

Synthesis and Dyeing Performance of Some Novel Heterocyclic Azo Disperse Dyes

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A síntese de novos azocorantes heterocíclicos derivados de 5-acetil-2-amino-4-metiltiazol (1) utilizando-se de vários *N*-alquil derivados da anilina (2a-e) e suas performances como corantes dispersos foram avaliadas em tecidos de poliéster e nylon. As propriedades espectrais desses corantes foram determinadas. Os tecidos tingidos mostraram fixação moderada a boa na presença de luz, boa estabilidade à fricção, transpiração, lavagem e excelente estabilidade à sublimação. Esses corantes forneceram tonalidades de cor variando entre laranja e vermelho com boa profundidade e distribuição nos tecidos.

The synthesis of some novel heterocyclic azo disperse dyes derived from 5-acetyl-2-amino-4-methylthiazole (1) using various *N*-alkyl derivatives of aniline (2a-e) and their dyeing performance as disperse dyes have been assessed on polyester and nylon fabrics. The spectral properties of these dyes were measured. The dyed fabrics show moderate to good light fastness, very good rubbing, perspiration, washing fastness and excellent sublimation fastness. These dyes have been found to give bright orange-red colour hues with very good depth and levelness on fabrics. The dye bath exhaustion on fabrics has been found to be very good.

Keywords: 5-acetyl-2-amino-4-methylthiazole, disperse dyes, dyeing, exhaustion, fastness

Introduction

Heterocyclic diazo components have been used extensively in the preparation of disperse dyes with outstanding dischargeability on cellulose acetate. These dyes are characterised also by having generally excellent brightness and high extinction coefficients, relative to azo dyes derived from substituted anilines. These properties encouraged work on dyes prepared from heterocyclic diazo components suitable for dyeing synthetic fabrics.

Early interest in heterocyclic diazo components was stimulated by the need for blue disperse dyes with improved dischargeability and gas fastness (oxide of nitrogen) for cellulose acetate. Before 1950, almost all the disperse dyes used were prepared from the anthraquinone class and had the limitations of poor dischargeability and sensitivity to oxides of nitrogen. Red and blue azo dyes with good dischargeability for use in printing were developed. Investigation of the use of heterocyclic diazo components was stimulated by the discovery of Dickey JB of Eastman Kodak in 1950. In 1953, they prepared bright blue heterocyclic

azo disperse dyes¹ from 2-amino-5-nitrothiazole with adequate light fastness combined with excellent dischargeability, gas fastness and dyeability on cellulose acetate. The commercial success of such bright blue azo disperse dyes for cellulose acetate showing considerable interest in this class of dyes. With the exception of the 5-nitro derivatives for discharge printing of dyeing cellulose acetate fabrics, 2-thiazolylazo dyes have so far achieved only secondary importance as bright blue dyes for polyester. Greenish blue dyes can be prepared by choosing a coupler containing electron donating groups such as 5-acetamido-2-methoxyaniline derivatives. Additional early work on the 2-thiazolylazo dyes resulted in violet dyes from 2-amino-5-alkylsulphonylthiazole² and even more bathochromic dyes from 2-amino-4-alkylsulphonyl-5-nitrothiazole³. The pronounced bathochromic shift of the 5-nitro-2-thiazolylazo dyes, compared with the red azo dyes derived from the corresponding nitroaniline⁴, was of great interest. Early dyes showed moderate light fastness on cellulose acetate and polyesters, and light fastness on polyamides was very poor. Also, on polyesters the dyes had poor sublimation fastness for the thermofixation method of dyeing and showed loss of colour under high temperature exhaust dyeing conditions, particularly at high pH values. Dyes with increased light

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fastness and/or sublimation fastness were prepared from aniline type coupling components containing one or more *N*-alkyl groups substituted with groups such as cyano⁵, alkoxy⁶, pyridinium⁷ and sulphato⁸ were used as coupling components.

During the last ten years, the level of interest as indicated by the patent literature has grown in the field of thiazolylazo disperse dyes⁹⁻¹². There has been a considerable growth in the volume of data reporting outside of patent literature¹³⁻²⁰. It seems that no report is available on the use of 5-acetyl-2-amino-4-methylthiazole in the synthesis of disperse dyes by coupling with various *N*-alkylanilines. Hence, it was thought worthwhile to synthesise a series of disperse dyes from 5-acetyl-2-amino-4-methylthiazole (**1**) using various substituted *N*-alkyl-*N*-(2-hydroxyethyl) aniline derivatives **2a-e** as coupling components. The resulting dyes were applied to polyester and nylon fabrics and their dyeing performance has been studied.

