



STUDIES ON SYNTHESIS OF REACTIVE DYES AND THEIR APPLICATIONS ON FABRICS

TIRTH H THAKER*, PRINSA UPADHYAY, AAKASHKUMAR TIWARI, FORAM
CHAUDHARY AND NIRMAL PATEL

Department of chemistry, Parul Institute of Applied Science, Parul University, Waghodia,
Vadodara – 391760, Gujarat, India

*Corresponding Author: Dr. Tirth H. Thaker: E Mail: tirth6582@gmail.com; Tel.:9974030992

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ABSTRACT

The synthesis involves the diazotization of 2-amino-5-(2-sulfoxy) ethyl sulfonyl) benzene sulfonic acid followed by azo coupling in acidic medium with 2,4-diamino benzene sulfonic acid respectively for yellow dye (1c). Similar series of reaction were carried out for orange dye (1'c) which involves the diazotization of 2-amino-5-(2-sulfoxy) ethyl sulfonyl) benzene sulfonic acid) followed by azo coupling in acidic medium with 7-amino-4-hydroxy naphthalene-2-sulfonic acid respectively. Exhaust dyeing process for reactive dyes was performed which showed both the dyes were showing the highest shade in cotton followed by nylon, wool, acrylic, acetate & polyester.

Keywords: Azo dye, Coupling reaction, Diazotization

INTRODUCTION

Reactive dyes having large color gamut, flexibility in application, and good fastness properties when colored on wool, silk, cotton, and regenerated cellulosic fibers, that makes reactive dyes a very successful class of modern synthetic dyes [1, 2]. Reactive dyes are with pedant groups capable of establishing covalent

connections with nucleophilic sited in fibrous substrates, to use a broad definition. The colorations wash fastness capabilities will be excellent if these covalent bonds are stable under the conditions experienced laundry. Reactive dyes are for wool are seen as alternatives to chrome dyes and have becomes more extensively employed

on polyamide materials as a means of producing dyeing's and designs with great fastness. When dyeing at the boil and above, certain types of reactive dyes have a favorable effect on the quantity of wool damage caused. The reader is directed to highly valuable works on reactive dyes and their use [1-8]. In addition to the extensive explanations provided in this review. Reactive dyes are azo dyes that are well-known for their ability to form a covalent link with their substrates [9, 10]. Reactive dyes have gained commercial significance due to their great brilliancy, range of colors, high wet fastness, ease of handling, and adaptability [11, 12]. The number and kind of reactive groups have an impact on dye depletion and fixing on fibers [13]. The fixation effectiveness of dyes with two reactive groups is higher than that of dyes with only one reactive group. Bifunctional reactive dyes have a strong affinity for fibers due to the two reactive groups in the dye molecule. Furthermore, the presence of vinyl sulphone bonds in suitably reactive systems allows for higher fixation levels, which improves the fastness characteristic and resistance to acid, alkali and peroxide [14, 15].

