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Preparation of novel oligomeric azo dye

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ABSTRACT

The novel oligomeric acid azo dyes prepared by coupling reaction of m-cresol-thiourea resin with diazonium salts of various substituted naphthol sulfonic acid with. The novel oligomeric acid azo dyes demonstrate outstanding dyeing possessions on a variety of textile fibers. They shows that the formed dye have dominant fixation properties. The dyes fixed on the fiber with nearly minor unemployed dye. The best part of the dyes have prominent fixation on textile at a less important quantity of exhaustion. While using these dyes commercially it may influence the environmental saving by a lesser amount of dye effluents from textiles.

Keywords: Oligomeric azo dyes, Spectral studies, Thermogravimetry analysis, Light fastness, wash fastness.

INTRODUCTION

In the modern day, a new class of materials, polymeric colorants, has gained recognition and applicability as an alternative to classical methods of coloration. The reaction of polymer and dye chemistries enables the chemist to design unique materials that exploit the best characteristics of both pigments and dyes. The synthetic dyes play the major role in textile fibers fashioning. Most of the synthetic dyes evolve from phenolic and naphtholic bases [1]. The azoic chromophore based dyes have particularly high tintorial properties on fibers [1]. The phenolics are known as matrix resins or binding resins for its various application. Phenolic resins are commodity materials for wide applications [2-4]. Particularly Phenolic are acid catalyzed products. Number of modifications of these resins is made for further application [5-9]. The phenol-formaldehyde resins are important material in industries [10,11]. The main advantages of phenolics are their easy availability and their excellent properties, like thermal stability, acid resistance, fire retardancy, ion-exchange resin, water treatment, and etc [12-17]. One such area where phenolic resins find use is as coupling agents in the formation of acid azo dyes or pigments. This area has received attention academically and industrially is spite of the advantages noted above. Only a few researches have reported the use of phenolic resins as coupling components in the formation of acid azo dyes [18-24]. These dyes are reported to have been used as ion ion-exchange resin [19-23]. Hence, the present article reports the studied on novel oligomeric azo dyes based on the condensation of phenolic resin with N,N'-Dimethylolthiourea, as coupling agent. The whole route for synthesis is shown in Scheme I.

MATERIALS AND METHODS

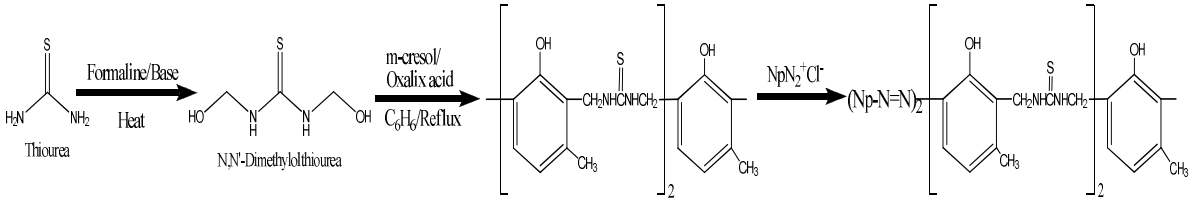
Experimental Details

m-cresol used was of analytical grade and were purchased from local markets. They purified from ethanol prior to use. Thiourea, formalin (37% w/v) oxalic acid and various aromatic amines were of laboratory grade.

Synthesis of N,N'-Dimethylolthiourea (DMTU)

To a solution of thiourea (7.61g, 0.1mole) in 100 ml water formalin (7.5 ml, 0.25 mole) was added and neutralize by alkali. Then the mixture was heated on water bath at 75 ºC. The resultant solution was then vacuum distilled under

reduced pressure to remove most of water molecules. The resultant syrup is stored in vacuum desiccators.