Experimental

General

All of the chemicals and various coupling components used were of commercial grade and were further purified by recrystallisation and redistilled before use. The solvents used were spectroscopic grade. Melting points were determined by open capillary method. The visible absorption spectra were measured in a Carl Zeiss UV/VIS Specord spectrometer. The elemental analysis were carried out on a Carlo Erba Elemental Analyser 1108. Infrared spectra were recorded on a Perkin-

Elmer model 983 spectrometer scanning between 4,000 to 400 cm^{-1} using a KBr pellets. Purification of the products was carried out by TLC (1 mm thickness glass plates 20 x 5 cm, using suspension of silica gel G in CHCl_3). The diazo component 5-acetyl-2-amino-4-methylthiazole (**1**) was prepared according to the literature²¹. Fastness to light, sublimation and perspiration were assessed in accordance with BS:1006-1978. The rubbing fastness test was carried out with a crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS:765-1979. The details of the method of colour fastness tests were described in the literature²². The dyeing of polyester and nylon fabrics were carried out according to the literature²². The percentage dyebath exhaustion of the dyed fabrics was determined according to the known method²³.

Synthesis of 5-acetyl-2-[4-[*N*-(2-hydroxyethyl)amino] phenylazo]- 4-methylthiazole (**1a**)

Dry NaNO_2 (1.38 g, 0.02 mol) was slowly added with stirring to concentrated H_2SO_4 1.1 cm^3 with stirring while allowing the temperature to raise to 65 °C. The solution was then cooled to 5 °C and 20 cm^3 of a mixture of AcOH/propionic acid (17:3 v/v) was added dropwise with stirring, allowing the temperature to raise to 15 °C. The reaction mixture was then cooled to 0-5 °C, and the diazo component 5-acetyl-2-amino-4-methylthiazole (**1**, 3.12 g, 0.02 mol) was added portionwise and stirring was continued at this temperature for 2 h. The excess nitrous acid (the presence tested by starch-iodide paper) was decomposed with the required amount of urea. The clear diazonium salt

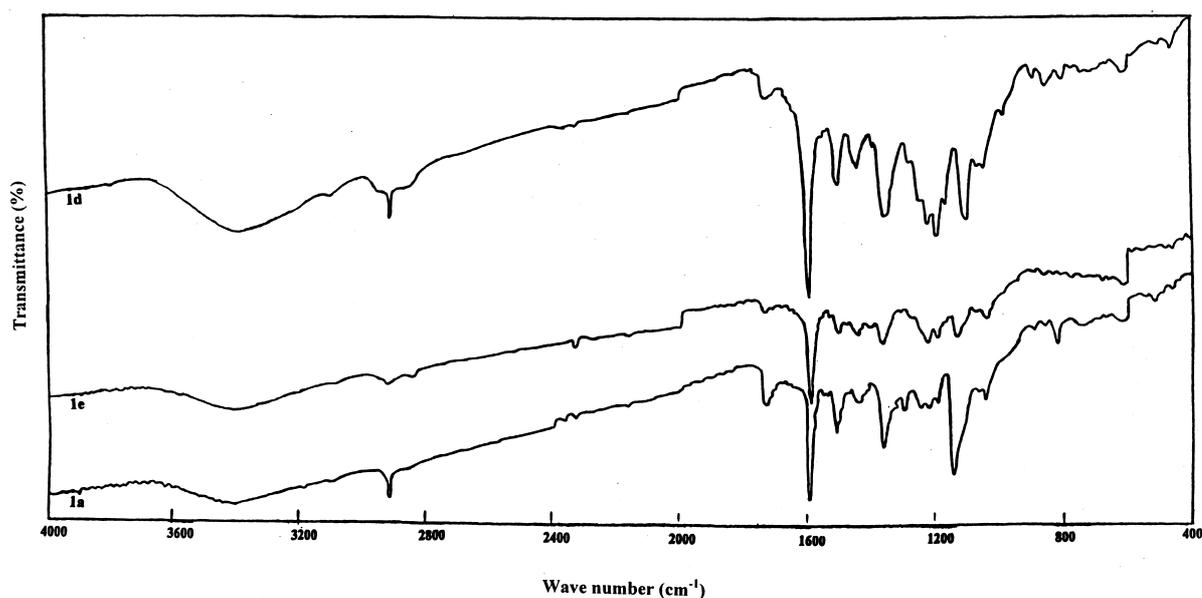
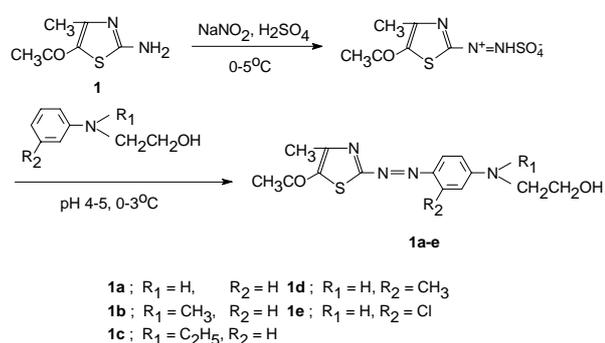


