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Novel azobenzene derivatives containing a glucopyranoside moiety. Part II: dyeing properties

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Abstract

Novel azobenzene dyes containing a glucopyranoside moiety were applied to polyethylene terephtalate and cellulose diacetate fibres. Isothermal rate-of-dyeing curves at different temperatures, calculations of the apparent activation energies, light and dry heating colourfastness are reported for polyester. For the cellulose diacetate fibres, bath exhaustions at equilibrium are considered. The data suggest that while the hydrophilic β-D-glucopyranose ring decreases toxicity, it also reduces the substantivity towards hydrophobic fibres. The analogue with an acetylated β-D-glucopyranose ring has dyeing properties comparable to traditional disperse dyes, and, in effluent treatment, is easily converted by hydrolysis of acetate groups to a non-toxic dye. © 2000 Elsevier Science Ltd. All rights reserved.

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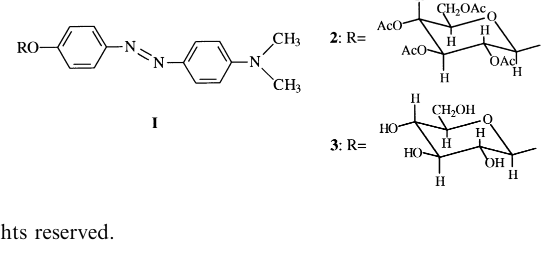
1. Introduction

The synthesis of novel dyes for textile application and the development of dyeing techniques are intended to improve technological performances and to reduce toxicity and negative impact on the environment. Recently, various coloured molecules containing hydrophilic substituents have been investigated.

In part I of the present work [1], the synthesis, thermal behaviour, structural characterisation and mutagenic properties of novel azobenzene dyes (general formula I) were reported. Dye **1** is a classic disperse azo dye and is useful for dyeing hydrophobic fibres but has a mutagenic nature [1]; dyes **2** and **3** bear a glucopyranoside ring with hydrophilic properties derived from the acetylation of hydroxy groups. Reduced mutagenicity has been observed when the more hydrophilic β-D-glucopyranose moiety is present (dye **3**).

This paper deals with the dyeing properties of these dyes on polyester and cellulose diacetate and some resulting colour fastness properties.



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2. Experimental

Details of the synthesis and purification of dyes **1**–**3** and their spectroscopic characterisation have been reported previously [1].

The dyeings were performed in a Linitest (Heraeus) apparatus with a temperature accuracy of ±1°C. Polyester (1.7 dtex, fibres) and cellulose (3.33 dtex, fibres) fabrics were used. Dye baths were set up using a liquor ratio of 1:30 and dyeing intensity 0.45% o.w.f. Dyes, suitably dispersed (average particle size 0.5–2 μm), were added to water, Sandozol KB (2 ml/l) and acetic acid (to pH = 5.5). The dispersion quality was checked by examining the homogeneity of the filtration pattern on filter paper. Dye **3** proved to be the most difficult to disperse.

Dyeing of polyester was performed isothermally at a range of temperatures while cellulose diacetate was dyed applying a non-isothermal process: starting temperature 40°C, heating rate 1°C/min, dyeing temperature 85°C for 60 min, cooling rate 1°C/min. After all dyeings, the fabrics were washed in 60 ml of deionized water and 25 ml of cold acetone to remove superficial dye. The residual dye bath and rinse water were diluted with *N*,*N*-dimethylformamide (1/3) and acidified with H_3PO_4 to pH = 5.5, to provide stable, optically clear solutions. Dye concentration in these solutions and the acetone washings was determined spectrophotometrically using a Shimadzu UV-265FW spectrophotometer and suitable calibration curves.

Fastness to light of dyed fabrics was performed according to ISO 105-B02, using a Xenotest 150S apparatus (Heraeus) and the photocromism was assessed accordance with ISO 105-B05. Fastness to dry heating was performed according to ISO 105-P01, using a Fixotest apparatus (Heraeus) and adjacent fabrics as described in the ISO 105-F.

3. Results and discussion

3.1. Dyeing of polyethylene terephthalate fabrics

Figs. 1–3 show the isothermal rate-of-dyeing curves for the three dyes at different temperatures, and in Fig. 4 the curves at 130°C are compared.

