

Dyeing Performance of Disperse Dyes Based on 2-aminothiazole for Cellulose Triacetate and Nylon Fibers

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(Received December 28, 2001; Revised March 9, 2002; Accepted March 16, 2002)

Abstract: A series of monoazo disperse dyes based on 2-amino-4-phenylthiazole was prepared using various *N,N*-dialkylaniline derivatives as the coupling component. The dyes were characterized by IR spectral studies, visible absorption spectroscopy and elemental analysis. The dyeing performance of these dyes was assessed on cellulose triacetate and nylon fibers. These dyes were found to give a wide range of colour shades varying from bright red to royal blue with very good depth, brightness and levelness on fibers. The dyed fibers showed good to very good light fastness and very good to excellent fastness to washing, perspiration, rubbing and sublimation. The dyebath exhaustion and fixation on the fibers were found to be very good.

Keywords: 2-amino-4-phenylthiazole, *N,N*-dialkylaniline, Cellulose triacetate, Disperse dyes, Dyeing, Fastness, Nylon

Introduction

The discovery of the fusion reaction between *p*-toluidine and sulphur to give dehydrothio-*p*-toluidine in 1887 constitutes the beginning of thiazole dyestuff technology. Colour Index described various basic, direct, vat, and disperse dyes wherein thiazole nucleus occurs[1].

Early interest in heterocyclic diazo components was stimulated by the need for blue disperse dyes with improved dischargeability and gas fastness (oxide of nitrogen). 2-aminothiazole diazo components have long been used in the manufacture of disperse dyes[2]. A major advance was made by research group of Dickey of Eastman Kodak in the 1950s in heterocyclic azo dyes and resulted in a classic paper on thiazole-based disperse dyes[3]. In 1953, they prepared bright blue heterocyclic azo disperse dyes[4] from 2-amino-5-nitrothiazole with adequate light fastness combined with excellent dischargeability, gas fastness, and dyeability on cellulose acetate. The commercial successes 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 fibers, 2-thiazolyazo 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-thiazolyazo dyes resulted in violet dyes from 2-amino-4-trifluoromethyl-5-carbalkoxythiazole[5], 2-amino-4-alkylsulphonylthiazole[6], 2-amino-4-methyl-5-cyanothiazole[7] and even more bathochromic dyes from 2-amino-4-alkylsulphonyl-5-nitrothiazole[8]. The commercial success of dyes for cellulose triacetate, which were derived

from 2-amino-5-nitrothiazole, resulted in considerable interest in this class of dyes. Early dyes showed moderate light fastness on cellulose triacetate and polyesters, and light fastness on polyamides was very poor. Dyes with increased light fastness and/or sublimation fastness were prepared from aniline type coupling components containing one or more *N*-alkyl groups substituted with cyano[9], amyl-carbonyloxy[10], alkoxy[11], sulphato[12], diphenylamine [13], pyridinium[14] dicarboximide[15], 1-naphthylamine[16], and *N*-alkyl-1,2,3,4-tetrahydroquinolines[17] were used as coupling components. These coupler types have the advantages of providing dyes, which have a neutral or green cast when exposed to artificial light, whereas the corresponding dyes from *N*-alkylaniline couplers have an extremely red cast. The improved fastness to light and sublimation provided by 3-acylaminoaniline types coupling components was not overlooked and dyes were patented[18-21].

During the last ten years, the level of interest as indicated by the patent literature has grown in the field of thiazolyazo disperse dyes[22-25]. There has been a considerable growth in the volume of data reporting outside of patent literature [26-36]. Earlier we had studied the disperse dyes based on 2-aminothiazole derivatives[37-41]. The encouraging results prompted to extend the study on thiazole moiety. Hence, a series of monoazo dyes was synthesized and tested as disperse dyes for cellulose triacetate and nylon fibers. In addition to the characterization of the dyes, an evaluation of their technical properties and a colour assessment was performed.

Experimental

Materials and Methods

All of the chemicals used in synthesis of dye **3** were of

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commercial grade and were further purified by crystallization and distillation. All solvents used were either of analytical grade or redistilled commercial grade. Melting points were determined by open capillary method. The visible absorption spectra were measured in a Carl Zeiss UV/VIS Specord spectrometer. Elemental analysis were carried out on a Carlo Erba Elemental Analyser 1108. Infrared spectra were recorded in KBr pellets, on a Perkin-Elmer model 983 spectrophotometer.

Preparation of 2-amino-4-phenylthiazole 1

The title compound was synthesized by the method reported in the literature[42].

Preparation of Dye 3

Diazotization of 2-amino-4-phenylthiazole 1 was carried out according to the method reported in the literature[43].