MATERIALS AND METHODS

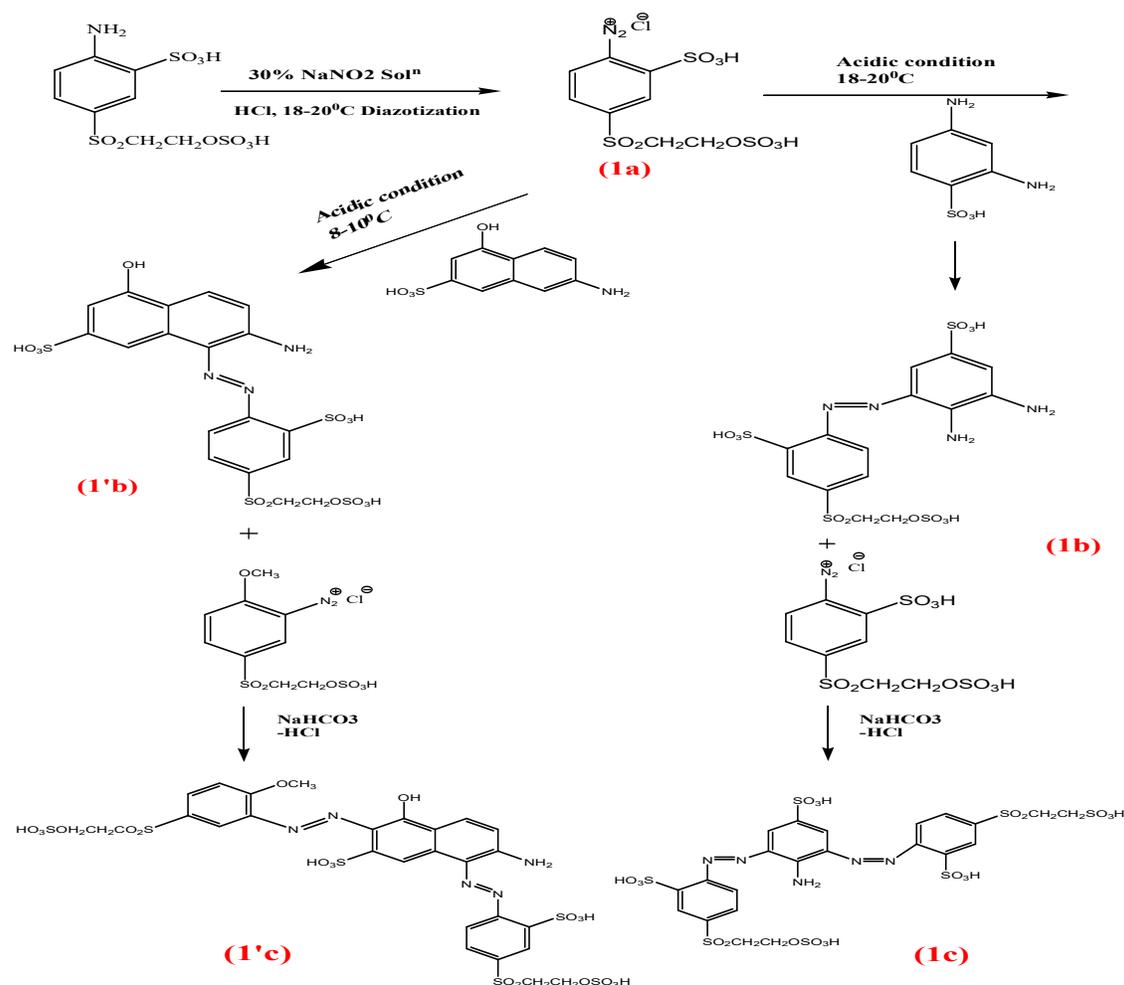
All the materials used were of high quality. Materials involves 2-amino-5-(2-sulfoxy) ethyl sulfonyl benzene sulfonic acid, 2,4-diamino benzene sulfonic acid, 7-amino-4-

hydroxy naphthalene 2-sulfonic acid, 2-(4-amino-3-methoxyphenylsulfonyl) ethyl hydrogen sulfate, Sodium nitrite (NaNO_2), Hydrochloric acid (HCl), Sulfamic acid. Different type of analysis was also performed such as IR, NMR, & HPLC for the determination of functional groups purity & solubility.

Experimental Section:

2-amino-5-(2-sulfoxy) ethyl sulfonyl benzene sulfonic acid (1a): Take 77.35gm of 2-amino-5-(2-sulfoxy) ethyl sulfonyl benzene sulfonic acid (for 70% purity, 0.15mole) in a beaker arranged with stirrer and thermometer & charge it with 100ml ice chilled water for 30 minutes. After 30 minutes add 30 ml HCl & 40% NaNO_2 solution (10.56gm) to the above mixture. The addition must be done between 18-20⁰C for about 60 minutes. After this, stir this mass for 90 minutes by maintaining temperature between 18-20⁰C. Check for starch iodide test if it is negative add a pinch of NaNO_2 & stir for some time & check SI again. Once positive destroy this excess nitrite with Sulfamic acid solution.

