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Synthesis of Azo Dyes Based on α-Naphthol-formaldehyde Oligomer and Their Application on Textile Fibres

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ABSTRACT

This paper reports the synthesis of oligomeric dispersed dyes based on α-naphthol-formaldehyde (NF) oligomer by coupling of various diazonium salt to α-NF oligomer. α-NF oligomer was prepared by the condensation of α-naphthol with formaldehyde in presence of oxalic acid. To achieve suitable oligomer in the present study, several variables namely molar ratios of reactants, temperature, time and catalyst have been optimized in the synthesis. A series of oligomeric azo dyes have been prepared by coupling various diazonium salts of aromatic amines to α-NF oligomer. Their dyeing on polyester, nylon and wool resulted in attractive hues on fibres. In this study of oligomeric azo-NF dyes the dyeing of the fibres completed in short time and most important is that no patches were observed on the fibres, while earlier reported oligomeric dyes form patches on the fibre. They were characterized in terms of their softening points, yield, colour, solubility and UV-visible spectra. Structure-property relationships are discussed and dyeing on polyester (PET), nylon-6,6 and wool are assessed to have excellent fastness properties.

Key Words: azo dyes, polyester, nylon-6,6 and wool, light fastness and washing fastness

INTRODUCTION

Phenolics are known as matrix resins or binding resins for various applications. The main advantages of phenolics are their easy availability and some of their excellent properties [1], such as high thermal stability, excellent acid resistance, high fire retardancy, etc. Naphthols are well-established intermediates for the synthesis of dyes. The uses of naphthol-formaldehyde condensates as coupling components in the formation of azo dyes and pigments have received little attention.

However, the use of phenolic resins as coupling components in the azo dyes has been reported [2–4]. The products are stated to be useful in dyeing of synthetic and natural fibres and also of leather. They

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have stated to have good fastness properties. H.S. Patel has recently studied the oligomeric dyes in this direction [5, 6]. Hence, in continuation of this work the present work comprises some azo dyes based on coupling of diazo salt of various aromatic amines to α-NF condensates.

EXPERIMENTAL

Materials

α-Naphthol used was of analytical grade and crystallized from ethanol prior to use. Formaline (37 %w/v) and oxalic acid used were of laboratory grades. Various aromatic amines were commercially available. The aromatic amines listed in Table 1 were used for the preparation of diazonium salts. They were supplied by Atul Product Ltd., Atul, India. Polyester (PET), Nylon-6,6 and wool fabrics were supplied by Atul Products as well.

Synthesis of α-Naphthol-formaldehyde Oligomer

In a 2 L three-necked, round bottom flask α-naphthol (1 mol), formalin (37 % w/v, 0.5 mol), oxalic acid (2.0 g) and benzene (500 mL) were agitated on magnetic stirrer for 1 h. The contents were then refluxed at 80 °C for 3 h. The reaction mixture was then filtered under reduced pressure (10–15 mm Hg) at 90–100 °C to remove benzene and water. The resulting liquid was washed with a large volume of petroleum ether (40–60 °C). The oligomer α-NF was collected as a thick liquid.

Table 1. Aromatic amines for the preparation of diazonium salt.

No.	Aromatic amines
1	4-Chloro-2-nitroaniline
2	2-Chloro-4-nitroaniline
3	2-Cyano-4-nitroaniline
4	6-Bromo-2-cyano-4-aniline
5	2,6-Dibromo-4-nitroaniline
6	2,6-Dichloro-4-nitroaniline
7	6-Bromo-2,4-dinitroaniline
8	6-Chloro-2,4-dinitroaniline
9	2,6-Dibromo-4-methylaniline
10	2-Methyl-4-nitroaniline
11	2-Methyl-5-nitroaniline
12	2,5-Dichloro-4-methylaniline

Characterization of α-NF Oligomer

Colour: dark brown

Efflux time: t = 102 s

M_n: 620±10

Preparation of Diazonium Salt Solution

The diazotization of various substituted aromatic amines (Table 1) were carried out by the method reported in literature [7].

Synthesis of Oligomeric Azo Dyes

To a cooled (0 °C) alkaline solution (pH=10–10.5) of the oligomer α-NF (0.1 mol), the diazonium salt solution was added dropwise at such a rate that the reaction proceeded at low temperature (exothermic reaction) while maintaining the pH between 10 and 10.5. After the completion of azo coupling then the reaction mixture was stirred for 1 h at 0–5 °C and then acidified to pH 5.5–6.0. The precipitated oligomeric dyes were then filtered, dried, and washed thoroughly with hot water. The dye was soxhlet-extracted with ether to purify from adventitious products presumably due to formation of simple dye from the coupling of diazo compounds with the free naphthols present in oligomer. The oligomeric azo-naphtholic dye was dissolved in DMF and reprecipitated by addition of water. The yield was about 80 %.