General Coupling Procedure

The *N,N*-dialkylaniline (0.02 mol) was dissolved in glacial acetic acid (10 ml) and water (5 ml) together with sodium acetate (5 g). This solution was cooled in an ice-bath 0-5°C

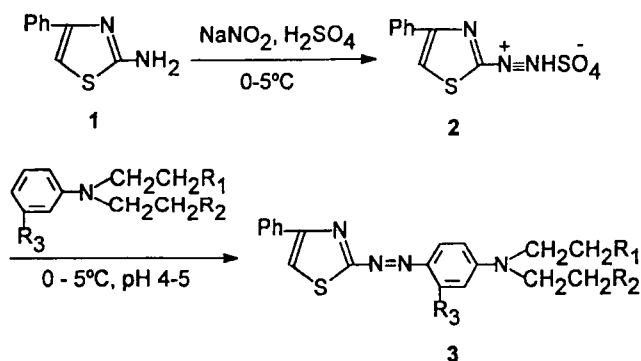
and the diazonium solution of 2 previously prepared was added dropwise over 30 minutes with vigorous stirring. The pH was maintained between 4 and 5 by simultaneous addition of 10% sodium acetate solution. Stirring was continued for 2 hours, allowing the temperature to rise to ambient. The dye was then filtered off, washed with warm and cold water until acid-free, dried at 50°C in an oven to give azo dye 3. Recrystallized from ethanol provided the pure dye (Scheme 1). The characterization data are given in Tables 1 and 2.

Dyeing Procedure

A convenient laboratory method for dyeing cellulose triacetate and nylon fibers is to employ high temperature (90-135°C) and high pressure (24-30 psi). The dyeing of cellulose triacetate and nylon fibers was carried out at 90°C for 1 hour. The detail of the dyeing method are mentioned in the literature[43].

Colour Fastness Test

The fastness to light, sublimation and perspiration was assessed in accordance with BS:1006-1978. The rubbing



Scheme 1. Synthetic route of dyes 3.

Table 2. Characterization data for dye 3

Dye no.	Substituents			Melting point (°C)	Yield (%)	R _f value
	R ₁	R ₂	R ₃			
3a	OH	OH	H	118-120	81	0.86
3b	OAc	OAc	H	125-127	86	0.78
3c	OH	OH	CH ₃	116-118	88	0.87
3d	OH	OH	Cl	135-136	74	0.94
3e	OH	OH	NHAc	109-110	90	0.85
3f	OAc	OAc	CH ₃	107-108	82	0.80
3g	Cl	Cl	H	137-138	82	0.85
3h	CN	CN	H	162-163	80	0.78
3i	CN	CN	CH ₃	135-137	86	0.90
3j	CN	CN	Cl	115-116	84	0.87

Table 1. Absorption maxima, intensities, exhaustion, and fixation of dye 3

Dye no.	Substituents			Absorption maxima (λ _{max})		log ε (DMF)	Cellulose triacetate		Nylon	
	R ₁	R ₂	R ₃	λ _{max} /nm (DMF)	λ _{max} /nm (conc. H ₂ SO ₄)		%E	%F	%E	%F
3a	OH	OH	H	520	587	4.47	75	90	72	91
3b	OAc	OAc	H	505	475	4.81	75	85	70	88
3c	OH	OH	CH ₃	690	480	4.86	80	90	79	90
3d	OH	OH	Cl	515	485	4.52	76	87	74	89
3e	OH	OH	NHAc	650	470	5.18	72	89	82	90
3f	OAc	OAc	CH ₃	515	500	4.98	77	84	75	86
3g	Cl	Cl	H	515	505	4.26	83	89	83	89
3h	CN	CN	H	510	505	4.87	77	86	75	89
3i	CN	CN	CH ₃	520	470	4.36	81	89	79	90
3j	CN	CN	Cl	500	490	4.76	83	90	83	92

fastness test was carried out using crockmeter (Atlas) in accordance with AATCC-1961 and the wash fastness test in accordance with IS:765-1979. The details of various fastness tests are mentioned in the literature[43].

Determination of the Percentage Exhaustion and Fixation (Dissolution Method)

The dyebath exhaustion percentage (%E) and fixation percentage (%F) of the dyed fibers were determined according to the known method[43].