2,4-diamino-5-(2-{2-sulfo-4-[2-(sulfoxy) ethane sulfonyl] phenyl} diazen-1-yl) benzene-1-sulfonic acid (1b): Weigh 86.37 gm (0.30 mole) of 2,4-diamino benzene sulfonic acid & add this to the above diazo mixture (1a) in 30 mins. Stir this whole reaction mass for 2 hours at 18-20⁰C to obtain the intermediate (1b).



2,4-diamino-3,5-bis(2-{2-sulfo-4-[2-(sulfoxy) ethane sulfonyl]phenyl}diazen-1-yl) benzene-1-sulfonic acid (1c): Take 77.35gm of 2-amino-5-(2-sulfo-4-[2-(sulfoxy) ethane sulfonyl] benzene sulfonic acid (for 70% purity, 0.15mol) in a 1L-3N-RBF and charged 100ml ice After 30 minutes. Add a mixture of 30 ml HCl & 40% NaNO₂ solution (10.56 gm, 0.15 mol) to the above mixture (1b). The addition must be done between 5-10°C for about 60 minutes. After this, stir this mass for 90 minutes by

maintaining temperature between 5-10°C. Observe the PH for this mixture (observed 3-3.30) & then maintained the PH between 5.5-6.0 by adding sodium bicarbonate to the mass. After the PH is maintained stir the reaction for 2 hours. Now filter the reaction mass and inject the filtrate to the spray dryer for obtaining the solid yellow dye 2,4-diamino-3,5-bis(2-{2-sulfo-4-[2-(sulfoxy)ethanesulfonyl]phenyl}diazen-1-yl) benzene-1-sulfonic acid (1c). Yield: 93.11%, C, H, N analyses: calculated C,

29.30%, H, 2.57%, N, 7.77% & S, 24.89%, observed C, 29.66%, H, 2.43%, N, 7.33% & S, 24.97%, IR analyses (cm⁻¹): 3420.74, 3367.33, 1605.16, 1520.25, 1226.95, 1103.49, 1074.82, 998.61 indicating all functional groups NH₂ group, SO₃H group, C-O stretch, N=N stretch, C=S stretch, C-N stretch, N-S band respectively. HPLC purity for yellow dye (1c) 98.33%

Preparation of Orange Dye (1'c):

7-amino-4-hydroxy-8-((2-sulfo-4-(2-(sulfoxy) ethyl sulfonyl) phenyl) diazenyl) naphthalene-2-sulfonic acid(1'b): Weigh 33.72gm (0.127 mol) of 7-amino-4-hydroxy naphthalene-2-sulfonic acid & add this to 1(a) (0.127 mol) in 30 mins. Stir this whole reaction mass for 2 hours at 5-10⁰C to obtain the intermediate (1'b).

7-amino-4-hydroxy-3-((2-methoxy-5-(2-(sulfoxy) ethyls sulfonyl) phenyl) diazenyl)-8-((2-sulfo-4-(2-(sulfoxy) ethylsulfonyl)phenyl)diazanyl)naphthalene-2-sulfonic acid (1'c): Take 41.56 gm of 2-(4-amino-3-methoxyphenylsulfonyl) ethyl hydrogen sulfate (for 95% purity), 0.127 mole) and 100ml ice chilled water in a 1L-3N-RBF and stirred for 30 minutes. Add 30ml HCl & 40% NaNO₂ solution (8.9gm, 0.127 mol) in 30 to 60 mins. Stir for 1 Hr. To the above mixture add above prepared 1b' solution in 30-40 mins. The addition must be done between 5-7⁰C for about 60 minutes. Observe the pH for this mixture