The dyes show different behaviour both in dyeing rate and in equilibrium saturation values as determined after 8 h. Dye **1** reaches equilibrium more quickly; i.e. it diffuses rapidly in the fibre, in

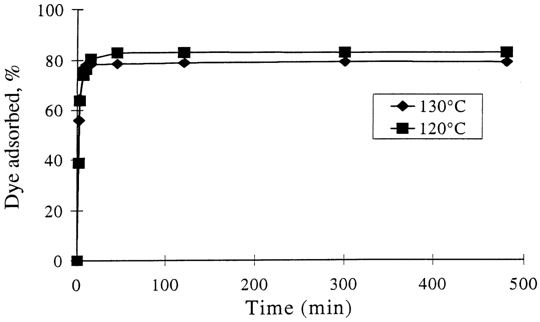

Fig. 1. Isothermal rate-of-dyeing of dye **1** on polyester at different temperature..

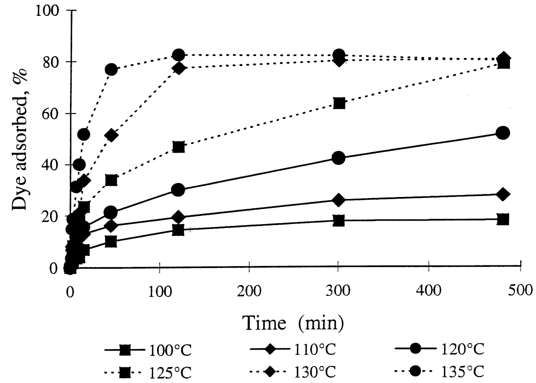

Fig. 2. Isothermal rate-of-dyeing of dye **2** on polyester at different temperature..

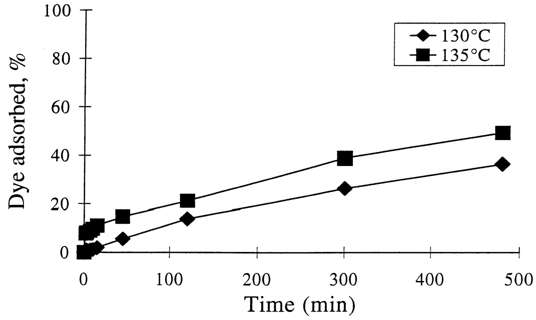

Fig. 3. Isothermal rate-of-dyeing of dye **3** on polyester at different temperature.

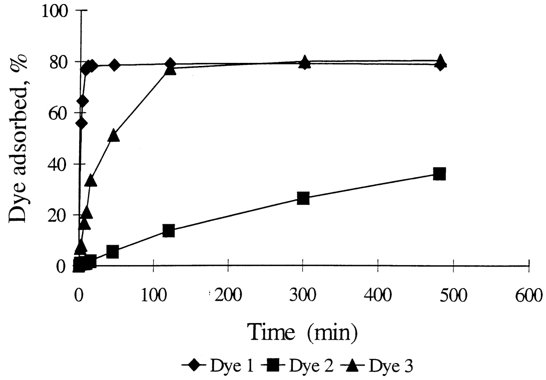

Fig. 4. Comparison of the isothermal rate-of-dyeing on polyester at 130°C.

keeping with its smallest molecular volume. It is a typical disperse dye with a suitable hydrophobic character for dyeing polyester fabrics, as the high equilibrium saturation values confirm. The temperature influences the final amount of adsorbed dye; it decreases as the temperature rises, in accordance with the exothermic nature of the dyeing process [2]. Dye **3**, containing a β-D-glucopyranosyl ring, has a higher molecular weight and hydrophilic properties; consequently, it dyes slowly and has low fibre affinity. After 8 h at 130°C, equilibrium has not been reached and the extrapolated saturation value is very low. Dye **2** has a molecular weight comparable to that of dye **3**, and less hydrophilic character due to the acetylation of the hydroxy groups. Together, these structural elements give a slow dyeing rate and a saturation value comparable at high temperatures to that of dye **1**. Consequently, dye **2** has properties more like those of traditional disperse dyes.

The parabolic Eqs. (1) and (2) and the Cegarra–Puente Eq. (3), widely used to describe disperse dyeing process [3,4], were used for a quantitative analysis of kinetic data:

$$C_t = k\sqrt{t} \tag{1}$$

$$C_t/C_\infty = k\sqrt{t} \tag{2}$$

$$1n\left[1 - \frac{C_t^2}{C_\infty^2}\right] = -kt \tag{3}$$

where k is the rate-of-dyeing constant, and C_t and C_∞ are the concentration of dye after time t and at equilibrium, respectively. Table 1 summarises the rate-of-dyeing constants (k) at 130°C for dyes **1**–**3** and the related correlation coefficients. The closest-fitting has been obtained applying the Cegarra–Puente Eq. (3).

