Journal of Current Chemical & Pharmaceutical Sciences

J. Curr. Chem. Pharm. Sc.: 3(3), 2013, 181-186
ISSN 2277-2871

NOVEL OLIGOMERIC AZO DYES

BHAVESH P. DAVE[a], BINDU C. PATEL[a] and PURVESH J. SHAH[*]

Department of Chemistry, Shri A. N. Patel P.G. Institute, ANAND – 388001 (Guj.) INDIA
[a]Department of Chemistry, M. B. Patel Science College, ANAND – 388001 (Guj.) INDIA

(*Received : 06.05.2013; Accepted : 20.05.2013*)

ABSTRACT

The reaction between m-cresol and N,N'-dimethylolthiourea gives a novel m-cresol-Dimethylolthiourea (MCDMTU) oligomers. These oligomer then treated with various aromatic diazonium salts afforded a series of novel oligomeric acid azo dyes. The newly formed compounds were characterized by dyeing assessment properties on various textile fibers, which was excellent. 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.

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

INTRODUCTION

Azo compounds are a very important class of chemical compounds receiving attention in scientific research. The synthetic azo dyes play a 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 applications[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 thermosetting resin etc[12-18]. 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[19-23]. These dyes, which are reported here; have been used as ion ion-exchange resin[20,21]. Hence, the present article reports the studieds 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 1.

Available online at www.sadgurupublications.com
[*]Author for correspondence; E-mail: purvesh23184@gmail.com, drbppatel14@gmail.com

EXPERIMENTAL

Materials

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

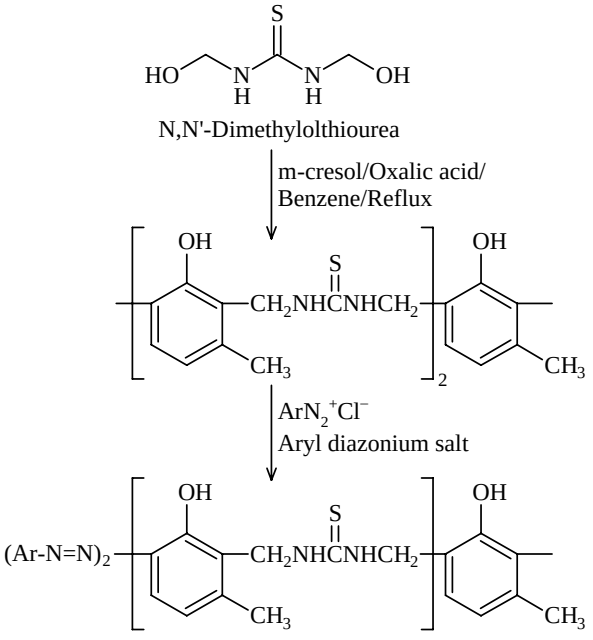
Procedure

Synthesis of N, N'-Dimethylolthiourea (DMTU)

To a solution of thiourea (7.61 g, 0.1 mole) in 100 mL water, formalin (7.5 mL, 0.25 mole) was added and neutralized by alkali. Then the mixture was heated on water bath at 75ºC. The resultant solution was then vacuum distilled under reduced pressure to remove most of water molecules. The resultant syrup is stored in vacuum desiccators.

Synthesis of m-cresol-Dimethylolthiourea (MCDMTU) oligomers

A mixture of m-cresol (21.6 g, 0.2 mole), N,N'-Dimethylolthiourea (DMTU) (13.6 g, 0.1 mole), oxalic acid (2.0 g) 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 (10-15 mm) 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 (400 MHz, 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 1.



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 1

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

Dye	Color	M.P. (°C)	Yield (%)	Molecular formula	Mol. weight	Elemental analysis							
						C(%)		H(%)		N(%)		S(%)	
						Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
azo-MCDMTU-a	Yellowish white	213-215	67	$C_{32}H_{34}N_8O_2S_2$	626	61.34	61.33	5.43	5.41	17.89	17.86	10.22	10.20
azo-MCDMTU-b	yellow	204-206	64	$C_{32}H_{34}N_8O_4S_2$	658	58.36	58.34	5.17	5.16	17.02	17.00	9.73	9.71
azo-MCDMTU-c	Reddish brown	219-221	68	$C_{34}H_{38}N_8O_2S_2$	654	62.39	62.35	5.81	5.80	17.13	17.11	9.79	9.76
azo-MCDMTU-d	yellow	217-219	66	$C_{32}H_{34}N_8O_2S_2Cl_2$	697	55.09	55.07	4.88	4.86	16.07	16.06	9.18	9.15
azo-MCDMTU-e	Brown	222-224	62	$C_{34}H_{38}N_8O_4S_2$	686	59.48	59.46	5.54	5.52	16.33	16.32	9.33	9.30

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

Oligomers MCDMTU (27.4, 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 (0.1 mole) 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 20 g of NaCl and heated on a water bath for 30 minutes. The resultant dyes azo-MCDMTU (a-e) were filtered, washed with water and air-dried.

