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Novel oligomeric azo dye of thiourea-phenol resin

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ABSTRACT

A series of novel oligomeric acid azo dyes were prepared by coupling various aromatic diazonium salts have been prepared and characterized the dyeing assessment of such dyes on various textile fibers reveals that excellent are achieved. During the dyeing assessment it was observed that the produced dye have powerful fixation properties. The dyes fixed on the fiber with almost negligible unused dye. Most of the dyes have high fixation on textile at less percentage of exhaustion. While using these dyes commercially it may affect the environmental saving by less percentage of dye effluents from textiles.

Keywords: Azo dyes, Textile fiber, IR, Spectral studies, Thermogravimetry, Light and wash fastness, Textile industries effluents

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INTRODUCTION

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 [18-20]. These dyes are reported to have been used as ion ion-exchange resin [19-20]. 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.

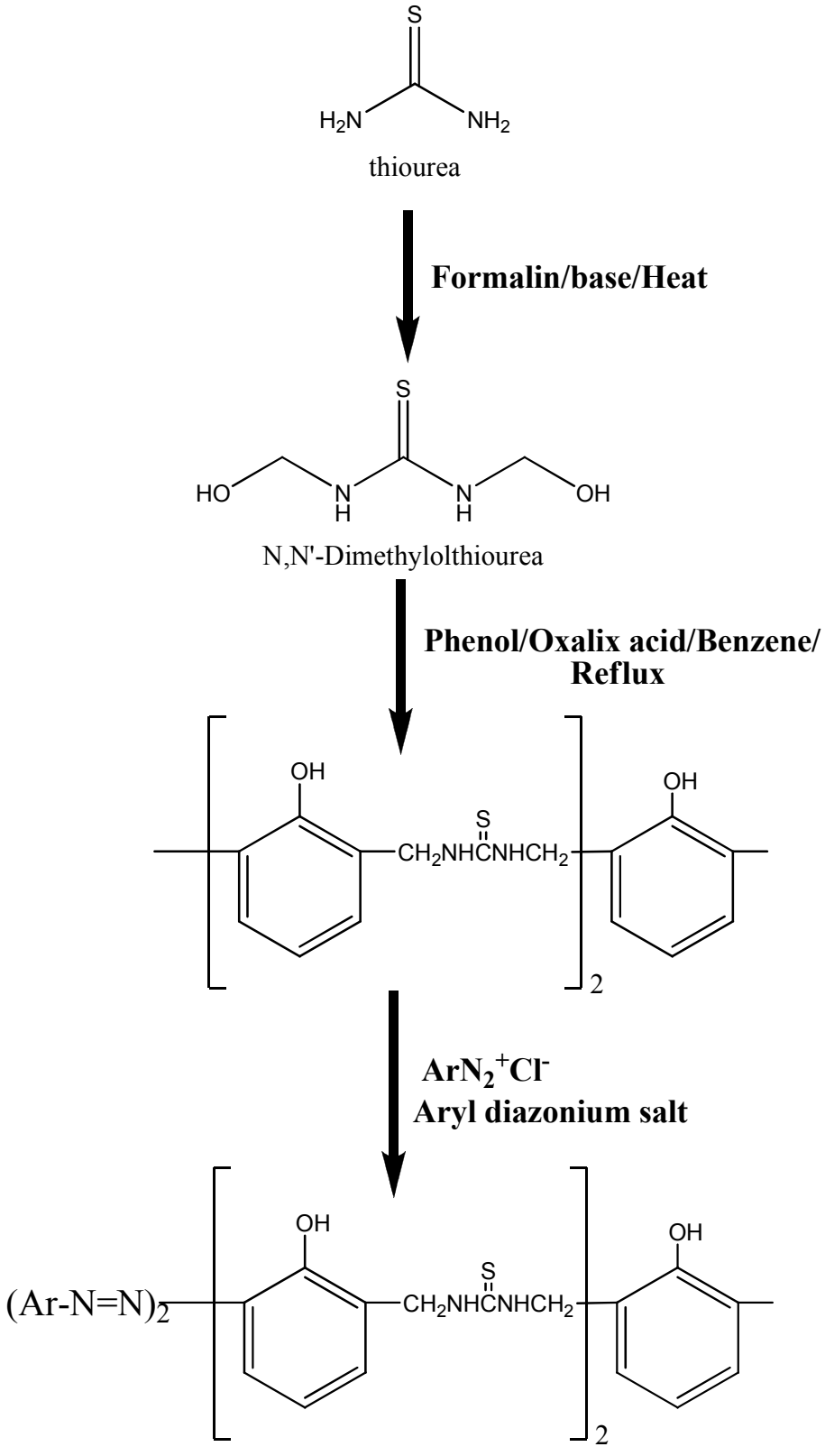
MATERIALS AND METHDS

Phenol 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.