The effect of temperature on the rate-of-dyeing constants has been evaluated by the Arrhenius Eq. (4):

$$k = k_o e^{-E_{\mathrm{ap}}/RT} \tag{4}$$

where k (min^{-1}) is the rate-of-dyeing constant at temperature T calculated by Eq. (3), k_o (min^{-1}) is the pre-exponential factor, R (kcal/mol·K) is the universal gas constant, and T (kelvin) is the absolute temperature.

The apparent activation energy E_{ap} (kcal/mol) is graphically obtainable from the slope of the plot ln$k$ versus $1/T$. In Fig. 5 the data for dye **2** are reported. Two different straight lines have been obtained with a notable change of slope at about 120°C; consequently, two different E_{ap} values can

Table 1
Dyeing of polyester: calculated rate constants (k) and correlation coefficients (R^2)

Equation	Dye **1**		Dye **2**		Dye **3**	
	k	R^2	k	R^2	k	R^2
(1)	26.529	0.8526	2.1572	0.9825	1.3800	0.9661
(2)	0.3700	0.8526	0.0837	0.9825	0.0157	0.8526
(3)	0.3485	0.9216	0.0130	0.9837	0.0003	0.9744

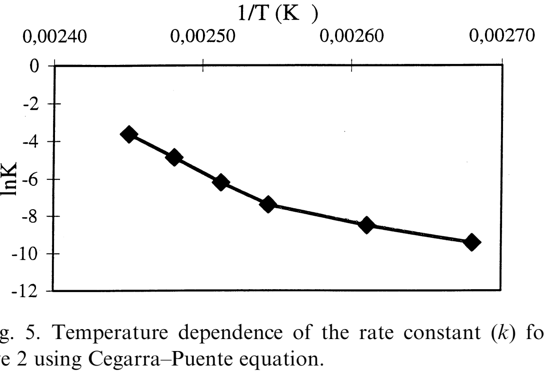

Fig. 5. Temperature dependence of the rate constant (k) for dye 2 using Cegarra–Puente equation.

be extrapolated. This variation is attributable to the glass transition of the fibre. Table 2 summarises the E_{ap} values for dyes **1**–**3** and the molecular weight of the substituent R in general formula I, used to describe the molecular hindrance of dyes. Although the accuracy of the values of parameter E_{ap} is limited owing to the reduced number of dyeing tests, the values can be considered acceptable in their order of magnitude and used for comparison.

Table 2
Dyeing of polyester: apparent activation energy and molecular weight of the substituent *R*

Dye/temperature range	E_{ap} (kcal/mol)	MW of *R* (g/mol)
1 (120°C–130°C)	2.382	15
2 (120°C–135°C)	80.259	331
(100°C–120°C)	29.210	
3 (130°C–135°C)	45.132	163

Table 3
Dyeing of cellulose diacetate: equilibrium exhaustion at 85°C

Dye	Equilibrium exhaustion
1	97.30
3	21.79
2	64.16

E_{ap} values correlated with the molecular weight of the substituent *R*, which suggests the following. The lowest E_{ap} value of dye **1**, confirms its suitability for polyester. The hydrophobic character and the lowest hindrance of substituent ($R=CH_3$) provide the high saturation value and a fast diffusion rate, little affected by temperature. Dye **2** shows the highest E_{ap} value, so a high dyeing temperature has to be employed to promote diffusion. This high dependence of diffusion on temperature is attributable to the presence of a hindering substituent (*R* = acetylated glucose) that depresses the diffusion of dye into fibre. On the whole, dye **2** is hydrophobic as the hydrophobic polyester requires; so, at high temperatures, it shows saturation values comparable to those of dye **1**. Dye **3** is the most hydrophilic of the series owing to the free hydroxy groups of the glucosidic substituent. Consequently, it has a very low affinity for the hydrophobic polyester as evidenced by the low saturation value. The intermediate hindrance of the glucosidic substituent gives an intermediate E_{ap} value but the excessive hydrophilic nature of dye **2** limits its affinity for the polyester fibre.

