

Effects of additives on the dyeing of nylon-6 with dyes containing hydrophobic and hydrophilic moieties

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Dedicated to Arnold T. Peters, a clever scientist, a skilled colourist, a friend

Abstract

A series of azo disperse dyes with variable hydrophobic chain length and hydrophilic (hydroxy or glucosyl group) head were synthesised. ^1H and ^{13}C NMR spectra indicated that the glucosyl moiety was linked to the azo structure with a β anomeric bond. The dyeing properties on polyamide fibres were assessed with dyeing isotherms and Linitest experiments. The positive effects of additives, as ternary systems (SDS, Brij 35 and octanol) or cyclodextrins, on the dyeing uniformity were shown by tristimulus colorimetry. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Disperse dyes; Glucosyl dyes; Cyclodextrins; Dyeing isotherms; Dyeing tests; Colour measurements; NMR spectra

1. Introduction

In previous work, the effects of “precursors of microemulsions” on the dyeing of hydrophobic fibres with disperse dyes were studied [1–5]. Recently, cyclodextrins were used as additives in the dyeing of polyamide fibres with acid dyes [6], with the aim of improving dye levelling and of reducing the content of organic matter in waste waters. In particular, cyclodextrins were chosen for their natural origin and their biodegradability. Cyclodextrins (Fig. 1) are industrially obtained by the degradation of starch carried out by a large number of micro-organisms, e.g., *Bacillus macerans* [7].

In the present work the effects of cyclodextrins and other additives on the dyeing of nylon-6 were investigated. Dialkylaminoazobenzene dyes with variable alkyl chain length and hydrophilic head, such as an alcoholic group or a glucosyl moiety, were used (Fig. 2). The glucosyl moiety was chosen, because it could increase both the hydrophilic properties and the dispersibility of the dyes.

2. Experimental

Compounds **1–3** were prepared by the reported method [8].

Dyes **4–8** were synthesised by coupling dialkylamines **1–3**, *N,N*-diethylaniline and *N,N*-dimethylaniline with the diazonium salt prepared from 2-(4-aminophenyl)ethanol. All the dyes were purified by flash chromatography on silica gel 60

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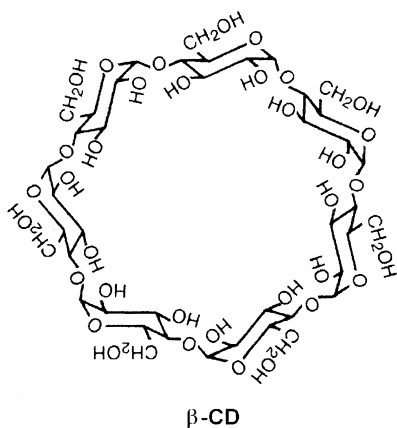


Fig. 1. β-Cyclodextrin.

(230–400 mesh, Merck), petroleum ether/ethyl acetate 70:30 v/v as eluent, and crystallised from ethanol. Physical properties and yields are reported in Table 1 and the NMR data in Table 2.

Dyes **9** and **10** were prepared by substitution of the alcoholic group in dyes **5** and **7** with a glucosyl residue [9].

2.1. 2-[4-(4-Diethylaminophenylazo)phenyl]ethyl-β-glucopyranoside, **9**

A solution of 2-[4-(4-diethylaminophenylazo)phenyl]ethanol, dye **5**, (5 g, 16.8 mmol) and penta acetylglucose (20 g, 50.4 mmol) in dry dichloromethane (50 ml) was treated dropwise at 0°C with boron trifluoride diethyl etherate (4.8 g, 33.6 mmol). The ice bath was removed after 2 h and the mixture was kept at room temperature for 20 h. The reaction mixture was then treated with a saturated aqueous solution of sodium hydrogencarbonate (50 ml). The organic phase was washed with water, dried (Na₂SO₄) and the solvent removed. The solid residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (80:20 v/v) as eluent. Three fractions were collected, the second was identified as the unreacted dye **5**. The first fraction was identified as the acetyl derivative of dye **5** via ¹H NMR (δ CH₃CO = 2.00 ppm). The third fraction was eluted with petroleum ether/ethyl acetate 50:50 v/v. TLC analysis (silica gel 60 F-254, Merck, petroleum ether/ethyl acetate 80:20 v/v)

showed the presence of two compounds, which were separated and identified as pentaacetylglucose and dye **9**. To isolate dye **9** the whole fraction was vacuum concentrated and the solid mixture dissolved in methanol/aqueous ammonia (30%) 20:2 v/v to hydrolyse the acetyl esters. The solvent was vacuum removed and the residue (dye **9**) was carefully washed with deionised water and crystallised from methanol.

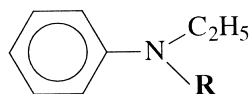
2-[4-(*N*-Ethyl-*N*-octylaminophenylazo)phenyl]ethyl-β-glucopyranoside, dye **10**, was similarly obtained starting from 2-[4-(*N*-ethyl-*N*-octylaminophenylazo)phenyl]ethanol, dye **7**. Physical properties, yields and NMR data are reported in Tables 1 and 3 respectively.

