Dyeing Properties of Reactive Cationic Dyes Containing a Vinyl-sulphonyl Group on Acrylic Fibre Blends

K. NISHIDA
T. TAMURA
K. TAKAYAMA
Y. ANDO and
T. MORIMOTO

Department of Industrial Chemistry
Tokyo University of Agriculture and Technology
Koganei–shi
Tokyo 184
Japan

H. IWAMOTO and
H. TODA

The Textile Research Institute of Tokyo Metropolitan Government
Honzyo
Sumita–ku
Tokyo 130
Japan

The preparation of reactive azo cationic dyes containing a vinylsulphonyl group derived from 2-aminobenzothiazole and its derivatives is described. Their dyeing properties on blends of acrylic–cellulosic, polyester–cellulosic fibre and on cotton and synthetic fibres are investigated. The relationship between absorption spectra and pH of dye solution is assessed.

Introduction

Numerous fibre blends containing acrylic fibre have been developed to exploit its excellent properties. The dyeing method used for these blends usually entails a two-bath procedure. However, if a one-bath method could be developed, the process would be simpler and the cost of dyeing could be reduced significantly.

Reactive cationic dyes for cellulosic fibre have been reported, but little information is available on their dyeing properties. It is thought that, in alkaline solution, the dyes react with the hydroxyl or amino groups which are present in the fibres employed as blend components.

Experimental

INTERMEDIATES AND DYES

The intermediates used in the present study were as follows:

Diazo Components:

(A) 2-Aminobenzothiazole – supplied by Dr B. Yamada (Nippon Kayaku Co. Ltd)

(B) 6-Nitro-2-aminobenzothiazole – prepared by a method reported in the literature [1]. [m.p. 242–243.5°C (Lit. 242–243°C)]

Coupling Component:

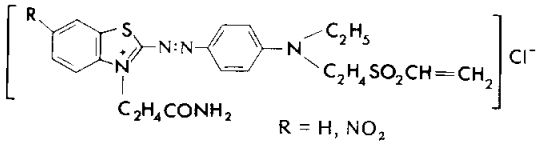
(I) *N*-Ethyl-*N*-vinylsulphonylethylaniline – prepared by a known method [2].

The methods for diazotization and coupling of these dyes have been described [3].

Quaternization of Dyes

A solution of 2.2 g of the dye intermediate in 14 ml of glacial acetic acid was heated to 90–95°C. 0.5 g of hydrochloric acid (36%) and 3.6 g of acrylamide were added to the solution, which was stirred for 6 h at the same temperature. After cooling to room temperature, the solution was poured into 150 ml of water, stirred, and a small amount of activated carbon was added. The solution was stirred again and then filtered.

18 g of NaCl and 0.6 g of $ZnCl_2$ were added to the filtrate. This was then filtered after allowing it to stand overnight at room temperature.



R = H, NO_2

MATERIALS

The acrylic fibre used was Cashimilon (Asahi–Kasei Co. Ltd). The dye sites contained in this fibre are sulphonic groups. Tetron (Tei-Jin Co. Ltd) was used as the polyester fibre. All other fibres used in this study were common products.

DYEING AND TESTING PROCEDURE FOR CATIONIC DYES

2-g samples of each of polyester, polyester–cotton (65/35) and polyester–wool (65/35) fibre were dyed as follows:

A solution of dye was prepared by mixing the finely divided dye (0.15 g), ethanol (10 ml) and nonionic surfactant (1–2 ml) (based on a condensate of ethylene oxide and a long-chain alcohol) in the presence of a carrier (*o*-dichlorobenzene (2 ml)). The mixture was added to a dyebath (100 ml) and dyeing was carried out for 40 min at 100°C.

The dyeing of the other fibres (cotton, wool, acrylic, acrylic–cotton, acetate and nylon 6) was carried out by the following procedure:

Using 2% dye, 1% acetic acid and 2% sodium acetate, at a 100:1 liquor-to-goods ratio, the goods are entered at 50°C, the temperature raised rapidly to 80–85°C (in 10 min). The temperature was then raised to the boil over 30 min and dyed at the boil for 90 min. The dyebath was cooled slowly and the samples washed off thoroughly [5].

An aqueous solution of ammonia was then added to the dyebath, until its concentration in the dyebath reached 10%, and the fabric treated for 24 h at room temperature in the solution. Finally, the dyed fabric was rinsed with water.

