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ORIGINAL ARTICLE

Synthesis and evaluation of a series of symmetrical hot brand bis azo reactive dyes using 4,4′-methylene-bis-metanilic acid on various fibre

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KEYWORDS

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Abstract 4,4′-Methylene-bis-metanilic acid (A) was synthesized by the reaction between metanilic acid and formaldehyde. The compound (A) was used as a bifunctional middle component in the preparation of several symmetrical hot brand bis azo reactive dyes. The compound (A) was tetrazotized and coupled with various *m*-nitro anilino cyanurated coupling component to give various hot brand bis azo reactive dyes. The entired compounds have been identified by IR, ^{1}H NMR spectra and elemental analysis. The dyes were applied on silk, wool and cotton fabrics and their fastness properties were evaluated. All the dyes give good fastness properties. The percentage dye bath exhaustion was also been studied.

1. Introduction

The introduction of reactive dyes is an important landmark in the history of synthetic dyes (Shenai, 1994). Reactive dyes constitute a very important class for dyeing cellulosic fibres and a high rate of growth is predicted in future (Patel et al., 2004). These dyes under the dyeing condition form covalent bond with hydroxyl groups of cellulose or amino group of protein (Bird and Boston, 1975). Improvement in the structure of reactive dyes chromogens and in the structure, selection and number of reactive group have led to an increased used of reactive dyes (Renfrew and Taylor, 1994; Hanke, 1986; Abeta et al., 1984). Over a last decade a number of major changes have been taken place, primarily aimed at minimizing the major weakness of reactive dyes for facilitating new application condition. In this period bis azo reactive dyes (Patel et al., 1998, 2000, 2003) have been established as a major group for fixation to cellulose. Ayyangar et al. (1987, 1991) reported that bis azo dyes are tinctorially stronger than mono azo dyes making them potentially more economic. Patel et al. (2002, 2007) reported bis azo reactive dyes shows good properties on cotton fabric.

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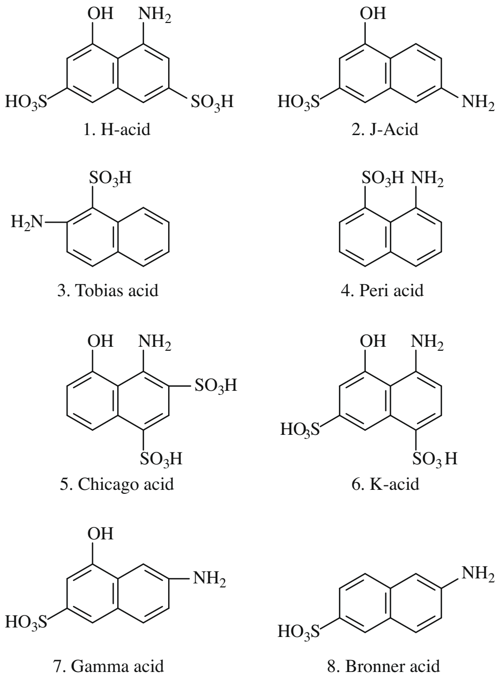
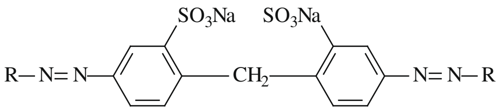


Chart 1 The coupling component used in the preparation of bis azo reactive dyes (D_1–D_8).

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



where R = various *m*-nitro anilino cyanurated coupling component.

4,4′-Methylene-bis-metanilic acid was tetrazotised and coupled with various *m*-nitro anilino cyanurated coupling component at alkaline pH to yield the reactive dyes (**D_1–D_8**).

The coupling components used are given in Chart 1.