¹H NMR spectra were recorded with a Jeol EX 400 spectrometer in DMSO-*d*₆ solution (2%). The two-dimensional COSY experiment was performed with a spectral width of 3000 Hz over 2000 data points. The two-dimensional ¹³C-¹H HETCOR spectrum was recorded with spectral windows of 18000 and 3400 Hz in the F₂ and F₁ dimensions respectively. Both acquisitions involved 64 scans for 256 experiments and the data were collected and transformed using a sine bell squared function.

The electronic spectra were determined on a Unicam UV2 spectrophotometer in ethanol solution.

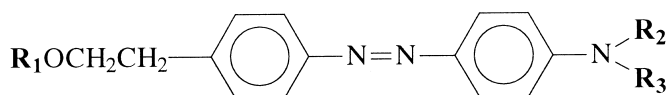
R_f values were determined on RP-18 WF 254s plates (Merck), using methanol as eluent, or on Silica Gel 60 F-254 TLC plates (Merck), using as eluent: (a) ethyl acetate–petroleum ether 30:70; (b) methanol–ethyl acetate 80:20; (c) butanol–acetic acid–water (BAW) 4:1:5 (organic layer).

Laboratory dyeing tests were carried out on a Linitest apparatus (Hanau-Germany) at liquor to goods ratio 20:1, 10:1 and 5:1, 1% o.w.f., pH 7 (Tris buffer), in the presence of SDS (sodium dodecyl sulphate), Brij 35 (polyoxyethylene (23) lauryl ether) as dispersing agents and octanol as oil phase. In some cases, the baths were sonicated to improve the dispersion of the dye (ultrasonic apparatus Vibra-cell 120 W). Nylon 6 fabric (filling dtex 78/24, warp dtex 67/12, Sniafibre Italy) were introduced into the dye-bath at 40°C and the temperature raised to 80°C (2°C/min) and maintained for 1 h. The dyed fibre was then removed, washed at 40°C with water solution containing



Compounds 1-3

Compounds	R
1	C ₄ H ₉
2	C ₈ H ₁₇
3	C ₁₂ H ₂₅



Dyes 4-10

Dyes	R ₁	R ₂	R ₃
4	H	CH ₃	CH ₃
5	H	C ₂ H ₅	C ₂ H ₅
6	H	C ₂ H ₅	C ₄ H ₉
7	H	C ₂ H ₅	C ₈ H ₁₇
8	H	C ₂ H ₅	C ₁₂ H ₂₅
9		C ₂ H ₅	C ₂ H ₅
10		C ₂ H ₅	C ₈ H ₁₇

Fig. 2. Dyes and intermediates structures.

soap (2.5 g/l) and sodium carbonate (2 g/l), rinsed and dried in hot air.

Colour measurements were carried out with a Minolta CR 200 instrument. The dyed samples were evaluated by means of colour difference in CIE Lab space (ΔE) between dyed and undyed fabrics. ΔE represents a measure of the dye uptake

on the fibre and is the mean of five determinations on different positions for each specimen. The standard deviation of ΔE ($\sigma_{\Delta E}$) is a measure of colour levelling [2]. Best dyeings correspond to highest ΔE and lowest $\sigma_{\Delta E}$ values. Dye concentration in the bath, before and after the dyeing, was measured by means of spectrophotometric

Table 1
Physical properties and reaction yields of dyes 4–10

Dye	m.p. (°C)	λ_{\max} (nm)	Log ϵ	Yield (%)
4	125	408	3.19	95
5	90	416	3.26	80
6	Viscous oil	417	3.21	74
7	Viscous oil	416	3.19	27
8	48–9	417	3.22	12
9	100–1	417	4.49	14
10	92–3	417	4.40	22

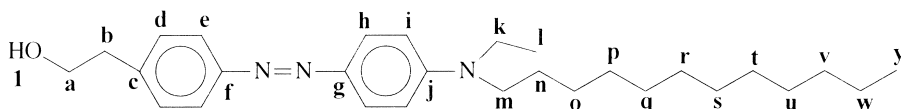
analysis (water/ethanol 1:1). These data allowed bath exhaustion to be calculated. Quantitative dyeing measurements were performed in a dyeing bath prepared dissolving suitable amounts of dye and additives (SDS, Brij 35 or SDS, Brij 35 and octanol) in acetone (10 ml). The solvent was gently removed to obtain a concentrated syrup to whom

buffer solution and water were added to obtain a final volume of 250 ml. Dyeing was carried out at 80°C in the apparatus previously described in [10]. Sorption rate curves were obtained measuring in continuum the absorbance of the bath at 420 nm and calculating the corresponding concentration in the fibre. Measurements were pursued until concentrations attained constant values for at least 2 h. In order to obtain reliable equilibrium values (C_{∞}) the experimental points were treated according to the linear form of Vickerstaff equation.

$$\frac{t}{C_{f,t}} = \frac{1}{k * C_{f,eq}^2} + \frac{1}{C_{f,eq}} * t$$

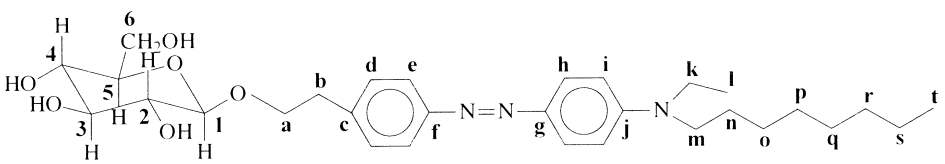
t = time, $C_{f,t}$ = dye concentration in the fibre at the time t , $C_{f,eq}$ = equilibrium dye concentration in the fibre, k = Vickerstaff constant.