Measurements

The elemental analysis of azo-MCDMTU (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-m-cresol-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-MCDMTU (a-e) dye solution in water (100 mL) (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 fiber. The dye bath was constantly revolving in a thermo stated 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 azo-MCDMTU (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-MCDMTU (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 377 to 527 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-MCDMTU (a-e) dyes start their decomposition between 150-170ºC, weight loss being completed between 190 to 220ºC depending upon the structural variation. The oligomeric acid azo-MCDMTU (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-MCDMTU (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-MCDMTU (a-e) dyes varied from 75% to 100%, 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 60 % to 80%.

Table 2: Visible absorption spectra and fastness properties of the azo-MCDMTU (a-e) dyes

Dyes	λ_{max} (nm)	log ε	Dyeing on Nylon		Dyeing on Wool	
			Light fastness	Wash fastness	Light fastness	Wash fastness
azo-MCDMTU-a	527	4.45	4-5	4	3-4	3
azo-MCDMTU-b	417	4.25	4-5	4	4	3-4
azo-MCDMTU-c	377	4.91	3-4	4	3-4	4
azo-MCDMTU-d	392	5.33	4-5	4-5	3-4	4
azo-MCDMTU-e	512	4.59	3-4	3-4	1-2	2-3

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

In this study of oligomeric and acid azo-MCDMTU (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-MCDMTU (a-e) dyes were synthesized by coupling various aromatic diazonium salts to MCDMTU. 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.

REFERENCES

1. B. C. Dixit, H. M. Patel and D. J. Desai, J. Serb. Chem. Soc., **72**, 119 (2007).
2. W. Hesse, Phenolic Resins, in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim (2002) p. 156.
3. S. D. Alexandratos, Ind. Eng. Chem. Res., **48**, 388 (2009).
4. M. L. Kuo, D. Adams, D. Myers, D. Curry, H. Heemstra, J. L. Smith and Y. Bian, Forest Prod. J., **48(2)**, 71 (1998).
5. L. H. Baekeland, Ind. Eng. Chem., **1(8)**, 545 (1909).

6. O. A. Cruickshank and D. O. Braithwaite, Ind. Eng. Chem., **41**, 472 (1949).
7. A. Gardziella, L. A. Pilato and A. Know, Phenolic Resins: Chemistry, Application, Standardization, Safty and Ecology, New York, Springer (2000) p. 205.
8. H. El-Saied, A. M. A. Nada, A. A. Ibrahem and M. A. Yousef, Angew. Makromolek. Chem., **122**, 169 (1984).
9. R. E. Ysbrandy, R. D. Sanderson and G. F. R. Gerischer, Adhesives from Autohydrolysis Bagasse Lignin, Part-I, Holzforschung, **46(3)**, 249 (1992).
10. T. B. Shah, H. S. Patel, R. B. Dixit and B. C. Dixit, Int. J. Polym. Anal. Charact., **8**, 369 (2003).
11. D. K. Patel and Arun Singh, E-J. Chem., **6(4)**, 1017 (2003).
12. A. Knop and W. Scheib, Chemistry and Application of Phenolic Resins, Spronger Veriag, Berlin, Heidelberg, New York (1979) p. 60.
13. D. T. Masram, K. P. Kariya and N. S. Bhave, Der Pharma Chemica, **3(3)**, 124 (2011).
14. D. T. Masram, K. P. Kariya and N. S. Bhave, Epolymers, **75**, 618 (2007).
15. S. A. Raja, A. Mohamed, A. Riswan, J. Duraisamy and R. B. Abdul, Iranian Polymer J., **18(10)**, 821 (2009).
16. M. M. Jadhao, L. J. Paliwal and N. S. Bhave, J. Appl. Polym. Sci., **96(5)**, 1605 (2005).
17. M. M. Jadhao, L. J. Paliwal and N. S. Bhave, Desalination, **247**, 456 (2009).
18. S. Vasudevan, composites, US8153706 (2012).
19. B. D. Lad, Ph.D. Thesis, Sardar Patel University (1985).
20. J. R. Patel, K. S. Nimavat and K. B. Vyas, J. Chem. Pharm. Res., **3(6)**, 483 (2011).
21. J. R. Patel, K. S. Nimavat and K. B. Vyas, Der Pharma Chemica, **3(4)**, 102 (2011).
22. B. P. Dave and P. J. Shah, Der Chemica Sinica, **3(6)**, 1343 (2012).
23. B. P. Dave, B. C. Patel and P. J. Shah, J. Chem. Pharmaceut. Res., **5(3)**, 112 (2013).