), 4.16 (s, 1H), 6.78-8.47 (m, 24H, Ar-H), 7.26 (2H, NH), 9.01 (s, 4H, -OH).
H ₅	3531 (N-H), 1596 (-N=N-), 1341, 1161 (-S=O asym., sym.), 1183, 1010 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 6.80-8.54 (m, 24H, Ar-H), 7.26 (s, 2H, -OH).
H ₆	3525 (N-H), 1591 (-N=N-), 1342, 1156 (-S=O asym., sym.), 1180, 1009 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 4.62 (s, 4H, -NH ₂), 6.80-8.47 (m, 24H, Ar-H), 9.01 (s, 2H, -OH).
H ₇	3522 (N-H), 1593 (-N=N-), 1341, 1159 (-S=O asym., sym.), 1191, 1019 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 5.12 (s, 4H, -NH ₂), 6.80-8.97 (m, 24H, Ar-H).
H ₈	3523 (O-H & N-H), 1589 (-N=N-), 1340, 1158 (-S=O asym., sym.), 1180, 1013 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 5.12 (s, 4H, -NH ₂), 6.80-8.47 (m, 26H, Ar-H).
H ₉	3528 (N-H), 1593 (-N=N-), 1340, 1162 (-S=O asym., sym.), 1190, 1011 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 5.32 (s, 4H, -NH ₂), 6.80-8.66 (m, 26H, Ar-H).
H ₁₀	3529 (O-H & N-H), 1601 (-N=N-), 1352, 1162 (-S=O asym., sym.), 1181, 1004 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 5.32 (s, 4H, -NH ₂), 6.80-8.47 (m, 24H, Ar-H).
H ₁₁	3523 (N-H), 1582 (-N=N-), 1346, 1164 (-S=O asym., sym.), 1183, 1010 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 5.32 (s, 4H, -NH ₂), 6.80-8.74 (m, 26H, Ar-H).
H ₁₂	3522 (O-H), 1584 (-N=N-), 1345, 1166 (-S=O asym., sym.), 1186, 1014 (-S=O asym., sym.).	1.62 (s, 3H, -CH ₃), 4.16 (s, 1H), 5.32 (s, 4H, -NH ₂), 6.80-9.05 (m, 24H, Ar-H).

Table-2: Characterization of acid dyes (H_{1-12})

Dye no.	Coupling comp. (R)	Colour observed	λ_{max} (nm)	Molecular formula	Mol. Wt. (g/mol)	Yield (%)	m. p. ($^{\circ}\text{C}$)	R _f Value
H ₁	J-acid	Cream	475	C ₄₆ H ₃₄ O ₁₄ N ₆ S ₄ Na ₂	1069.03	80	>300 $^{\circ}\text{C}$	0.44
H ₂	H-acid	Light Orange	534	C ₄₆ H ₃₂ O ₂₀ N ₆ S ₆ Na ₄	1271.96	78	>300 $^{\circ}\text{C}$	0.41
H ₃	G-acid	Light Cream	467	C ₄₆ H ₃₀ O ₂₀ N ₆ S ₆ Na ₄	1243.07	83	>300 $^{\circ}\text{C}$	0.40
H ₄	N-methyl J-acid	Light brown	498	C ₄₈ H ₃₈ O ₁₄ N ₆ S ₄ Na ₂	1097.08	78	>300 $^{\circ}\text{C}$	0.45
H ₅	Chromotropic acid	Light Brown	515	C ₄₆ H ₃₂ O ₁₆ N ₄ Na ₂	1070.99	82	>300 $^{\circ}\text{C}$	0.40
H ₆	Gamma acid	Light yellow	504	C ₄₆ H ₃₄ O ₁₄ N ₆ S ₄ Na ₂	1069.03	84	>300 $^{\circ}\text{C}$	0.42
H ₇	C-acid	Dull	426	C ₄₆ H ₃₂ O ₁₈ N ₆ S ₆ Na ₄	1241.11	78	>300 $^{\circ}\text{C}$	0.39

		Brown						
H ₈	Bronner acid	Light orange	485	C ₄₆ H ₃₄ O ₁₂ N ₆ S ₄ Na ₂	1037.03	75	>300 °C	0.37
H ₉	Tobias acid	Orange	471	C ₄₆ H ₃₄ O ₁₂ N ₆ S ₄ Na ₂	1037.03	79	>300 °C	0.37
H ₁₀	Koch acid	yellow	488	C ₄₆ H ₃₂ O ₁₈ N ₆ S ₆ Na ₄	1244.11	75	>300 °C	0.40
H ₁₁	Napthanoic acid	Light Red	491	C ₄₆ H ₃₄ O ₁₂ N ₆ S ₄ Na ₂	1037.03	81	>300 °C	0.42
H ₁₂	Sulphotobias acid	Light cream	465	C ₄₆ H ₃₂ O ₁₈ N ₆ S ₆ Na ₄	1241.11	79	>300 °C	0.45

Table 3. Results of Exhaustion and Fixation study of H₁₋₁₂ 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
H ₁	73.40	87.19	74.60	90.48	71.90	85.54
H ₂	77.44	85.23	75.14	88.50	74.20	89.62
H ₃	73.10	88.24	72.66	86.71	70.30	90.33
H ₄	74.30	86.14	76.00	90.13	73.50	82.31
H ₅	81.76	90.51	81.30	89.18	77.15	86.18
H ₆	75.24	91.71	71.10	92.12	70.30	80.37
H ₇	76.20	86.61	79.12	85.31	77.40	85.27
H ₈	71.62	82.38	72.42	88.37	69.62	81.87
H ₉	79.48	87.44	80.22	89.75	80.18	89.80
H ₁₀	74.56	84.50	72.92	85.02	72.06	86.73
H ₁₁	80.04	88.71	82.06	91.40	79.80	85.21
H ₁₂	75.30	87.65	76.18	88.61	74.60	83.11

Table-4: Fastness properties of acid dyes on wool, silk and nylon fabrics (H₁₋₁₂).