Table 2
 ^1H NMR chemical shifts of dyes 4–8



Proton	Dye				
	4	5	6	7	8
a	3.67	3.67	3.67	3.67	3.67
b	2.81	2.81	2.81	2.81	2.80
d	7.38	7.37	7.37	7.37	7.37
e	7.72	7.70	7.70	7.70	7.70
h	7.79	7.77	7.76	7.76	7.76
i	6.83	6.79	6.78	6.77	6.78
k	3.05	4.45	3.46	3.44	3.46
l		1.15	1.14	1.13	1.15
m	3.05	4.45	3.36	3.37	3.36
n		1.15	1.57	1.57	1.57
o			1.34	1.29	1.25
p			0.94	1.29	1.25
q				1.29	1.25
r				1.29	1.25
s				1.29	1.25
t				0.87	1.25
u					1.25
v					1.25
w					1.25
y					0.86
l	4.74	4.71	4.70	4.71	4.69

Table 3
 ^1H and ^{13}C NMR chemical shifts of dyes **9** and **10**



Position ^a	^1H NMR spectrum		^{13}C NMR spectrum	
	9	10	9	10
a			69.34	69.87
a'	4.00	3.98		
a''	3.70	3.68		
b	2.90	2.90	35.54	35.91
c			140.61	141.02
d	7.39	7.37	129.85	130.26
e	7.65	7.65	121.78	122.20
f			150.04	150.63
g			142.17	142.55
h	7.72	7.70	125.12	125.48
i	6.75	6.66	111.06	111.43
j			151.12	151.52
k	3.39	3.33	44.16	45.12
l	1.10	1.04	12.63	12.69
m	3.39	3.22	44.16	50.23
n	1.10	1.45	12.63	27.62
o		1.17		26.92
p		1.17		29.25
q		1.17		29.42
r		1.17		31.77
s		1.17		22.63
t		0.78		14.45
1	4.22	4.21	103.01	103.28
2	2.99	2.99	73.57	73.81
3	3.18	3.18	76.90	76.97
4	3.08	3.07	70.20	70.45
5	3.12	3.12	77.05	77.18
6			61.23	61.49
6'	3.70	3.68		
6''	3.45	3.45		

^a Signals of methylene protons **6** and **a** were split in the ^1H NMR spectrum, and are indicated as **6'**, **6''**, **a'**, **a''**.

The statistical parameters of the linear relationships ($t/C_{f,t}$ vs. t) proved very good ensuring reliable $C_{f,\text{eq}}$ values. Dyeing isotherms were obtained plotting the equilibrium dye concentration in the fibre $C_{f,\text{eq}}$ versus the corresponding concentration in solution $C_{s,\text{eq}}$.

β -Cyclodextrin (Pharma grade) and methylcyclodextrin (average methylation degree 1.8, Pharma grade) were supplied by Wacker-Chemie and used as received.

3. Results and discussion

Dyes **4–8** represent a series of molecules with a different hydrophobic behaviour as a result of the variation in the length of the aliphatic chain. Compounds **9** and **10**, comparable to dyes **5** and **7**, present higher hydrophilic properties because of the presence of a glucosyl moiety.

R_f values, obtained by TLC on silica gel, generally increase with the hydrophobic properties of

the substrates (Table 4) whereas on RP-18 stationary phase the behaviour is reversed. These results are in agreement with the different polarity of the stationary phases and the hydrophobic properties of each compound. Dyes **9** and **10** illustrate the high hydrophilic character of glucosyl moiety.

The structure of dyes were determined by NMR spectra. Table 2 reports the protons chemical shifts of azo dyes **4–8**. The assignment of the chemical shifts of the aromatic protons was in agreement with previous investigations on similar dialkylaminoazobenzenes [11,12]. In the following discussion, the bold type letters refer to the formula at the top of Table 2. Protons **i** (ortho position with respect to the dialkylamino group) undergo shielding effects and are thus easily distinguished from protons **e** and **h** (ortho position to the azo group). Protons **d** show a chemical shift intermediate between protons **e**, **h** and **i**, in agreement with the electronic effects of the β -hydroxyethyl group exerted on protons **d**. The chemical shifts of protons **e** and **h** are identified by analysis of the coupling constants with protons **d** and **i** respectively ($J_{d,e}=8.2$ Hz, $J_{h,i}=9.0$ Hz). The signals of the aliphatic protons in compounds **4** and **5** are assigned by direct inspection. The length variation of the aliphatic chain exerts a small effect on the chemical shift of protons **i**. NMR spectra of compounds **9** and **10** were recorded in the presence of D₂O to induce H-D exchanges on glucosyl OH groups for an easier interpretation. 2-D NMR