Figure 1.

solution thus obtained was used immediately in the coupling reaction (see Scheme 1). Now *N*-(2-hydroxyethyl)aniline (**2a**, 2.74 g, 0.02 mol), was dissolved in 10 cm³ of AcOH, then cooled in an ice-bath at a 0 °C. The diazonium solution previously prepared was added dropwise over 1 h with vigorous stirring at 0-3 °C. The reaction mixture was stirred for further 2 h at 0-5 °C, then 10 % AcONa solution was dropped in slowly until the pH became 4-5. The product was then filtered off, washed with water until acid-free, dried at 50 °C in an oven to give azo dye **1a**, which was recrystallised three times from EtOH (4.98 g, 82 %). The mp 208-209 °C (EtOH).



Scheme 1.

The following dyes **1b-e** were prepared in similar manner using various coupling components **2b-e**.

1b: 5-acetyl-2-[4-[*N*-methyl-*N*-(2-hydroxyethyl)amino]phenylazo]-4-methylthiazole.

1c: 5-acetyl-2-[4-[*N*-ethyl-*N*-(2-hydroxyethyl)amino]phenylazo]-4-methylthiazole.

1d: 5-acetyl-2-[4-[*N*-(2-hydroxyethyl)amino]-2-methylphenylazo]-4-methylthiazole.

1e: 5-acetyl-2-[4-[*N*-(2-hydroxyethyl)amino]-2-chlorophenylazo]-4-methylthiazole.

The characterisation data of dyes **1a-e** are given in Table 1.

Results and Discussion

Preparation of Dyes

5-Acetyl-2-amino-4-methylthiazole (**1**) was diazotised satisfactorily at 0-5 °C by nitrosylsulphuric acid in AcOH. In order to determine the end point of diazotisation, it was found useful to check for the presence of unreacted diazo component on TLC by sampling the diazotisation mixture. Thus, when unreacted diazo component no longer persisted on TLC, the diazotisation was ended. The diazonium salt solution was used immediately since this decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the resulting diazonium salt continuously to the solution of coupling component in acetic acid. Coupling was usually accompanied by some evidence of decomposition; however 80-85 % yield of dye were usually obtained by careful addition of the diazonium salt solution at 0-3 °C to a solution of the coupling component in an acetic acid. To complete coupling, particularly for reactions using nitrosylsulphuric acid in the previous diazotisation, the pH of the reaction mixture was adjusted to approximately 4-5. Thus, an appropriate amount of 10 % sodium acetate solution was slowly added below 5 °C.

Physical properties of dyes

The purity of all the dyes was checked by TLC using methanol/water/acetic acid (12:3:7 v/v) as the solvent system. When adsorbed on silica chromatography plates, the dyes produced orange-red colours. All the recrystallised dyes exhibited well-defined melting points characteristic of pure compounds but it would be unwise to attempt to explain in detail their relative values, because of the complex dependence of the melting points on a number of factors (*e.g.* polarity, size, geometry, interaction etc).