3.2. Dyeing of cellulose diacetate fabrics

Dyes **1**–**3** have been tested in the dyeing of cellulose diacetate fibres. The exhaustions at equilibrium have been used as semiquantitative indices

Table 4
Fastness to light and heat resistance of polyester fabrics

Dye	Dyeing temperature (°C)	Light	Change in colour			Staining on polyester adjacent fabric		
			150°C	180°C	210°C	150°C	180°C	210°C
1	120	5[a]	4–5	4–5	4	4	2	1
	130	4–5[a]	4–5	4–5	4	4	2	1
2	100	1–2	4	3–4	3	5	4–5	4–5
	110	3–4	4–5	4–5	4	5	4–5	4–5
	120	5	4–5	4–5	4–5	5	4–5	4
	125	5–6	5	4–5	4–5	5	4	3–4
	130	5	5	5	4–5	5	4	3–4
	135	5	5	5	5	5	4	3–4
3	130	1–2	5	4–5	4–5	5	4–5	3–4
	135	2	5	4–5	4–5	5	4	3–4

[a] Photochromism observed.

of the affinity of dye for the fibre. The data are collected in Table 3.

Dye **1** shows the best performance for the cellulose diacetate fibres as it did for polyester too. The high affinity is due to its low molecular hindrance and appropriate hydrophilic-hydrophobic balance. Dye **2** is less suitable, probably owing to its excessive hydrophobic character and molecular hindrance. In contrast, dye **3**, more polar and less hindered, shows a higher affinity for cellulose diacetate than its parent dye, but is still not comparable to that of dye **1**.

3.3. Colour fastness to light and to dry heating of dyed polyethylene terephtalate fabrics

A product, in order to be defined as a dye for textiles, in addition to suitable dyeing behaviour must exhibit good colourfastness. Table 4 shows the data on the colourfastness to light and to dry heating of the dyed polyester fabrics.

Fabrics dyed with dyes **1** and **2** at high temperature show the same medium light resistance; dye **1** exhibited photochromism. Samples dyed with dye **2** at different temperatures, show light fastness that increases as the dyeing temperature increases. This phenomenon can be ascribed to a lower diffusion of the dye into the fibre at low temperatures. The hydrolysis of acetate groups (dye **3**) reduces light fastness, even for fabrics dyed at high temperatures. Because the chromogen is the same in all three dyes, and the three R substituents exert the same electronic effect, (as UV–visible spectroscopy suggests [1]), the decreased colourfastness to light observed for dye **3** can be ascribed to low diffusion of dye into the fibre.

Generally, dyes **1–3** show little change in colour with dry heating. Fabrics dyed at low temperatures with dye **2** show greater change in colour, attributable to lower diffusion in the fibre. A slightly better fastness is observable for glucosidic dyes, in accordance with the increase of molecular weight that reduces the sublimation from the fibre. The difference in molecular weight influences the staining on polyester too. In the tests at 180 and 210°C, the fabric adjacent to the sample, dyed with the more sublimable dye **1**, appeared markedly coloured, while better performance was observed for the glucosidic dyes.

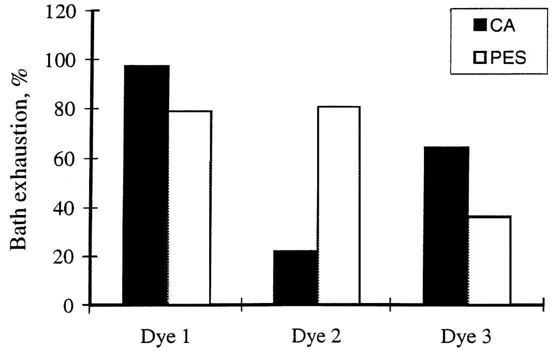

Fig. 6. Bath exhaustion for the dyeing of cellulose diacetate (CA) at 85°C and polyester (PET) at 130°C.

4. Conclusions

Fig. 6 collects the bath exhaustion values obtained on both fabrics under better dyeing conditions.

Dye **1** appears particularly suitable for both polyethylene terephtalate and cellulose diacetate fabrics, showing (i) exhaustion values near 80 and 100%, respectively, (ii) rapid diffusion, (iii) acceptable light fastness, (iv) good dry heating fastness in which, only the staining of adjacent fabric is unfavourable. Dye **2** appears suitable for polyester with a bath exhaustion comparable to that of dye **1** and generally acceptable fastness despite a need for high temperature and a long time of dyeing. In addition, the easy conversion of dye **2** to non-toxic dye **3** by hydrolysis makes the former interesting from the effluent treatment point of view. Dye **3** shows a bath exhaustion of 64 and 35% on cellulose diacetate and polyester, respectively. Data suggest that the hydrophilic β-D-glucopyranose ring decreases toxicity [1], but also decreases affinity for hydrophobic fibres to a marked extent but not as fully as does the sulphonic acid group. Novel dyes containing both a glucose moiety and hydrophobic groups, e.g. bulky alkoxy substituents [5], could show decreased toxicity and useful dyeing properties for hydrophobic fibres; their synthesis is in progress.

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