COSY experiments allowed the chemical shifts assignments of glucosyl protons. These experiments offer a means of determining the correlations of pairs of *J*-coupled nuclei in a molecule by allowing the observations of cross-peaks [13]. Fig. 3a and b show the spectrum of compound **10**, whose chemical shifts are reported in Table 3 (bold type letters are now referred to the formula at the top of Table 3). The aromatic signals in the range 6.66–7.70 are easily interpreted by both the comparison with the spectra of compounds **4–8** and the observation of the cross-peaks (Fig. 3b). In the aliphatic region the two triplets at 1.04 and 0.78 ppm correspond to protons **l** and **t**, respectively. Actually, the signal at 0.78 ppm shows a cross-peak with protons **s** at 1.17 ppm (signals of protons **o–s** are overlapped), while the triplet at 1.04 ppm is coupled with the methylene group (**k**) at 3.33 ppm. The signal at 1.45 ppm is assigned to protons **n** for the presence of two cross-peaks with protons **o** and protons **m** (3.22 ppm). The chemical shifts of protons **m** and **n** are in agreement with the electron withdrawing effect exerted by the nitrogen atom on the adjacent positions. The doublet at 4.21 ppm is assigned to the glucosyl proton **1**, bonded to an “acetalic” carbon. The value of the coupling constant J_{12} (8.0 Hz) is typical of a *trans* diaxial constant [14] and confirms a β -glucosyl bond. A cross-peak connects the signal due to H₁ to the apparent triplet centred at 2.99 ppm (proton **2**). Protons **3** and **4** give signals at 3.18 and 3.07 ppm, respectively. Proton **5** gives a multiplet through coupling with proton **4** and with the two split and non-equivalent protons **6'** (3.68 ppm) and **6''** (3.45 ppm), as confirmed by a 2-D heteronuclear carbon-proton experiment (Fig. 4) (coherence signals between 61.49 ppm and 3.68, 3.45 ppm). Protons **6'** and **6''** give rise to a complex overlapped signal. The HETCOR experiment shows the non-equivalence of **a'** and **a''** (coherence signals between 69.87 ppm and 3.98, 3.68 ppm), as expected by the closeness to the chiral centre in the glucosyl position **1**. The multiplet centred at 3.98 ppm is attributed to proton **a'**, confirmed by the two cross-peaks with protons **a''** and **b** (2.90 ppm). The assignment of ¹³C spectrum is helped by the HETCOR experiment. The identification of the quaternary aromatic carbon is possible by

Table 4
R_f data of compounds **1–10**

Compounds	RP-18	Silica gel	
	Methanol	Petroleum ether/ethyl acetate 70:30	BAW
1	0.54	0.85	0.90
2	0.39	0.91	0.90
3	0.21	0.93	0.85
4	0.71	0.18	0.90
5	0.66	0.19	0.80
6	0.65	0.19	0.84
7	0.49	0.28	0.85
8	0.28	0.22	0.90
9	0.84	0	0.70
10	0.61	0	0.76