Where Np= (a) 8-Amino-1-naphthol-6,8-disulfonic acid (b) 6-Amino-1-naphthol-3-sulfonic acid

(c) 7-Amino-1-naphthol-3-sulfonic acid (d) 8-Amino-1-naphthol-5,7- disulfonic acid

Scheme I

Synthesis of m-cresol-Dimethylolthiourea (MCDMTU) oligomers

A mixture of m-cresol (21.6g, 0.2mole), N,N'-Dimethylolthiourea (DMTU) (13.6g, 0.1 mole), oxalic acid (2.0 gm) and benzene (250 ml) was refluxed at 80°–82°C for 3 hrs in a three necked round bottom flask. The resultant viscous mass was distilled under reduced pressure at (10-15mm) to remove unreacted m-cresol, benzene and eliminated water as much as possible. The thick viscous liquid resin washed with a large amount of petroleum ether (40ºC –60°C). It was kept in vacuum desiccators.Yeild-62%,M.P.278-280°C(uncorrected). Analysis for $C_{10}H_{13}N_2OS$,Cal: %C 57.42,% H 6.22,% N 13.40,% S 15.31;Found: % C 57.4, % H6.2,% N 13.3,% S 15.2.IR(KBr,cm^{-1}): 3456(OH),3328(NH stretching of secondary amine), 3040, 1650,1530(C=C stretching of aromatic ring),1189(C=S group),2850,2950(C-H of CH_2, CH_3 group); ^{1}H-NMR(400MHz, DMSO-d_6, δ/ppm): 5.36 (H,s,-OH), 2.23 (2H,s,NH), 7.12-6.85 (4H,m,aromatic),4.77,2.91(4H,s,-CH_2),2.38(3H,s,CH_3).The predicted structure of m-cresol- Dimethylolthiourea (MCDMTU) oligomers is shown in Scheme-I.

Synthesis of oligomeric acid dyes, NCDMTU (a-d):

General method: Oligomers MCDMTU (26.0g, 0.1 mole) was dissolved in 10% (v/v) aqueous NaOH (75 ml) and the pH of solution was adjusted to 10-10.5. The solution was cooled to 0°C. To this diazonium salt solution of naphthol sulfonic acid (0.1mole) solution was added drop wise at temperature below 5°C and maintains the pH 10-10.5. The completion of azo coupling was confirmed by starch-iodide paper. After the addition is over, the reaction mixture was stirred for 1hr at 0°C. The reaction mixture was acidified to pH 5.5-6.0. The precipitated dye was stirred well with 20g of NaCl and heated on a water bath for 30 minutes. The resultant dyes NCDMTU (a-d) were filtered, washed with water and air-dried.

Measurements

The elemental analysis of NCDMTU (a-d) dyes were carried out by C,H,N Analyzer (Carlo Erba, Italy). Melting points were determined in open capillary tubes and were uncorrected. The IR spectra were recorded in KBr pellets on a Nicolet 400D spectrometer and ^{1}H NMR spectra were recorded in DMSO with TMS as internal standard on a Bruker spectrometer at 400 MHz. Absorption spectra were recorded on a Beckman DK-2A spectrophotometer in various solvents. The thermal stability of all the dyes synthesized in the present study was assessed on a DuPont 951 thermal analyzer in air at a heating rate 10ºC min^{-1}.

Dyeing of Oligomeric Acid NCDMTU Dyes on Wool and Nylon

For dyeing, wool and nylon were scoured in soap (0.2%) solution containing ammonia (0.1% w/v) at 45ºC–50ºC for 10 min, washed with water, squeezed and dried. The treated wool and nylon fibers were heat set for 5 min at 80ºC in a dilute acid solution of pH 3 for wool and pH 5 for nylon.

The dye bath was set with the required amount of dye and dilutes sulphuric acid. The M: L ratio was maintained as 1:50. The exact quantity of oligomeric acid NCDMTU(a-d) dye solution in water (100ml) (containing 0.04 g of the dye) was used for dyeing wool and nylon (2.0 g weight of each fibers), so as to get 1% shade of the dye on the fibre. The dye bath was constantly revolving in a thermostated bath at 85ºC. Dyeing was continued up to the equilibrium.

RESULTS AND DISCUSSION

Novel oligomeric azo dyes based on the condensation of phenolic resin with N,N- Dimethylolthiourea has not been reported previously. All the dyes were obtained as an amorphous powders ranging in color from yellow to Brown. All the oligomeric acid NCDMTU (a-d) dyes were soluble in common organic solvents such as 1,4-dioxane, DMF and DMSO.