Procedure

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 **Ar**= (a) C_6H_5 (b) p-OHC_6H_4 (c) p-$CH_3C_6H_4$

(d)p-ClC_6H_4 (e)p-$OCH_3C_6H_4$

Scheme I

Synthesis of Phenol-Dimethylolthiourea(PDMTU) oligomers

A mixture of Phenol (18.8g, 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 phenol, 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-65%, M.P.272-274°C(uncorrected). Analysis for $C_9H_{11}N_2OS$,Cal: %C 55.38,% H 5.64,% N 14.36,% S 16.41;Found: % C 55.3, % H 5.6,% N14.3,% S 16.4. 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(C-H of CH_2group);^{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).The predicted structure of Phenol-Dimethylolthiourea (PDMTU) oligomers is shown in Scheme-1.

General method for the synthesis of oligomeric acid dyes, azo-PDMTU(a-e):

Oligomers PDMTU (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 solution Aryl diazonium salt (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 azo-PDMTU (a-e) were filtered, washed with water and air-dried.

Measurements

The elemental analysis of azo-PDMTU (1-5) 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 Azo-phenol-DMTU 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 azo-PDMTU(a-e) 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 85 ºC. Dyeing was continued up to the equilibrium.

Table 1: Elemental analysis data for azo-PDMTU (a-e) Dye

Dye	Color	M.P(°C)	Yield (%)	Molecular formula	Molecular weight	Elemental Analysis							
						C(%)		H(%)		N(%)		S(%)	
						Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
azo-PDMTU-a	Yellow	202-204	62	$C_{30}H_{30}N_8O_2S_2$	598	60.20	60.1	5.02	5.0	18.73	18.7	10.70	10.6
azo-PDMTU-b	Pale yellow	197-199	65	$C_{30}H_{30}N_8O_4S_2$	630	57.14	57.1	4.76	4.7	17.78	17.7	10.16	10.1
azo-PDMTU-c	Reddish yellow	186-188	66	$C_{32}H_{34}N_8O_2S_2$	626	61.74	61.7	4.82	4.8	18.01	17.9	10.29	10.2
azo-PDMTU-d	Pale yellow	213-215	64	$C_{30}H_{30}N_8O_2S_2Cl$	667	53.97	53.9	4.20	4.1	16.79	16.7	9.60	9.5
azo-PDMTU-e	Brown	201-203	60	$C_{32}H_{34}N_8O_4S_2$	658	58.36	58.3	5.17	5.1	17.02	17.0	9.73	9.7

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 azo-PDMTU (a-e) dyes were soluble in common organic solvents such as 1,4-dioxane, DMF and DMSO.

The absorption spectral characterization, molar extinction co-efficient and Fastness Properties for acid azo-PDMTU (a-e) 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 445 to 525 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 azo-PDMTU (a-e) dyes start their decomposition between 150-170ºC, weight loss being completed between 190 to 220 ºC depending upon the structural variation.

The oligomeric acid azo-PDMTU (a-e) dyes were dyed on nylon and wool fibres at 1% shade and gave blue, brown, red and orange shades. Thus, the oligomeric acid azo- PDMTU (a-e) 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 azo-PDMTU (a-e) dyes varied from 75% to 100%, depending upon the nature of the oligomeric dye, while it was observed that in simple phenol azo dyes the exhaustion and fixation varied from 60 % to 80 %.

Table 2: Visible absorption spectra and Fastness Properties of the azo-PDMTU (a-e) Dyes

Dyes	$\lambda_{max(nm)}$	log ε	Dyeing On Nylon		Dyeing On Wool	
			Light fastness	Wash fastness	Light fastness	Wash fastness
azo-PDMTU-a	445	5.27	3-4	4	3-4	4
azo-PDMTU-b	480	4.35	3	3	2-3	3
azo-PDMTU-c	525	4.46	2-3	3	1-2	2
azo-PDMTU-d	512	4.38	4-5	4	3-4	3
azo-PDMTU-e	498	4.59	4-5	4	3	3

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

In this study of oligomeric and acid azo- PDMTU (a-e) 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 symptoms 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-PDMTU (a-e) dyes were synthesized by coupling various aromatic diazonium salts to PDMTU. The use of these compounds in the dyeing on wool and nylon shows poor to very good light fastness as well as washing fastness properties. Fixation of dyes on fiber is also high.

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