2. Experimental

2.1. Materials and methods

Melting points were determined in open capillaries and are uncorrected. The IR spectra were recorded on Perkin–Elmer-881 spectrometer using KBr pallets. ^{1}H NMR spectra were scanned on Bruker DRX-300 FT-NMR spectrometer at 300 MHz, using TMS as an internal standard and DMSO-d_6 as solvent (chemical shift in δ ppm). The purity of all the dyes was checked by TLC (Fried and Sharma, 1982). Elemental analysis of C, H and N were carried on Carlo Erba 1108 Instrument. The light fastness was assessed in accordance with BS: 1006-1978 (Standard test method, 1978, 1994). The rubbing fastness test was carried out with a Crockmeter (Atlas) in accordance with AATCC-1961 (AATCC Test Method, 1961) and the wash fastness test in accordance with IS: 765-1979 (Indian Standard ISO, 1979). The tensile strength has been measured by single thread test.

The preparation of first dye using H-acid consist of four parts, they are

(1) Preparation of 4,4′-methylene-bis-metanilic acid.
(2) Tetrazotization of 4,4′-methylene-bis-metanilic acid.
(3) Preparation of *m*-nitro anilino cyanurated H-acid (R).
    (i) Cyanuration of H-acid (R′);
    (ii) Coupling with *m*-nitro aniline.
(4) Formation of dyes D_I.

*Preparation of 4,4′-methylene-bis-metanilic acid (*Nafziger, 1985; Cruros, 1971*):* metanilic acid (17.3 g, 0.1 mol) was dissolved in water (125 m1) and 36.5% hydrochloric acid (25 ml) at 50 °C. The reaction mixture was then reacted with 3% aqueous formaldehyde (35 ml) solution at 60 °C with stirring for an hour and neutralized with 10% sodium hydroxide, yellowish precipitates obtained were filtered, washed with hot water, dried and recrystalized from acetic acid. Yield 89%, m.p. 210 °C, IR (KBr): $\nu_{\max}$ (cm^{-1}) 3510, 3440 (Asym. and sym. N–H stretching), 2860 (C–H stretching), 1160, 1030 (Asym. and sym S=O stretching). Elemental analysis: Found C-43.51%; H-3.88%; N-7.78%; $C_{13}H_{14}O_6N_2S_2$ (MF requires C 43.57%; H 3.94%; N 7.82%). ^{1}H NMR (DMSO-d_6) (chemical shift in δ ppm): 3.28 δ (4H, s, –NH_2), 1.25 δ (2H, s, –CH_2), 7.05 δ 7.85 δ (6H, m, Ar–H).

Tetrazotisation of 4,4′-methylene-bis-metanilic acid: 4,4′-methylene-bis-metanilic acid (1.79 g, 0.005 mol) was suspended in H_2O (60 ml). Hydrochloric acid (0.36 g) was added dropwise to this well stirred suspension. The mixture was gradually heated up to 70 °C, till clear solution obtained. The solution was cooled at 0–5 °C in an ice bath. A solution of $NaNO_2$ (0.6 g) in water (4 ml) previously cooled to 0–5 °C, was then added over a period of 5 min with stirring. The stirring was continued for an hour, 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-A at 0–5 °C was obtained and used for subsequent coupling reaction.

Preparation of m-nitro anilino cyanurated H-acid (R): The preparation of *m*-nitro anilino cyanurated H-acid involves two steps.

(i) Cyanuration of H-acid (R′) and;
(ii) Condensation with *m*-nitro aniline.

Preparation of cyanurated H-acid (R′): cyanuric chloride (1.85 g, 0.01 mol) was stirred in acetone (25 ml) at a temperature below 5 °C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01 mol) in aqueous sodium carbonate solution (10% w/v) was then added in small lots in about an hour. 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 clear solution was obtained. The cyanurated H-acid solution was used for subsequent coupling reaction.

Condensation with m-nitro aniline: the temperature of ice-cooled well stirred solution of cyanurated H-acid (4.67 g, 0.01 mol) was gradually raised to 45 °C for half an hour. To this cyanurated H-acid the *m*-nitro aniline (1.39 g, 0.01 mol)