Results and Discussion

Preparation of Thiazole Dye 3

4-substituted thiazoles are prepared by reacting the appropriate ketone with thiourea in presence of bromine. Acetophenone was reacted overnight on a steam bath with thiourea in equimolar ratio in the presence of one mole bromine gave compound 1[42]. The thiazole derivative obtained from the reaction mixture agreed in elemental analysis and physical properties with those reported in the literature[42]. For diazo component 1, an anhydrous diazotization can only achieved using nitrosylsulphuric acid obtained from dry solid sodium nitrite and concentrated sulphuric acid. Thus, the thiazole intermediate 1 was diazotized satisfactorily at 0-5°C by addition of nitrosylsulphuric acid to a suspension of the amine in a mixture of acetic acid and propionic acid. All products required recrystallization to eliminate contaminants arising from diazo decomposition and/or by-products present in the industrial sourced coupling components used. In addition, removal of undiazotized amine necessary in dyes. In order to determine the end point of diazotization, it was found useful to check for the presence of unreacted diazo component on thin layer chromatography (T.L.C.) by sampling the diazotization mixture and extracting with ethyl acetate. Thus, when unreacted diazo component no longer persisted on T.L.C., the diazotization was ended. All dyes were purified by recrystallization from ethanol. Purity of the dyes

was confirmed by T.L.C. and satisfactory elemental analysis (Table 3). The diazonium salt solution 2 was generally used within a few hours since it decomposed on standing, even when cold. Subsequent coupling reactions took place readily on adding the resulting diazonium salt solution 2 continuously to the solution of coupling component in acetic acid. Coupling was usually accompanied by some evidence of decomposition; however, by careful addition of the diazonium salt solution 2 at 0-5°C to a solution of the coupling component in an aqueous acetic acid, high yields (74-90%) of the dye were usually obtained. To complete coupling, particularly for reactions using nitrosylsulphuric acid for the diazotization, the pH of the reaction mixture was eventually adjusted to approximately 4-5. Thus, an appropriate amount of 10% sodium acetate solution was slowly added below 5°C.

Physical Properties of Dye 3

All the solid dyes are dark reddish-brown in colour. The purity of the dyes was checked by T.L.C. using methanol: water:acetic acid (12:3:7) as the solvent system. When adsorbed onto silica chromatography plates, each dyes produced a reddish-brown colour spot. All the recrystallized dyes exhibited well-defined melting points characteristic of pure compounds. It would be premature to attempt to explain in detail their relative values because of the complex dependence of the melting point on a number of factors (e.g., polarity, geometry, size, and molecular interaction).

Visible Absorption Spectroscopic Properties of Dye 3

The visible absorption spectroscopic properties of dye 3 were recorded in DMF and concentrated sulphuric acid solution, and are presented in Table 1. The value of the logarithm of molar extinction coefficient ($\log \epsilon$) of the dye 3 was in the range of 4.26-5.18, consistent with their very high intensity of absorption. One cause of the increased intensity might be attributed to the greater planarity of the thiazole dyes, because of the lower steric interaction of a five-membered thiazole ring. The colour of the dye 3 is affected

Table 3. Elemental analysis of dye 3

Dye no.	Substituents			Molecular formula	Molecular weight	C%		H%		N%	
	R ₁	R ₂	R ₃			Require	found	Require	found	Require	found
3a	OH	OH	H	C ₁₉ H ₂₀ N ₄ O ₂ S	368	61.95	61.69	5.43	5.23	15.21	15.08
3b	OAc	OAc	H	C ₂₃ H ₂₄ N ₄ O ₄ S	452	61.06	60.88	5.30	5.10	12.38	12.20
3c	OH	OH	CH ₃	C ₂₀ H ₂₂ N ₄ O ₂ S	382	62.82	62.65	5.75	5.60	14.65	14.50
3d	OH	OH	Cl	C ₁₇ H ₁₅ N ₄ O ₂ SCl	358.5	56.90	56.71	4.18	4.01	15.62	15.76
3e	OH	OH	NHAc	C ₂₁ H ₂₃ N ₅ O ₃ S	425	59.29	59.06	5.41	5.28	16.47	16.28
3f	OAc	OAc	CH ₃	C ₂₄ H ₂₆ N ₄ O ₄ S	466	61.80	61.52	5.57	5.41	12.01	11.72
3g	Cl	Cl	H	C ₁₉ H ₁₈ N ₄ SCl ₂	405	56.29	56.10	4.44	4.20	13.82	13.58
3h	CN	CN	H	C ₂₁ H ₁₈ N ₆ S	386	65.28	65.09	4.86	4.48	21.76	21.43
3i	CN	CN	CH ₃	C ₂₂ H ₂₀ N ₆ S	400	66.00	65.76	5.00	4.81	21.00	20.76
3j	CN	CN	Cl	C ₂₁ H ₁₇ N ₆ SCl	420.5	59.92	59.65	4.04	3.80	19.97	19.70

by substituents in the coupler constituent. The bathochromism of the dyes is an inherent property of the thiazole system itself; the bathochromism does not derive from the substituent groups. However, the greater polarizability of the thiazole system (relative to the benzene system), in addition to affecting a general bathochromism in dyes. As can be seen from the data in Table 1, additional bathochromic shifts can also be obtained by enhancing the electron donor properties of the coupler ring.