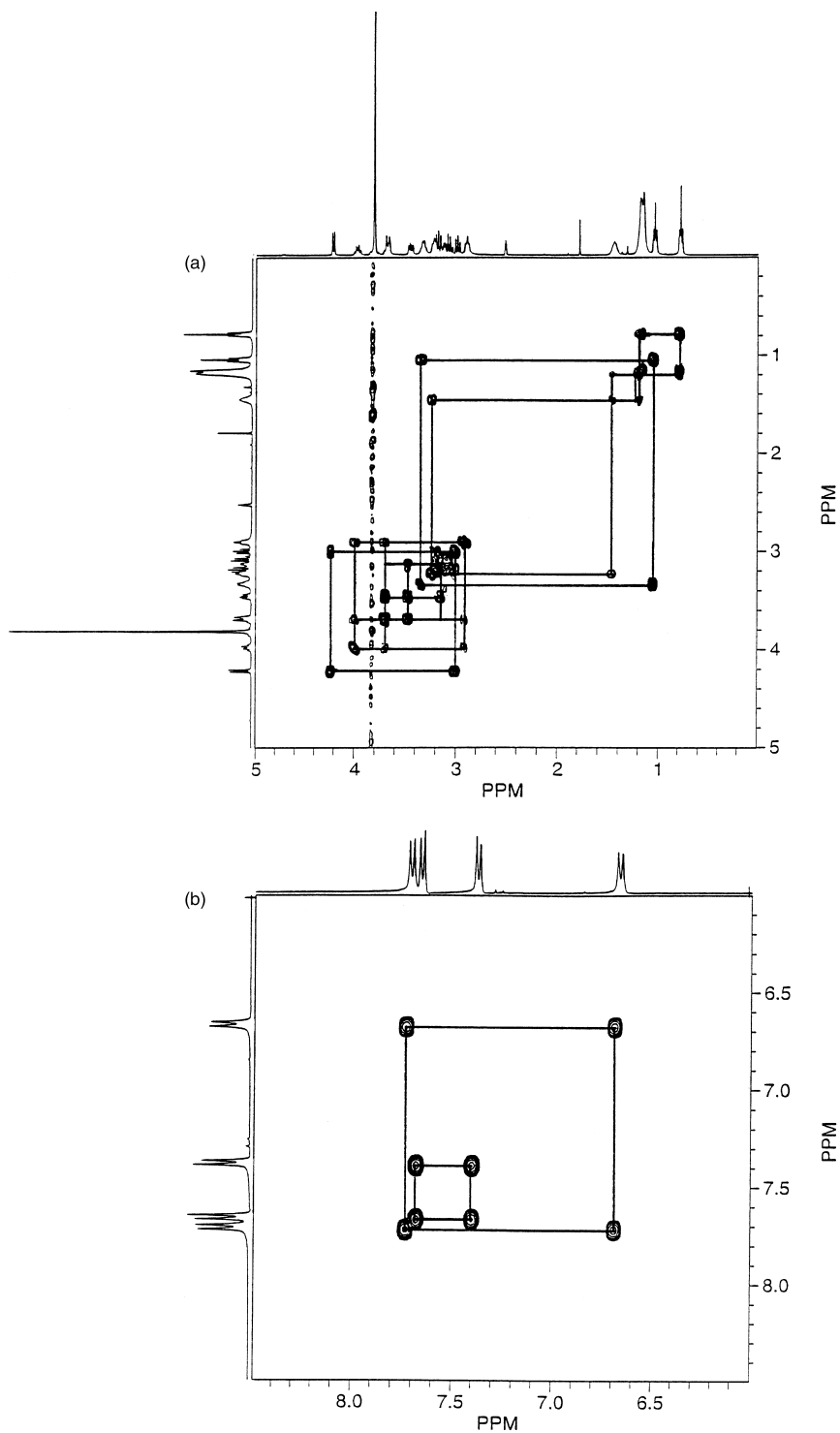


Fig. 3. Dye 10: ^1H - ^1H COSY spectrum: (a) aliphatic region; (b) aromatic region.

comparing spectra of analogous dyes [15]. The assignment of the aliphatic carbons is based on chemical shifts calculated by additive rules of shielding effects [16]. The whole data agree with the expected structure and confirm the presence of only one glucosyl moiety.

The interactions between dyes and the polyamide fibre were studied by recording the dyeing isotherms. The effects of the presence of “microemulsion precursors” (SDS, Brij 35 and octanol mixture) in comparison to surfactants (SDS, Brij 35) were investigated. The applications of “microemulsion precursors” in dyeing processes (surfactant + cosurfactant + oil phase in low concentration range compared to the usual one typical for microemulsions) are well known [1–5]. In all cases, the isotherms were linear indicating a dye–fibre interaction of the Nernst type (Fig. 5). The straight line slopes represent the Nernst partition

constants K . The presence of the glucosyl group (dyes **9** and **10**) does not change this pattern. Table 5 shows the values of the Nernst partition constants in the presence of the additives in order to highlight the effects of “microemulsion precursors”. In the presence of SDS–Brij 35 as additives, with or without octanol, the Nernst constants of dyes **4–8** decrease with the increase of dye hydrophobicity associated with the variation of the aliphatic chain length. For all the dyes, the constant increases in the presence of octanol. Dyes **9** and **10**, containing a glucosyl moiety, give rise to a large decrease of the constants which are influenced neither by the hydrophobic part of the molecule nor by the presence of “microemulsion precursors”. The glucosyl group, with its great hydrophilic properties, seems to be a crucial factor in the dyeing of fibres because of the capacity to form stronger dipole–dipole interactions and hydrogen