All fastness tests were carried out as recommended by the Japanese Industrial Standard Committee (JIS). Generally, these tests correspond to those recommended by ISO. It was assumed that the material was sufficiently pure for dyeing tests if only one distinct thin layer chromatographic spot on silica gel was obtained in 25% aqueous pyridine.

ABSORPTION SPECTRA

The visible spectra of the dyes in ethanolic or aqueous solution were recorded on a Hitachi Model 124 recording spectrophotometer, using a 1-cm cell.

pH

The pH of the solution was measured by a pH meter (Demki–Kagaku Keiki Co. Ltd (Model MG–7)). The dyes were dissolved in conc. HCl and NaOH.

Results and Discussion

SPECTRAL CHARACTERISTICS

Absorption maxima in ethanolic solution are listed in Table 1. The quaternization of the dyes enhances the polarity in the heterocyclic ring and, therefore, results in a bathochromic shift.

TABLE 1

Absorption Maxima of Reactive Cationic Dyes containing Vinylsulphonyl Groups as Coupling Components

	Purified Yield* (%)	M.p. (°C)†	λ_{max}(nm)
A→I	42.3	144–146	493
B→I	40.0	146–148	515
Quaternized by acrylamide			
A→I	54.3	112–114	608
B→I	18.5	130–132	602

*The quaternized dyes prepared were repeatedly recrystallized from ethyl alcohol until only one t.l.c. spot on silica gel appeared. 25% aqueous pyridine was used as a developer. The yields of the dyes which were purified by such procedures are shown. The dye samples used for dyeing were also purified in this way.

†Recrystallized from alcohol

Dye concentration: about 1×10^{-5} mol/l in ethanol

A = 2-Aminobenzothiazole

B = 6-Nitro-2-aminobenzothiazole

I = *N*-Ethyl-*N*-vinylsulphonylethylaniline

In the case of the cationic dye, B→I, the existence of an NO_2 group in the position which is of high electronegativity, inhibits the localization of the electron and, as a result, quaternization becomes difficult. The yield of B→I was low.

DYEING AND FASTNESS PROPERTIES

The dyeing results and the fastness properties are given in Table 2. Some of these dyes have excellent dyeing properties. Unfortunately, the fastness to light of the dyes is low except on the acrylic and on the acrylic–cotton blend fibres. These dyeings show good fastness to light. The substantivity of the dyes for acrylic–cotton (55/45) blends and for acrylic, wool, acetate and nylon 6 fibres is good, but only moderate for the 65/35 polyester–cotton blends.

Owing to the lower content of the cotton in the blends, the one-bath method described produces level and bright dyeings. In the dyeing of wool and nylon 6, the formation of a chemical bond through the vinylsulphonyl group as well as an electrostatic bond is of importance in the processing of dyeing. A large part of the absorbed dyes on the cotton could not be removed by treatment with 25% aqueous pyridine. This suggests that, as well as the electrostatic forces of attraction between dye and fibre, the dyes have combined chemically with the cotton through the vinylsulphonyl group.

The polyester component also combined strongly with these dyes. It may be that there is a chemical reaction with the terminal –COOH group in the polyester fibre.

TABLE 2

Fastness Properties of Reactive Cationic Dyes containing the Vinylsulphonyl Group as the Coupling Component