Table 1. Characterisation data for dyes **1a-e**

Dye no.	Substituents		Yield (%)	mp (EtOH) (°C)	Molecular formula (Mol. Wt.)	Elemental analysis, %			λ_{\max} /nm (DMF)	log ϵ	R _f
	R ₁	R ₂				Calc.	(Found)	N			
1a	H	H	82	208-209	C ₁₄ H ₁₆ N ₄ O ₂ S (304)	55.26 (55,10)	5.26 (5,08)	18.42 (18,28)	498	4.13	0.81
1b	CH ₃	H	85	215-216	C ₁₅ H ₁₈ N ₄ O ₂ S (318)	56.60 (56,48)	5.66 (5,51)	17.61 (17,52)	505	4.08	0.79
1c	C ₂ H ₅	H	81	192-194	C ₁₆ H ₂₀ N ₄ O ₂ S (332)	57.83 (57,75)	6.02 (5,91)	16.86 (16,71)	508	4.82	0.74
1d	H	CH ₃	80	186-188	C ₁₅ H ₁₈ N ₄ O ₂ S (318)	56.60 (56,45)	5.66 (5,60)	17.61 (17,52)	510	4.83	0.80
1e	H	Cl	84	198-199	C ₁₄ H ₁₅ N ₄ O ₂ SCl (338.5)	49.63 (49,49)	4.43 (4,32)	16.54 (16,46)	495	4.56	0.92

Table 2. Colour fastness properties and exhaustion of dyes **1a-e** on polyester fabric

Dye no.	Colour hue on polyester	Exhaustion (%)	Light fastness	Wash fastness	Rubbing fastness		Perspiration fastness		Sublimation fastness
					Dry	Wet	Acid	Alkaline	
1a	Orange	78	3-4	4-5	4-5	4-5	4	4-5	5
1b	Red	81	3-4	4	4-5	4-5	4	4	5
1c	Reddish orange	80	3-4	4	4-5	4-5	4-5	4-5	5
1d	Dark red	82	4-5	4-3	4-5	4-5	4-5	4	5
1e	Red	78	4-5	4-5	4-5	4-5	4-5	4-5	5

Table 3. Colour fastness properties and exhaustion of dyes **1a-e** on nylon fabric

Dye no.	Colour hue on nylon	Exhaustion (%)	Light fastness	Wash fastness	Rubbing fastness		Perspiration fastness		Sublimation fastness
					Dry	Wet	Acid	Alkaline	
1a	Reddish orange	81	4	4-5	4-5	4-5	4-5	4-5	5
1b	Deep red	85	4	4-5	4-5	4-5	4-5	4-5	5
1c	Red	82	4	4-5	4-5	4-5	4	4-5	5
1d	Bright red	86	4	4	4-5	4	4-5	4-5	5
1e	Reddish orange	83	4	4-5	4	4	4	4-5	5

Spectral properties of dyes

Absorption maxima of dyes **1a-e** were recorded in DMF solution and are shown in Table 1. As far as absorption maxima are concerned, λ_{\max} values are directly proportional to the electronic power of the substituents in the coupled ring system. The value of the logarithm of molar extinction coefficient ($\log \epsilon$) of the dyes were in the range of 4.13-4.83, consistent with their high intensity of absorption. The introduction of electron-donating or electron-attracting groups at suitable positions in the coupled ring affect the absorption characteristics of the dyes. As can be seen from the data in Table 1, the bathochromic shift can be obtained by enhancing the electron donor properties of the coupled ring, *e.g.* by introducing a methyl group *ortho* to the azo group, as in dye **1d**. This gave considerable shift of 15 nm relative to dye **1e**. Thus, electron displacement can be enhanced by electron donating substituents on the coupled ring. The resulting increase polarisability should result in bathochromism. An additional small bathochromic shift of 3 nm also resulted from increasing the alkyl chain length of dye **1c**; for example, when replacing the methyl group by ethyl group, the resulting dye **1c** absorbed at 508 nm.

Infrared spectra of dyes

The infrared spectra of dyes **1a**, **1d** and **1e** are shown in Figure 1. The characteristic band at 3400-3420 cm^{-1} indicates the N-H and O-H stretching. The strong bands observed at 1600-1610 cm^{-1} indicate stretching vibration of the C=O. The bands at 820-830 cm^{-1} and 1320-1360 cm^{-1} correspond to *para* disubstituted ring and -C-N-C stretching, respectively. The azo group is confirmed at 1515-1520 cm^{-1} . The band at 1450-1460 cm^{-1} is due

to the alkyl chain. The methyl group is confirmed at 2895-2900 cm^{-1} .