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
H ₁	4	3-4	4	3-4	3-4	4	3-4	3	3-4	3-4	3-4	3-4	3-4	4	4	3	3-4	3
H ₂	4	4	4	3	3-4	4	3-4	3-4	4	3-4	3-4	4	3-4	3-4	4-5	3-4	3	4
H ₃	4-5	3	3-4	4	3	3	4	3	3	4	3	3	3	3	3	3	3	3
H ₄	3-4	4	3-4	3-4	4	4	3	3-4	3-4	3	3-4	3-4	3	3-4	3-4	3	3-4	3-4
H ₅	4	4-5	4-5	4	4-5	4	3-4	4	4	3-4	4	4	4	4-5	4	3-4	4-5	3-4
H ₆	5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5	4	4-5	4-5	4	4-5	3-4	3-4	4
H ₇	4	4	4	3-4	3	3	3-4	3	3	3-4	3	3	3-4	4	3	3	3-4	3
H ₈	4-5	5	4-5	4-5	4	4	4	4	4	4	4	4	3-4	4-5	4	3-4	4	4
H ₉	4	3-4	3-4	3	3-4	3-4	4	3-4	3-4	4	3-4	3-4	3-4	4	4	3-4	4	4
H ₁₀	3-4	4-5	3-4	3-4	4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3	4	3-4	3	4	3
H ₁₁	5	4-5	4-5	4	4	4	4	4	4	4	4	4	3-4	4	4	3	3-4	4
H ₁₂	3	4	3-4	3	3-4	3-4	3	4	3-4	3	4	3-4	3	3-4	4	3	3-4	4

III. Result and Discussion

Exhaustion and Fixation Study:

The result of acid azo dyes obtained in **series-1 (H₁₋₁₂)** showed the percentage exhaustion values for wool ranges from 71% to 81%, in which dye H₅ shows maximum exhaustion value 81.76% while dye H₈ shows minimum exhaustion value 71.62%; for silk ranges from 71% to 82%, in which dye H₁₁ shows maximum exhaustion value 82.06% while dye H₆ shows minimum exhaustion value 71.10%; and for nylon ranges from 69% to 80%, in which dye H₉ shows maximum exhaustion value 80.18% while dye H₈ shows minimum exhaustion value 69.62 %.

The percentage fixation values of dyes **series-1 (H₁₋₁₂)** for wool varied from 82% to 91%, in which dye H₆ shows maximum fixation value 91.71% while dye H₈ shows minimum fixation value 82.38%; for silk varied from 85% to 92%, in which dye H₈ shows maximum fixation value 92.12% while dye H₁₀ shows minimum fixation value 85.10%; and for nylon varied from 80% to 90%, in which dye H₃ shows maximum fixation value 90.33% while dye H₆ shows minimum fixation value 80.37%.

Fastness Properties:

The acid azo dyes of **series-1** 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 H₅, H₆, H₈, H₁₁ showed good light fastness and very good washing, perspiration, rubbing fastness properties.

IV. 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.

References

- [1]. Choudhary A K.; "Tex. Prep. And Dye.", Science Publishers, USA, 2006.
- [2]. Booth And Gerald.; "Dyes, General Survey". Ullmann's Encyclopedia Of Industrial Chemistry. Weinheim: Wiley-VCH, 2000.
- [3]. Trowbridge Filippone, Peggy. "Food Color Additives". 2016.
- [4]. Klaus H.; Ed. Industrial Dyes: Chemistry, Properties, Applications Weinheim: WILEY-VCH Verlag, 2003.
- [5]. Mechanism Of Dyeing With Acid Dyes. *Textile Learner. Mazharul Islam Kiron*, 2012.
- [6]. Clark And Jim.; Intermolecular Bonding - Van Der Waals Forces, 2012.
- [7]. Colourage, , 39, 1989, 16-30.
- [8]. Bruckner M Z.; Basic Cellular Staining, 2013.
- [9]. Frazier R.A.; CAPILLARY ELECTROPHORESIS | Food Additives. Elsevier, 2007.
- [10]. Vega M.; Encyclopedia Of Separation Science. Elsevier, 2000.
- [11]. 11. Vanessa T., Sebastien F., Vevey F., Yan C., Jacques L., Cote M.F., Masson J.Y. And Rene C.G.; J. Med. Chem., 55, 6194, 2012. [11]
- [12]. Reema A.K., Ghassan A.S., Mahmoud A.S., Ghadeer A. And Mutasem T.; Med. Chem. Res., 21, 3669, 2012.
- [13]. Bechamp A.J.; Ann. Chim. Phys., 42(3),186,1854.
- [14]. Hazlet S.E. And Dornfeld C.A.; J. Am. Chem. Soc., 66, 1781, 1944.
- [15]. Frirz-David H.E. And Blengy L.; Fandamental Process Of Dye Chemistry, 3rd Ed, Willy: New York, 1949.
- [16]. Vogel A.I.; Atextbook Of Practical Organic Chemistry