The colour properties of the dyeing corresponded with absorption maxima of the dyes in solution, the positions of which were consistent with expectations. For example, bathochromic shifts were observed on replacing terminal CN group in the *N*-alkyl chains with hydroxyl functions, or locating an electron releasing group meta to the terminal amino function. When replacing the Cl and CN groups in dye **3g** and **3h** by the OH group, the resulting dye **3a** is absorbed at 520 nm. The bathochromic shift is due to an increase in the donor strength of the coupler ring. Similarly, introducing a methyl group meta to the terminal amino function in dyes **3c**, **3f**, and **3i** produced bathochromic shift of 170 nm and 10 nm compared to the dyes **3a**, **3b**, and **3h** respectively. The CN group is a more powerful electron acceptor (dye **3h**) than the Cl group (dye **3g**) and hypsochromic shift of 5 nm is observed. Curious coupling component substituent effect on absorption maxima are evident; for example, acetylation of terminal OH groups in dyes **3a** and **3c** typically bring about modest hypsochromic shift of 15 nm and 175 nm in dyes **3b** and **3f** respectively. Introducing an acetamido group ortho to the azo group, as in dyes **3e** gave shift of 130 nm relative to dye **3a**. The acetamido group is a weak electron donor, but more importantly, it can take part in hydrogen bonding with the azo group. This enhances the planarity of the dye containing the acetamido group. The value of $\log \epsilon$ of the dye **3e** is 5.18 indicating highest intensity of absorption attributed to greater planarity of the dye.

The results summarised in Table 1, clearly show that the incorporation of electron withdrawing group in coupler ring

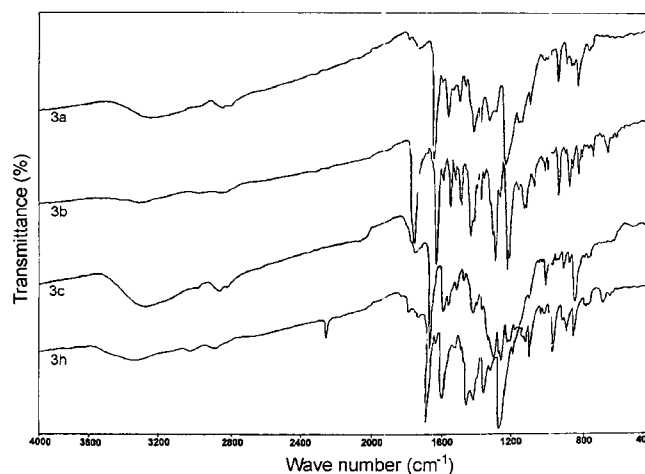


Figure 1. Infrared spectra of dye **3a**, **3b**, **3c**, and **3h**.

leads to hypsochromic shift, similarly, when the electron donating ability of the coupler is enhanced, the deeper in colour of the resulting dyes. In order to bring the shift in absorption maxima to longer wavelengths, electron donating group strategically placed in the coupler ring which increase in polarisability of the dye molecule resulting from enhanced electron density movement from the donor groups (coupler) to the acceptor group (diazo ring). The thiazole ring, being more electron deficient, is accordingly a poor electron donor. The bathochromicity of thiazole dyes is not attributable to a contribution of 3d atomic orbital of sulphur atom of the heterocyclic ring[44].

Infra-red Spectra of Dyes

The infra-red spectra of dyes **3a**, **3b**, **3c**, and **3h** are shown Figure 1. The C-H stretching vibrations of aromatic ring appear at 710-805 and 1580-1595 cm^{-1} . The strong absorption bands in the range 1500-1510 cm^{-1} and 1190-1210 cm^{-1} are corresponding to C-N stretching vibration. The N-H stretching vibration confirmed at 3400-3450 cm^{-1} . The azo and O-H group stretching vibration band appear at 1500-

Table 4. Results of dyeing and various fastness properties of dye 3 onto cellulose triacetate