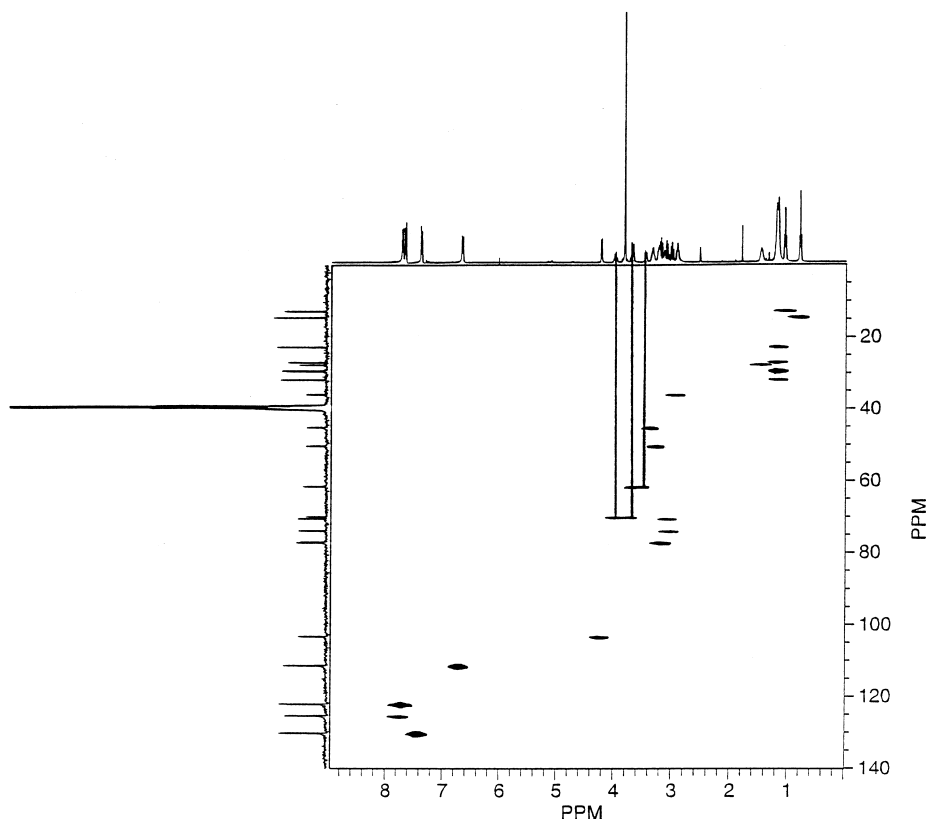


Fig. 4. Dye **10**: ^1H – ^{13}C HETCOR spectrum.

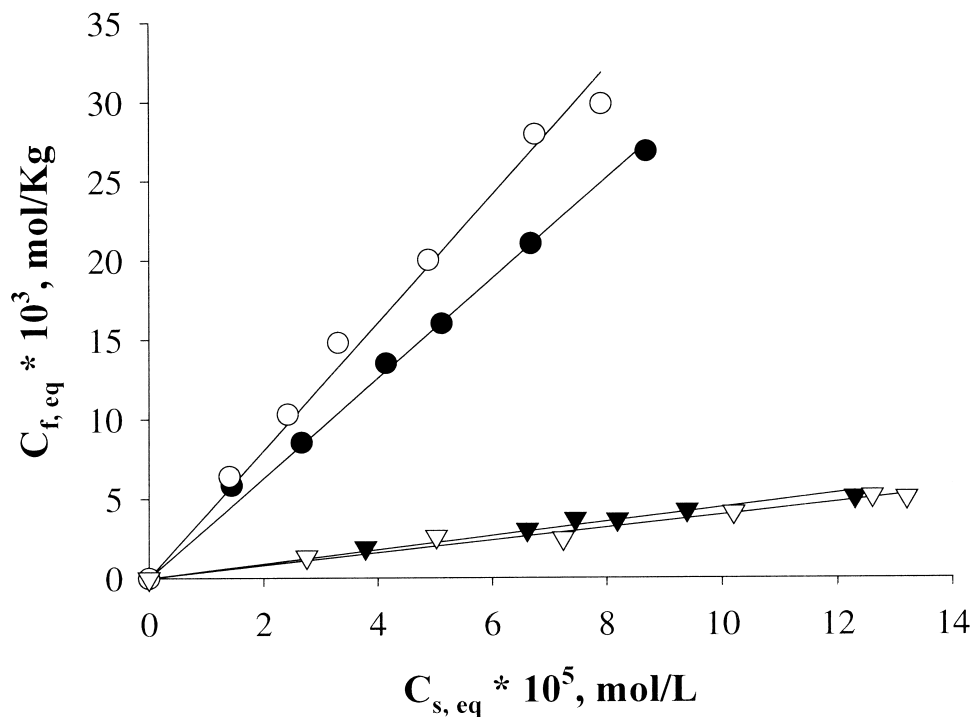


Fig. 5. Dyeing isotherms. Dye **5**: ● SDS 0.76 g/l, Brij 35 0.24 g/l; ○ SDS 0.62 g/l, Brij 35 0.19 g/l, octanol 0.19 g/l. Dye **9**: ▼ SDS 0.76 g/l, Brij 35 0.24 g/l; ▽ SDS 0.62 g/l, Brij 35 0.19 g/l, octanol 0.19 g/l.

Table 5
Partition constants

Dye	Total additives (g/l)	SDS (g/l)	Brij 35 (g/l)	Octanol (g/l)	K (l/kg)
4	1	0.76	0.24	–	367±7
5	1	0.76	0.24	–	303±7
6	1	0.76	0.24	–	254±20
7	1	0.76	0.24	–	187±17
8	1	0.76	0.24	–	139±10
4	1	0.62	0.19	0.19	405±10
5	1	0.62	0.19	0.19	384±15
6	1	0.62	0.19	0.19	356±18
7	1	0.62	0.19	0.19	229±17
8	1	0.62	0.19	0.19	163±8
9	1	0.76	0.24	–	42±2
10	1	0.76	0.24	–	43±3
9	1	0.62	0.19	0.19	40±3
10	1	0.62	0.19	0.19	39±2
9	0.5	0.38	0.12	–	78±2
10	0.5	0.38	0.12	–	111±8

bonds with both the polyamide fibre and the dyeing bath. Isotherms show lower K values probably due to stronger dye interactions with the bath than with the fibre. The greater water solubility of dyes **9** and **10** enables the isotherms to be studied with an halved additives concentration. In this case the constants show a significant increase. Dye **10** (the most hydrophobic one) is particularly sensitive and a threefold increase of K is observed when the additives concentration is halved.