Dyeing properties of dyes

The disperse dyes **1a-e** were applied at 2 % depth on polyester and nylon fabrics. Their dyeing properties are given in Tables 2 and 3. Change for these dyes are gave red hues with good levelness, brightness and depth on the fabrics. The variation in the hues of the dyed fabric result from both the nature and position of the substituent present on the coupler ring. The dyeings showed good to very good fastness to light, washing, rubbing and perspiration and excellent fastness to sublimation. A remarkable degree of levelness after washing indicates good penetration and affinity of these dyes to the fabrics.

Conclusion

The diazo component 5-acetyl-2-amino-4-methyl-thiazole (**1**) possessed sufficiently basicity to warrant the employment of various condition for diazotisation. It was found that nitrosylsulphuric acid was needed for satisfactory diazotisation. A series of azo disperse dyes containing various *N*-alkyl-*N*-(2-hydroxyethyl)aniline coupling moiety have been synthesised by conventional method and their colour properties examined in solution, and applied to polyester and nylon fabrics.

These dyes derived from **1** provided reddish orange rather than blue hues on polyester and nylon fabrics. These dyes, however, are noteworthy in its excellent affinity and intensity of colour. Outstanding characteristics of these dyes are that they give deep and bright hues with level dyeing. The bright hue might be attributed to the greater planarity of the thiazole dyes, because of the lower steric interaction of a five membered ring.

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References

1. Dickey, J. B.; Towne, E. B. *US Patent 2.659.719* **1953**.
2. Merian, E. *US Patent 3.007.915* **1961**.
3. Towne, E. B.; Dickey, J. B.; Bloom, M. S. *US Patent 2.839.523* **1958**.
4. Dickey, J. B.; Towne, E. B.; Bloom, M. S.; Moore, W. H.; Hill, H. M.; Heynemann, H.; Hedberg, D. G.; Sievers, D. C.; Otis, M. V. *J. Org. Chem.* **1959**, *24*, 187.
5. Gosei Senryo Gijupsu Kenktu Kumiai, *Jpn Kokai Tokkyo Koho JP 59.215.355* **1983**.
6. Mitsubishi Chemical Industries Co Ltd, *Jpn Kokai Tokkyo Koho 80.133.458* **1980**.
7. Parton, B. *British UK Patent 2.028.856* **1981**.
8. Sumitomo Chemical Co Ltd, *Jpn Kokai tokkyo Koho JP 57.161.653* **1982**.
9. Nakamura, Y.; Murata, J. *Jpn Kokai Koho 5.155.870* **1993**.
10. Hahn, E.; Wiesenfeldt, M.; Reichelt, H.; Gruettner, S. *German Offen 4.120.362* **1993**.
11. Sens, R.; Eitzbach, K. -H. *German Offen 4.426.023* **1996**.
12. Tsien, H.; Chu, K. -P.; Chang, H. *US Patent 5.652.344* **1997**.
13. Bello, K. A.; Martins, C. M. O. A.; Adamu, I. K. *Colourage* **1995**, *42*, 29.
14. Desai, K. R.; Modi, B. R.; Mistry, B. D. *J. Indian Chem. Soc.* **1995**, *72*, 141.
15. Bello, K. A. *Dyes Pigm.* **1995**, *27*, 45.
16. Griffiths, J.; Riepl, C. J. *Chem. Commun.* **1998**, *13*, 1349.
17. Hallas, G.; Choi, J. -H. *Dyes Pigm.* **1999**, *42*, 249.
18. Chikhalia, K. H.; Desai, K. R. *J. Inst. Chem. (India)* **1998**, *70*, 142.
19. Rangnekar, D. W.; Kanetkar, V. R.; Shankarling, G. S.; Malanker, J. V. *J. Indian Counc. Chem.* **1998**, *15*, 28.
20. Towns, A. D. *Dyes Pigm.* **1999**, *42*, 3.
21. Kochergin, P. M. *Zhur. Obshchei. Khim.* **1956**, *26*, 2897.
22. Maradiya, H.R.; Patel, V.S. *High Perform. Polym.* **2000**, *12*, 335.
23. Maradiya, H.R.; Patel, V.S. *Bull. Chem. Technol. Macedonia* (in press).

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