



Research Article

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## Synthesis and characterization novel oligomeric azo dye

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### ABSTRACT

The diazonium salts of various substituted naphthol sulfonic acid couple with phenol-thiourea resin afforded novel oligomeric acid azo dyes. The novel oligomeric acid azo dyes show excellent dyeing properties on various textile fibers. They shows that the produced dye have powerful fixation properties. The dyes fixed on the fiber with nearly minor unemployed dye. The majority of the dyes have elevated fixation on textile at a lesser amount of exhaustion. While using these dyes commercially it may influence the environmental saving by a lesser amount of dye effluents from textiles.

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

### INTRODUCTION

In the present day a new class of materials, polymeric colorants, has gained recognition and applicability as an alternative to classical methods of coloration. The marriage 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 in 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 [18-23]. 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.

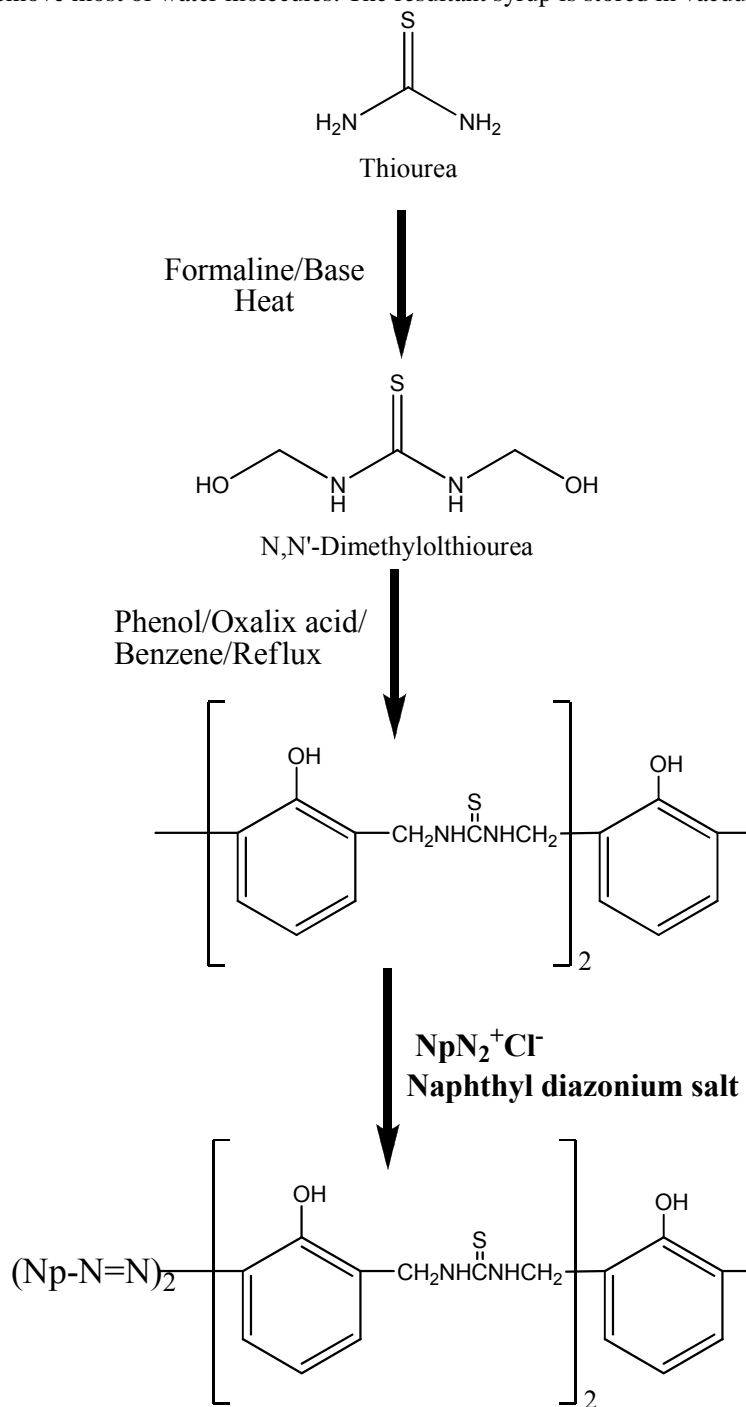
### EXPERIMENTAL SECTION

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.

#### 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 °C. 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 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 (40°C –60°C). It was kept in vacuum desiccators. Yield-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, % N 14.3, % 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  $CH_2$  group);  $^1H$ -NMR(400MHz, DMSO- $d_6$ ,  $\delta$ /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, NPDMTU (a-d):

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 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 NPDMTU (a-d) were filtered, washed with water and air-dried.

#### Measurements

The elemental analysis of NPDMTU (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  $^1H$  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  $10^\circ C \text{ min}^{-1}$ .

#### Dyeing Of Oligomeric Acid NPDMTU Dyes On Wool And Nylon

For dyeing, wool and nylon were scoured in soap (0.2%) solution containing ammonia (0.1% w/v) at 45°C–50°C for 10 min, washed with water, squeezed and dried. The treated wool and nylon fibers were heat set for 5 min at 80°C 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 NPDMTU(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 85 °C. Dyeing was continued up to the equilibrium.