The dyes were also tested in Linitest laboratory experiments in order to evaluate their practical applicability. The dyeing temperature was kept low (80°C) to avoid possible self levelling phenomena. In these conditions the colour levelling effects exerted by additives are measurable. The dyed specimens were tested by tristimulus colorimetry using a well stated methodology [2,3,5,6]. The results are reported in Tables 6–8 in terms of colour intensity (ΔE) and colour uniformity

Table 6

Colour yield (ΔE) and colour uniformity ($\sigma_{\Delta E}$)

Dye	Total additives (g/l)	SDS (g/l)	Brig 35 (g/l)	Octanol (g/l)	Liquor to goods ratio 20:1			Liquor to goods ratio 10:1		
					ΔE	$\sigma_{\Delta E}$	Bath exhaustion (%)	ΔE	$\sigma_{\Delta E}$	Bath exhaustion (%)
4	1	0.62	0.19	0.19	100.3	0.4	98	99.9	0.5	98
5	1	0.76	0.24	–	100.1	0.3	96	101.6	0.1	99
	1	0.62	0.19	0.19	100.3	0.3	97	101.9	0.2	99
6	1	0.76	0.24	–	100.8	0.3	93	102.0	0.3	96
	1	0.62	0.19	0.19	100.9	0.1	95	102.0	0.4	96
7	1	0.76	0.24	–	100.6	0.3	70	99.6	0.6	70
	1	0.62	0.19	0.19	100.0	0.3	76	98.3	0.6	76
8	1	0.76	0.24	–	93.7	1.0	48	89.1	1.6	51
	1	0.62	0.19	0.19	87.9	1.0	53	91.1	0.3	55
9	1	0.76	0.24	–	95.4	0.2	69	97.8	0.4	89
	1	0.62	0.19	0.19	96.9	0.2	76	99.1	0.1	91
10	1	0.76	0.24	–	88.4	0.3	43	91.2	0.2	56
	1	0.62	0.19	0.19	90.5	0.3	46	91.9	0.3	59
5	0.5	0.38	0.12	–	101.5	0.4	99	101.8	0.4	99
9	0.5	0.38	0.12	–	98.5	0.3	82	99.6	0.4	94
7	0.5	0.38	0.12	–	100.4	0.5	85	100.0	0.6	91
10	0.5	0.38	0.12	–	92.2	0.3	51	93.0	0.6	64
5	0	–	–	–	91.4	1.0	* ^a	96.2	1.1	*
9	0	–	–	–	85.4	0.7	*	88.7	0.7	*
7	0	–	–	–	78.6	1.7	*	82.2	3.3	*
10	0	–	–	–	79.6	2.1	*	79.7	2.5	*

^a * Data not reported owing to dye precipitation.

Table 7

Colour yield (ΔE) and colour uniformity ($\sigma_{\Delta E}$)

Dye	Total additives (g/l)	SDS (g/l)	Brij 35 (g/l)	ΔE	$\sigma_{\Delta E}$	Bath exhaustion (%)
5	1	0.76	0.24	101.5	0.7	98
9	1	0.76	0.24	100.1	0.2	96
7	1	0.76	0.24	93.3	0.7	96
10	1	0.76	0.24	99.9	0.5	59

($\sigma_{\Delta E}$). The Linitest experiments were carried out at a liquor to goods ratio 20:1 and 10:1 (Table 6) with all the dyes. The additives concentration was kept constant (1 g/l) while the composition of the additive system was varied to study the influence of octanol on the levelling. Dyeing uniformity is generally good (at liquor to goods ratio 20:1) as shown by the low values of $\sigma_{\Delta E}$. The presence of octanol marginally improves the dyeing uniformity. Only dye **8**, with the longest aliphatic chain, shows a high value of $\sigma_{\Delta E}$. The use of liquor

Table 8

Cyclodextrins effect on colour yield (ΔE) and colour uniformity ($\sigma_{\Delta E}$)

Dye	Additive	ΔE	$\sigma_{\Delta E}$	Bath exhaustion (%)	Liquor to goods ratio
5	Methyl- β -CD	86.0	0.5	72	20:1
9	Methyl- β -CD	79.8	0.1	58	20:1
7	Methyl- β -CD	92.1	0.2	59	20:1
10	Methyl- β -CD	92.9	0.3	56	20:1
5	β -CD	99.4	0.3	93	20:1
9	β -CD	92.5	0.2	80	20:1
7	β -CD	98.6	0.9	97	20:1
10	β -CD	91.0	3.4	91	20:1
9	Methyl- β -CD	82.1	0.5	61	10:1
9	Methyl- β -CD	82.6	0.3	63	5:1

to goods ratio 10:1 gives rise to a general, but limited, decrease in the colour uniformity.