Table 1: Elemental analysis data for NCDMTU (a-d) Dye

Dye	Color	Yield (%)	Elemental Analysis							
			C(%)		H(%)		N(%)		S(%)	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
NCDMTU-a	Brownish red	85	50.70	50.68	4.23	4.22	13.15	13.13	15.02	15.00
NCDMTU-b	Reddish brown	82	56.18	56.15	4.29	4.28	14.56	14.54	12.48	12.46
NCDMTU-c	Reddish brown	79	56.18	56.17	4.29	4.27	14.56	14.53	12.48	12.47
NCDMTU-d	Reddish brown	81	50.70	50.67	4.23	4.20	13.15	13.12	15.02	15.01

The absorption spectral characterization, molar extinction co-efficient and Fastness Properties for acid NCDMTU (a-d) dyes are shown in Table 2. The wavelength of maximum absorption is attributed to the excitation of azo groups in the dye, which is observed around 490 to 560 nm. The variations in λ_{max} may be attributed to the structural variations in the oligomers and the amine coupling components.

TGA measurements reveal that the solid powder oligomeric acid NCDMTU (a-d) dyes start their decomposition between 160-180ºC, weight loss being completed between 200 to 230 ºC depending upon the structural variation.

The oligomeric acid NCDMTU (a-d) dyes were dyed on nylon and wool fibres at 1% shade and gave blue, brown, red and orange shades. Thus, the oligomeric acid NCDMTU (a-d) dyes gave a variety of attractive hues on dyed Nylon and wool fibers. The results of percentage dye bath exhaustion and fixation in dyeing of Nylon and wool by all the oligomeric acid NCDMTU (a-d) dyes varied from 68% to 87%, depending upon the nature of the oligomeric dye, while it was observed that in simple m-cresol azo dyes the exhaustion and fixation varied from 53 % to 68 %.

Table 2: Visible absorption spectra and Fastness Properties of the NCDMTU (a-d) Dyes

Dyes	λ_{max} (nm)	log ε	Dyeing on Nylon		Dyeing on Wool	
			Light fastness	Wash fastness	Light fastness	Wash fastness
NCDMTU-a	525	4.65	4-5	4	3-4	3-4
NCDMTU-b	497	4.85	4-5	4-5	5	4-5
NCDMTU-c	552	5.93	4-5	4	3	3
NCDMTU-d	552	4.59	4	3-4	4	3-4

The light-fastness and Wash fastness properties of all oligomeric acid NCDMTU (a-d) dyes (Table 2) were determined according to standard methods. Examination of the data reveals that the light-fastness of all acid NCDMTU (a-d) dyes on nylon and wool fibres was particularly appreciable. The light-fastness of oligomeric acid azo dyes varied from 3 to 6 (very good) on wool and 3 to 5 (good) on nylon fiber. Most acid NCDMTU (a-d) dyes having a rating of 4 (very good) and 5 (very good) rating on nylon and wool, respectively. The wash-fastness of all acid NCDMTU (a-d) dyes varied from 2 to 5 on nylon and wool fibers. It was concluded that the light fastness of dyeing by oligomeric acid NCDMTU (a-d) dyes on nylon and wool varied from poor to very good.

In this study of oligomeric and acid NCDMTU (a-d) dyes, the dyeing on the fiber is completed in short time (45 min on nylon, 30 min on wool) and low temperature.

Fixation of dyes on fiber is also high and most importantly no patches were observed on the fibers. The difference in the dyes on the nylon and the wool fibers was due to the structural variation of these fibers. This may good indication for industrial point of views. The conventional dyes have great effluent water pollution today. If these dyes will be viable commercially, it will solve the water pollution. Ultimately save the water pollutions.

CONCLUSION

A novel series of oligomeric acid azo dyes NCDMTU (a-d) were synthesized by coupling reaction of various substituted naphthol sulfonic acid of PDMTU. The use of these prepared compounds in the dyeing on wool and nylon shows good light fastness as well as washing fastness properties. These prepared compounds shows excellent fixation properities on fiber.

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