Dye††	Light fastness (Fade–Ometer)	Washing test			Perspiration test						Dry-cleaning test			Rubbing		Colour on fibre	Degree of Exhaustion
					Acid			Alkali									
Polyester–Cotton (65/35)		CC	S	SP	CC	S	SP	CC	S	SP	CC	S		Wet	Dry		
A→I	1	2	4–5^{+}	5	4	2–3^{+}	4	4	2–3^{+}	5	5	5		3–4	5	Pale bluish violet	Moderate
B→I	1	2–3	3–4^{+}	5	4–5	2–3^{+}	4–5	4	2–3^{+}	5	5	5		2–3	5	Pale red purple	Moderate
Polyester–Wool (65/35)																	
A→I	1	2–3	5*	5	4–5	2*	4	4–5	2–3*	4–5	5	5		4	4–5	Pale Violet	Good
B→I	1	4	5*	5	5	3–4*	5	5	4*	5	5	5		2–3	3	Dull yellow orange	Good
Polyester																	
A→I	1	4–5	5**	5	5	4**	5	5	4**	5	5	5		3–4	4–5	Pale pink	Moderate
B→I	1	4–5	5	5	5	4–5	5	4–5	4–5	5	5	5		4	4–5	Pale yellow orange	Moderate
Cotton																	
A→I	1	2	4–5	5	3–4	2–3	4	3–4	2–3	5	5	5		3	5	Pale bluish violet	Moderate
B→I	1	2–3	3–4	5	4–5	2–3	4–5	4–5	2–3	5	5	5		3	5	Purplish pink	Moderate
Wool																	
A→I	1	2–3	5*	5	4–5	2*	4	4–5	2	4–5	5	5		3	4–5	Dull purple	Good
B→I	1	4	5*	5	5	4*	5	5	4	5	5	5		2	3	Yellowish brown	Excellent
Acetate																	
A→I	1	4	5***	5	5	3–4***	3–4	5	3–4***	5	5	5		4	5	Light purple	Good
B→I	1	2	5***	5	3–4	3–4***	5	3–4	4***	5	5	5		3	5	Purplish red	Good
Nylon																	
A→I	1	3–4	5	5	5	4	5	4	4	5	5	5		4	5	Pale reddish violet	Good
B→I	1	4	5	5	5	4–5	5	5	4–5	5	5	5		3–4	4	Dark yellow orange	Good
Acrylic																	
A→I	4	5	5	5	5	5	5	5	5	5	5	5		3–4	4–5	Light violet	Good
B→I	4	4–5	5	5	5	5	5	5	5	5	5	5		2–3	4–5	Dark reddish violet	Excellent
Acrylic–Cotton (55/45)																	
A→I	3–4	4–5	5^{+}	3–4	5	5^{+}	2–3	5	5^{+}	2–3	5	5		3–4	5	Dull reddish violet	Good
B→I	4–5	4–5	5^{+}	3–4	5	5^{+}	2–3	5	5^{+}	2–3	5	5		1–2	3	Dull reddish violet	Good

CC = Change of colour, S = Staining on same kind of fibre as that used in dyeing, SP = Staining of Polyester, * = Staining of wool ** = Staining of nylon, *** = Staining of acetate, $^{+}$ = Staining of cotton $^{++}$ = Dyes that were quaternized by acrylamide

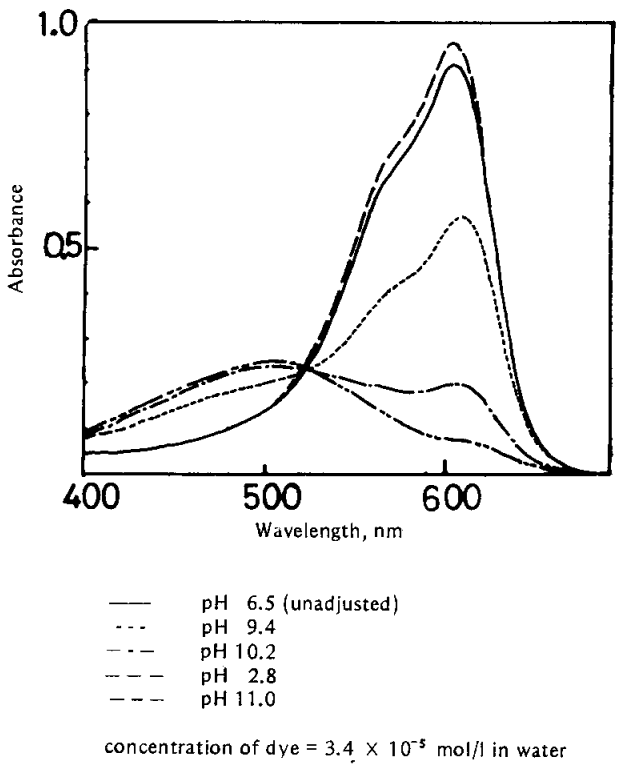


Figure 1 – Absorption spectra of quaternized 2-aminobenzothiazole→ N-ethyl-N-vinylsulphonylethylaniline

Figure 1 shows the pH-induced change in the spectra of the dye A→I. Unfortunately, when the dyeings are treated with aqueous ammonia to encourage formation of a chemical bond, the colour of the dyeings changed sharply from bright to dull in pH range 8–9.

It is very interesting to record that very bright dyeings are observed on acrylic fibre even when the pH range is >8. This could be a result of the acidic sulphonic groups, contained in the acrylic fibre (Cashimilon), acting as dye absorption sites.

* * *

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