Dye no.	Colour shade on cellulose triacetate	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
3a	Reddish blue	5	5-4	5-4	5-4	5	5	5-4
3b	Blue	5-4	5-4	4-5	5-4	5	5-4	5-4
3c	Reddish violet	5-4	5	5-4	5-4	5	5	5-4
3d	Scarlet red	5-4	5-4	5-4	4-5	5	5-4	5
3e	Indigo	8-7	5	5	5	5	5	5
3f	Indigo	5	5-4	5-4	5-4	5	5-4	5-4
3g	Reddish violet	5	5	5-4	5-4	5	5	5-4
3h	Maroon	6	5	5	5	5	5	5
3i	Red	6	5	5	5	5	5	5
3j	Maroon	6	5	5	5	5	5	5

Table 5. Results of dyeing and various fastness properties of dye 3 onto nylon

Dye no.	Colour shade on nylon	Light fastness	Wash fastness	Perspiration fastness		Sublimation fastness	Rubbing fastness	
				Acid	Alkaline		Dry	Wet
3a	Blackish violet	5-4	5-4	4-5	5-4	5	5-4	5
3b	Brilliant red	5-4	5	5-4	5-4	5	5	5
3c	Indigo	5	5-4	5-4	4-5	5	5	5
3d	Dark maroon	4-5	4-5	5-4	4-5	5	5	5
3e	Royal blue	7-8	5	5	5	5	5	5-4
3f	Deep red	5-4	5-4	5-4	5-4	5	5-4	5
3g	Reddish brown	5-4	5-4	5-4	4-5	5	5	5
3h	Brown	6-5	5	5-4	5-4	5	5	5
3i	Red	5-6	5	5	5-4	5	5	5
3j	Scarlet red	5-6	5	5	5	5	5	5

1525 cm^{-1} and 3500-3600 cm^{-1} respectively. The C-H stretching vibration of alkyl group appears at 2895-2900 cm^{-1} . The carbonyl stretching appears at 1715-1735 cm^{-1} .

Dyeing Properties of Dye 3

The disperse dye **3** were applied at 2% depth on cellulose triacetate and nylon fibers. Their dyeing properties are given in Tables 4 and 5. These dyes gave a wide range of attractive colour shades varying from red to royal blue shades with good levelness, brightness and depth on the fibers. The variation in the shades of the dyed fibers result from both the nature and position of the substituent present on the coupler ring. Introduction of an acetamido group ortho to the azo linkage in dye **3e** results in a significant improvement in the light fastness. This may be due to the intramolecular hydrogen bond formed between the acetamido group and azo group. The slight differences in the coupling components appear to have little effect: the addition of a CN group onto the end of the alkylamino chain would be expected have a beneficial effect on light and sublimation fastness with cellulose triacetate and nylon as the substrates. Light fastness ranges from good (4-5) to excellent (7-8). The observed slightly higher fastness (6) of dyes **3h**, **3i**, and **3j** with good fastness (5-4) of dyes **3a**, **3c**, and **3d** can be explained in terms of the reduction of the electron density at the azo group due to the inductive effect exerted by the CN group. All the dyes show very good (4-5) to excellent (5) fastness to rubbing, wash and perspiration on fibers. This may be attributed to good penetration and affinity of dyes to the fibers. The compactness of the dye structure provides for excellent sublimation fastness.

Conclusion

A series of thiazolylazo disperse dyes containing various *N,N*-dialkylaniline residues have been synthesized by conventional methods and their colour properties examined both in solution and on application to cellulose triacetate and nylon fibers. The dyes provide wide range of attractive

colour vary from red to royal blue fast shades on fibers and offer excellent affinity and intensity of colour. Their synthesis is generally convenient and economical. The small size of thiazolylazo dyes provided better dyeability. The intrinsic conjugation in the thiazolylazo structure results in very good colour strength. The outstanding property of the thiazolylazo dyes is their high sublimation fastness. The compactness of structure improves sublimation fastness. The nature of the substituent in the coupling components has a great influence on the visible absorption and shade of the dyeing. The introduction of an acetamido group ortho to the azo linkage results in a significant improvement in the light fastness. The heteroatom in the thiazolylazo structure results in bathochromicity and leads to brightness of shades. The CN substituted dyes, probably because of their poorer migration properties, have generally higher fastness than the hydroxylated analogues. Furthermore these dyes show very good exhaustion, fixation, level dyeing and display excellent dischargeability (an additional dyeing property, not exhibited by the carbocyclic azo and anthraquinone disperse dye structure). These properties, which have aided the rise to prominence of such diazo components as replacement for blue anthraquinone dyes on fibers.

The results suggest that the dyeing of cellulose triacetate and nylon fibers with thiazolylazo disperse dyes can be promising for practical uses, chiefly on account of the facility and cheapness of the dyes synthesis, the ease of application and the overall versatility of their use.

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