(observed 3.0-3.30) & maintain the PH between 5.5-6.0 by adding sodium bicarbonate to the mass. After the pH is maintained stir the reaction for 2 hours. Now filter the reaction mass & inject to the spray dryer for obtaining the solid orange dye 7-amino-4-hydroxy-3-((2-methoxy)-5-(2-sulfoxy) ethyl sulfonyl) phenyl diazenyl)-8-((2-sulfo-4-(2-(sulfoxy) ethyl sulfonyl) phenyl) diazenyl) naphthalene-2-sulfonic acid (1'c). C, H, N analyses: calculated C, 30.81%, H, 2.68%, N, 6.65% & S, 18.28%, observed C, 30.54%, H, 2.33%, N, 7.20% & S, 24.88%, IR analyses (cm⁻¹): 3415.21, 1613.99, 1506.16, 1231.39, 1146.92, 1078, 729.98, 719.98, 623.57, 148.55 indicating all functional groups NH₂ group, SO₃H group, N=N stretch, N-H bend, C=S stretch, C-H stretch, CH₂ group, C-O stretch, SO₂ group, C-H bend derivatives respectively. HPLC purity for orange dye (1'c) 98.13%

APPLICATION: EXHUAUST DYEING PROCESS FOR BOTH REACTIVE DYES (1c & 1'c): preparation of dye solution. (2% solution): Weigh 2 gm dye & dissolve in 100ml distilled water.

Preparation of Dyeing Pot: Dye solution (2%, 10ml), aqueous anhydrous Sodium Sulphate (Glauber salt) (20%, 20ml), Soda ash solution (20%,5ml).

First, the dye bath was filled with 20ml water, followed by 20ml of 20% Glauber salt solution. After that, 10ml reactive dye

was added to the dye bath. 5 gm of cotton fabric added to the dye bath. The dye bath was held for 60 minutes in dyeing apparatus. Dye depletion happened in the cloth during this time. 5 ml 20% Soda ash solution was added after 30 minutes at 60⁰ C. After 30 min remove the fabric from pots for washing.

Washing Process: First wash with cold water to remove color from fabrics then use hot water (90⁰C) once both the washing completed dry the fabric in the oven. Measurement of dry cloth (standard & sample) is done in spectrophotometer to check the strength of the dye. Both dyes shows significant effect on fabric.

RESULTS AND DISCUSSION

The diazotization of 2-amino-5-(2-sulfoxy) ethyl sulfonyl) benzene sulfonic acid was followed by Azo coupling in acidic medium using 2,4-diamino benzenesulfonic acid respectively in the synthesis approach. Later, in an alkaline medium, condensation diazotized key starting material with 2,4-diamino-5-(2-{2-sulfo-4-[2-(sulfoxy) ethane sulfonyl] phenyl} diazen-1-yl] benzene-1-sulfonic acid are used to produce the final yellow dye. It demonstrates that using an equimolar ratio of basic ingredients obtained a yellow dye (98.33 % purity). Yellow dye interpreted well in the infrared range. This dye is then subjected to the Exhaust Dyeing Process and gave excellent dyeing.

The synthesis methodology involved the diazotization of 2-amino-5-(2-sulfoxy) ethyl sulfonyl) benzene sulfonic acid followed by azo coupling in acidic medium with 7-amino-4-hydroxy naphthalene-2-sulfonic acid respectively. The later on condensation of above coupled intermediate in Alkaline medium with 2-(4-amino-3-methoxyphenylsulfonyl) ethyl hydrogen sulfate are used to produce the final orange dye. It shows using equimolar ratio of the raw materials give yield of the product orange dye (98.13% purity). In the IR spectrum of orange dye interpreted well. This dye is further exposed to Exhaust Dyeing Process and gave excellent dyeing.

CONCLUSION: This type of dyes comprises moderately reactive groups. As a result, dyeing was done at a higher temperature, between 60-70⁰C. C, H, N, IR and HPLC analyses were used to characterize the synthesized dye and that has shown promising result. With the help of spectrophotometer, the strength of the dye was measured in that we found cotton is having the highest shade followed by nylon, wool, acetate, acrylic, polyester respectively. Looking towards applications of synthesized dyes these makes great scope of commercialization.

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