Characterization

Carbon, hydrogen and nitrogen elemental analysis of the α-NF oligomer and oligomeric azo dyes was carried out on Carlo Erba, Italy elemental analyzer.

The absence of formaldehyde and naphthol in oligomer was determined according to the methods in the literature [8].

The mean number of azo groups in all the dyes was determined by the method reported in literature [9].

Visible spectra of all the dyes were recorded on a Beckman DK-2A spectrophotometer.

Dyeing of Polyester, Nylon and Wool Fibres with Oligomeric Azo Dyes

Oligomeric azo dispersed dye (40 mg) (Table 2) was taken in a 5 mL of *N,N'*-dimethyl formamide (DMF), along with the same quantity of satamol water, a dispersing agent, 2-3 drops of wetting agent (2% lauryl sulphate solution) and the dispersion of the azo naphtholic dye particle in water was prepared by vibration for 2 h. An exact quantity of dispersion (containing 0.04 g of dye in 100 mL water) was used for dyeing synthetic fibres (2 g weight of each fibres) so as to obtain 2% shade of the dye on fibres. The material to liquor (M:L) ratio was maintained at 1:50.

The fastness properties were determined according to international standards [10].

Details of the oligomeric azo dyes are given in Table 2.

RESULTS AND DISCUSSION

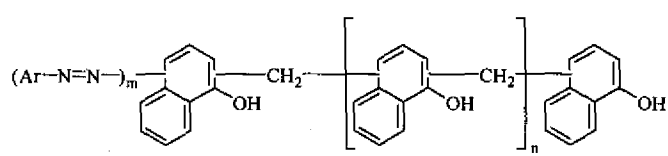
Infusible compounds of the dye studied have been used as pigments rather than dye due to their poor dyeability property [11]. Naphthol-formaldehyde oligomer with high molecular weight offered dye with poor dyeability and therefore more attempts were made to obtain oligomer of low molecular weight from the condensation of α-naphthol with formaldehyde.

Phenol-formaldehyde oligomer can be utilized in various applications and many synthetic methods for their formation are available. The synthesis of naphthol-formaldehyde oligomer has received less attention. To provide suitable oligomer for this present study, a number of variables in the synthesis, i.e., molar ratio of reactants, reaction temperature, catalyst and reaction time were optimized.

The α-NF oligomer was obtained as a viscous liquid, which remained in this form even after 6–7 months of storage in vacuum dessicator. The efflux time at room temperature (~32 °C) for the flow viscosity of α-NF oligomer remained constant during this storage period. The carbon and hydrogen contents for both α-NF oligomer are in agreement with the proposed structure of Scheme I, which also emphasize the probable heterogeneous nature of the products due to reaction proceeding of the ortho position, the more probable para position or a combination of the two.

All the oligomeric azo-NF dyes listed in Table 2 were soluble in solvents as ethanol 1,4-dioxane, DMF and DMSO. As the NF condensates are the mixtures of different molecular NF oligomeric chains and traces of free naphthol, the resulting azo-NF dyes could be non-heterogeneous and, on the premise [11] that simple naphthol based azo dyes are soluble in solvents such as ether, ethanol, 1:4-dioxane, DMF, and DMSO, the oligomeric azo-NF dyes were soxhlet-extracted with ether-ethanol (1:1) to remove both the simpler dyes resulting from traces of any low molecular weight oligomeric azo-NF dye. The values of the nitrogen content of the azo dye indicate that there may be two azo groups present per oligomer chain. This is in agreement with the estimated azo group content of samples in this series of oligomeric azo-NF dyes.

The UV-visible spectra of the azo-NF dyes were recorded in DMF and the value of absorption



α-Naphthol-formaldehyde azo dyes (I)

where, m=2, n=2 or 3 and Ar = corresponding to aromatic amines.

Scheme I

Table 2. Characterization of oligomeric azo-α-NF dyes.