The more hydrophilic properties of dyes **9** and **10** and their higher dispersibility suggest applications in low volume of dyeing bath. In these conditions

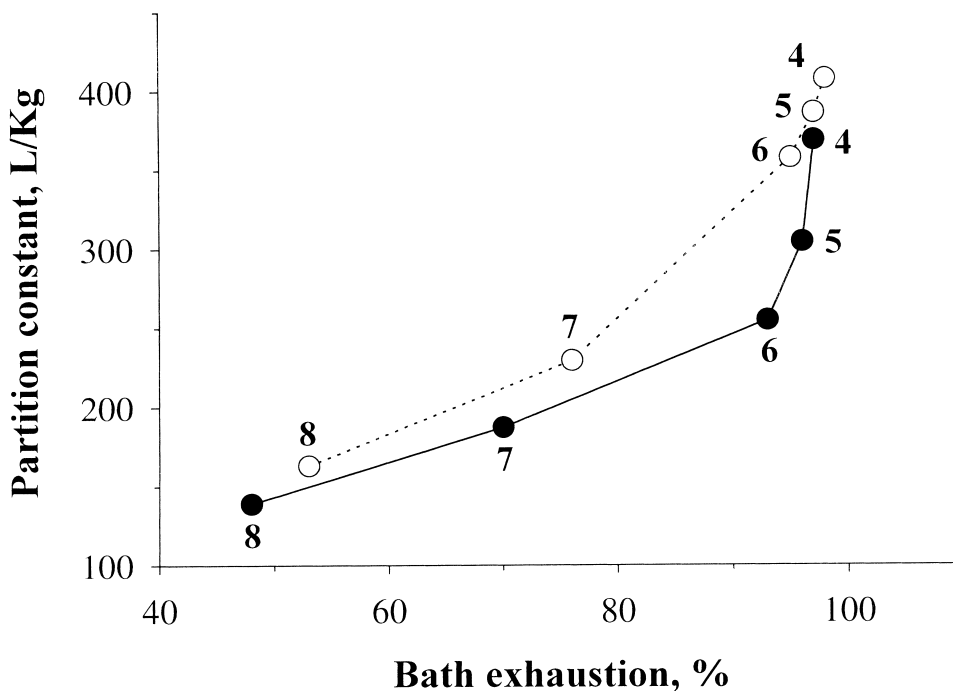


Fig. 6. Correlation between partition constants and bath exhaustion for dyes 4–8. ● SDS 0.76 g/l, Brij 35 0.24 g/l; ○ SDS 0.62 g/l, Brij 35 0.19 g/l, octanol 0.19 g/l. Bath exhaustion measured at liquor to goods ratio 20:1.

(liquor to goods ratio 5:1, Table 7) the increase of alkyl chain length reduces the colour uniformity, the same being observed for dyes 5 and 7. The better performances of dyes 9 and 10 in comparison with dyes 5 and 7 are due to the presence of the glucosyl group. Dye 9, with a short alkyl chain and a glucosyl moiety, shows the more interesting results.

Tests performed with reduced additives concentration (0.5 g/l) provide worse results even at liquor to goods ratio 20:1 (Tables 6). In the absence of additive systems the quality of goods is generally not acceptable with the exception of dye 9. Bath exhaustion is generally high, except for dyes 8 and 10, but decreases with increasing the length of the aliphatic chain and increases in the presence of octanol. The values of bath exhaustion are correlated with Nernst partition constants (Fig. 6), since both factors depend on the dye structure. The presence of a glucosyl moiety gives rise to lower bath exhaustion as well as lower partition constants. Effects analogous to those already reported for dyes 4–8 are observed in the

case of dyes 9 and 10 concerning both the chain length and the presence of octanol. The relative data are not reported in Fig. 6 because dyes 9 and 10 have a different structure.

The dyes 5, 7, 9 and 10 were also tested using cyclodextrins as additives (Table 8) especially since this topic has recently been studied in textile chemistry [6,17–23]. In the presence of methyl- β -cyclodextrin, dye 9 shows good dyeing uniformity even at low liquor to goods ratio. This additive drastically decreases the values of bath exhaustion. Good quality dyeings were obtained using β -cyclodextrin with dyes 5 and 9 and the values of bath exhaustion were comparable to those measured using conventional additives. The different behaviour of cyclodextrins can be correlated with the possible formation of inclusion complexes with dyes [6]. Methyl- β -cyclodextrin is more soluble than β -cyclodextrin [24] and generally their complexes show the same trend. The greater solubility of complexes with methyl- β -cyclodextrin may explain the lower bath exhaustion.

4. Conclusions

A family of model azo dyes has been synthesised, characterised and used to study the influence of additives in the dyeing of polyamide fibre. The effects depend on the hydrophobic properties of each molecule and on the presence of a glucosyl group. This group does not change the linear shape of the dyeing isotherms. Dipole–dipole interactions and hydrogen bonds are enhanced both with fibre and with bath components, being the latter more important. As a result, the affinity of the dye for the polyamide fibre is lowered but its dispersibility in the aqueous phase is enhanced. The presence of the oil phase (octanol) exerts a small but positive effect on both dyeing uniformity and bath exhaustion. Cyclodextrins also give positive effects on the quality of dyeings with disperse dyes.

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