Table 1: Elemental analysis data for NPDMTU (a-d) 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
NPDMTU-a	Reddish brown	212-214	87	$C_{34}H_{32}N_8O_9S_4$	824	49.51	49.4	3.88	3.8	13.59	13.5	15.53	15.5
NPDMTU-b	Red	207-209	73	$C_{34}H_{29}N_8O_6S_3$	741	55.06	55.0	3.91	3.9	15.11	15.1	12.96	12.9
NPDMTU-c	Reddish brown	196-198	84	$C_{34}H_{29}N_8O_6S_3$	741	55.06	55.0	3.91	3.9	15.11	15.1	12.96	12.9
NPDMTU-d	Reddish brown	223-225	92	$C_{34}H_{32}N_8O_9S_4$	824	49.51	49.4	3.88	3.8	13.59	13.5	15.53	15.5

## 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 NPDMTU (a-d) 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 NPDMTU (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  $\lambda_{max}$  may be attributed to the structural variations in the oligomers and the amine coupling components.

TGA measurements reveal that the solid powder oligomeric acid NPDMTU (a-d) dyes start their decomposition

between 160-180°C, weight loss being completed between 200 to 230 °C depending upon the structural variation.

The oligomeric acid NPDMTU (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 NPDMTU (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 NPDMTU (a-d) dyes varied from 70% to 90%, depending upon the nature of the oligomeric dye, while it was observed that in simple phenol azo dyes the exhaustion and fixation varied from 55 % to 70 %.

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

Dyes	$\lambda_{\max}(\text{nm})$	log $\epsilon$	Dyeing On Nylon		Dyeing On Wool	
			Light fastness	Wash fastness	Light fastness	Wash fastness
NPDMTU-a	497	4.85	5	4-5	4-5	4-5
NPDMTU-b	527	4.45	3-4	3	4-5	4
NPDMTU-c	552	5.93	3	3	4-5	4
NPDMTU-d	552	4.59	4	3-4	4	3-4

The light-fastness and Wash fastness properties of all oligomeric acid NPDMTU (a-d) dyes (Table 2) were determined according to standard methods. Examination of the data reveals that the light-fastness of all acid NPDMTU (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 NPDMTU (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 NPDMTU (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 NPDMTU (a-d) dyes on nylon and wool varied from poor to very good.

In this study of oligomeric and acid NPDMTU (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 NPDMTU (a-d) dyes were synthesized by coupling various substituted naphthol sulfonic acid of 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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## REFERENCES

- [1] B. C. Dixit, H. M. Patel, D. J. Desai, *J. Serb. Chem. Soc.*, **2007**,72,119.
- [2] Wolfgang Hesse "Phenolic Resins" in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim,**2002**.
- [3] S. D. Alexandratos, *Ind. Eng. Chem. Res.*,**2009**,48,388.
- [4] M. L. Kuo, D. Adams, D. Myers, D. Curry, H. Heemstra, J. L. Smith and Y. Bian., *Forest Products Journal*, **1998**,48(2),71.
- [5] L. H. Baekeland, *Ind. Eng. Chem.*, **1909**,1 (8), 545.
- [6] O. A. Cruickshank and D. O. Braithwaite,*Ind. Eng. Chem.*,**1949**,41,472.
- [7] A. Gardziella, L.A. Pilato and A. Know, *Phenolic Resins: Chemistry, Application, Standardization ,Safty and Ecology*, New York, Springer,**2000**,pp.205.
- [8] H. El-Saied, A.M.A. Nada, A.A. Ibrahim and M.A.Yousef, *Angew.Makromolek. Chem.* **1984**,122,169.
- [9] R. E. Ysbrandy, R.D. Sanderson and G.F.R. Gerischer,"*Adhesives from autohydrolysis bagasse lignin*",*part-I,Holzforchung*,**1992**,46(3),249.
- [10] T. B. Shah, H. S. Patel, R. B. Dixit and B. C. Dixit, *Int. J. of Polym. Anal. and Charact.* **2003**, 8,369.
- [11] D. K. Patel and Arun Singh, *E-Journal of Chemistry*, **2009**,6(4),1017.
- [12] A. Knop, W. Scheib, *Chemistry and Application of Phenolic Resins*, Spronger Veriag, Berlin, Heidelberg, New

York 1979, pp.60.

- [13] D.T. Masram, K. P. Kariya and N. S. Bhavé, *Der Pharma Chemica*, **2011**, 3(3),124.
- [14] D.T. Masram, K. P. Kariya, N.S. Bhavé, *epolymers*, **2007**,75,618.
- [15] S. A. Raja, A. Mohamed, A. Riswan, J. Duraisamy, R. B. Abdul, *Iranian Polymer Journal*,**2009**,18 (10), 821.
- [16] M. M. Jadhao, L. J. Paliwal, N. S. Bhavé, *J. Appl. Polym. Sci.*, **2005**, 96(5),1605.
- [17] M.M. Jadhao, L.J. Paliwal, N. S. Bhavé, *Desalination*, **2009**, 247,456.
- [18] B. D. Lad, *Ph.D. thesis*, Sardar Patel University,**1985**.
- [19] J. R. Patel, K. S. Nimavat and K. B. Vyas, *J. Chem. Pharm. Res.*,**2011**,3(6),483.
- [20] J. R. Patel, K. S. Nimavat and K. B. Vyas, *Der Pharma Chemica*,**2011**,3(4),102.
- [21] B. P. Dave and P. J. Shah, *Der Chemica Sinica*, **2012**,3(6),1343-1347.
- [22] D. R. Gosai, K. S. Nimavat and K. B. Vyas, *Der Chemica Sinica*,**2011**,3(4),491-500.
- [23] D. R. Gosai , K. S. Nimavat and K. B. Vyas, *Archives of Applied Science Research*, **2012**, 4(3),1395-1402.