Oligomeric azo-α-NF dyes	Colour on PET	Softening point (°C)	C (%) Found (Calc.)	H (%) Found (Calc.)	Found N (%)	Mean number of Azo	Yield (%)	$\bar{M}_n$ by VPO	λ_{max} (nm)
AN-31	orange	119–21	66.80 (67.0)	3.66 (3.64)	8.4	1.95	77	988	574.5
AN-32	brown	122–24	66.92 (67.0)	3.65 (3.64)	8.5	1.91	79	985	656.5
AN-33	brown	115–17	70.2 (70.15)	3.70 (3.69)	11.5	1.98	80	975	633.5
AN-34	light brown	112–14	60.60 (60.58)	3.10 (3.01)	9.9	1.94	75	1129	643.5
AN-35	orange	130–32	53.28 (53.27)	2.76 (2.74)	6.8	1.90	74	1239	652.5
AN-36	redish brown	123–25	62.40 (62.32)	3.24 (3.21)	7.9	1.99	83	1059	650
AN-37	dark brown	120–22	56.95 (56.89)	2.95 (2.93)	10.1	1.92	79	1112	635
AN-38	redish brown	111–12	61.70 (61.68)	3.18 (3.177)	11.0	1.97	84	1018	635
AN-39	orange	124–26	57.99 (57.92)	3.40 (3.387)	4.8	1.96	82	1181	452.5
AN-40	brown	121–23	72.18 (72.00)	4.45 (4.42)	8.8	1.9	79	950	544
AN-41	brown	119–21	71.95 (72.00)	4.41 (4.42)	8.79	1.98	88	956	515
AN-42	yellow	114–16	62.35 (62.32)	3.25 (3.22)	7.8	2.0	89	1055	642.5

	Dyeing on polyester		Dyeing on nylon		Dyeing on wool	
	Light fastness	Washing fastness	Light fastness	Washing fastness	Light fastness	Washing fastness
AN-31	2–3	4–5	2	3	2–3	4
AN-32	3–4	5	2–3	3–4	3	4–5
AN-33	2–3	4	3	4	2	4–5
AN-34	3	4–5	2–3	4	2–3	3–4
AN-35	2–3	4	2–3	3–4	3	4–5
AN-36	3	3–4	3–4	4–5	3	4–5
AN-37	2	3	2–3	4–5	3–4	5
AN-38	2–3	3–4	3	5	3	4
AN-39	3	4–5	2	3	2–3	3–4
AN-40	2	3	3	5	3–4	4
AN-41	2–3	4–5	2–3	4–5	4	5
AN-42	3	4	3	4–5	3–4	4–5

maximum (λ_{max}) is shown in Table 2. It is apparent that the wavelength of maximum absorption is related to the azo groups in the compounds and it is observed within the region 450–650 nm. Variations in λ_{max} being attributed to the nature of various substituted aromatic amines used as diazo component. The thermal stability of the azo-NF dyes was also assessed in terms of the loss in weight at different temperatures at a constant heating rate of 10 °C/min in air. This showed that the azo-NF dye began to decompose at around 190 °C with weight loss being complete at around 220 °C depending on the structural variations.

The oligomeric azo-NF dyes were dyed on polyester, nylon and wool fibres at 2% shade and gave brown, yellow, orange and red shades (Table 2). They resulted in variety of attractive hues on the dyed fibres. The results of percentage dye-bath exhaustion and fixation of all dyes varied from 70 to 98% depending upon the nature of oligomeric dye, while it was observed that in simple aryl azo (naphthol) [12] dyes the exhaustion (or fixation) varied from 60 to 70%.

The fastness of the oligomeric azo-NF dyes is shown in Table 2. The light fastness of the azo-α-NF azo dyes on polyester, nylon and wool fibre varied from moderate to good on polyester, good to very good on nylon and moderate to good on wool. The majority of the dyes are having higher ratings. The washing fastness (neutral detergents) varied from moderate to very good for all fibres. Compared with simpler azo-naphthol dye [10], the dyeing produced from the oligomeric azo-NF dyes had more moderate light fastness but slightly higher washing fastness. It is of interest to note that most of the polymeric dye previously reported [12], when dyed on various textiles, gave somewhat unleveled coloration's with the azo-NF dyes. Described in the present work and particularly when the dyeing was carried out for relatively short period of time (1.5 h on polyester, 1 h on nylon and 1 h on wool) and at low temperatures, the dyeing levels were obtained.

CONCLUSION

The key focus of the dyeing performance is that the most of these dyes are fixed almost completely on the fibre from dye-bath. Thus the use of such dyes can decrease water pollution. Today most of the textile industries have their effluent water pollution problem due to high exhaustion of commercial dyes. It is time to utilize the dye with high fixation or to treat the effluent water to complete decolouration and with no toxicity. The first criteria may be more useful economically as well as protecting the environment.

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