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Dyes and Pigments 60 (2004) 223–232

DYES and PIGMENTS

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Effects of additives on the dyeing of polyamide fibres. Part I: β-cyclodextrin

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Received 29 November 2002; received in revised form 16 June 2003; accepted 9 July 2003

Abstract

A series of 12 dyes were synthesised and used for the dyeing of nylon 6 and 6,6. β-Cyclodextrin was tested as a low environmental impact additive in dyeing processes. Interactions between dyes and β-cyclodextrin were studied by means of solubility isotherms, TGA and DTA analysis. β-Cyclodextrin showed good levelling properties in the dyeing of polyamide fibres. The observed effect can be due to the formation of complexes between β-cyclodextrin and dyes.

Keywords: β-cyclodextrin; Disperse dyes; Dyeing; Solubility isotherms; TGA; DTA

1. Introduction

Synthetic fibres are usually dyed in the presence of additives to obtain a levelling effect on goods' coloration. In the case of disperse dyes, additives also play an important role to enhance the solubility of dyes by the formation of a disperse system. Surfactants are commonly employed for this purpose. On the other hand, the formation of complexes between dyes and cyclodextrins has already been described [1–8] and can be used as an alternative. Low solubility of disperse dyes in water can be increased through the formation of the above mentioned complexes. α, β and γ-Cyclodextrins are the most widely used complexing agents. These are cyclic poly-α-1,4-glucopyranose systems differing in the number of glucopyranose units (6, 7 and 8, respectively). Cyclodextrins have a truncated cone shape (Fig. 1), with hydroxy groups on the extreme border and lone electrons pairs on the oxygens of glycoside bridges on the internal face. These structures give account of the water solubility and the ability of formation of inclusion complexes shown by cyclodextrins.

Cyclodextrins give rise to a selective formation of inclusion complexes only with compounds having a molecular size complementary to the cavity dimensions [9]. No covalent bond is established between host and guest, and consequently the dissociation–association equilibrium in solution becomes one of the most characteristic feature of the host–guest association.

In previous works, cyclodextrins have been examined as possible additives in dyeing processes [10–14].

In the present work a series of disperse dyes was synthesised and used for dyeing polyamide fibres

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doi:10.1016/S0143-7208(03)00142-6

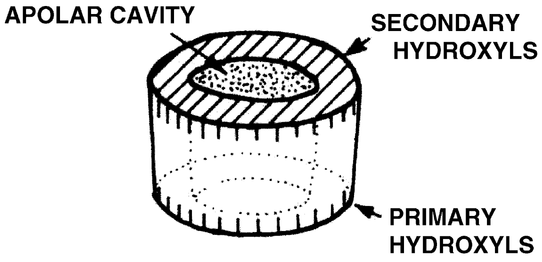


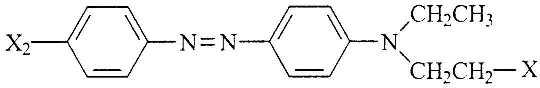
Fig. 1. Cyclodextrins structure.

(nylon 6 and nylon 6,6). β-Cyclodextrin was employed as levelling agent with low environmental impact in order to avoid resort to surfactants.

2. Experimental

Twelve dyes, with the general formula reported in Table 1, were synthesised by coupling the suitable dialkylanilines with the diazonium salts prepared from aniline, 4-methoxyaniline, 4-aminobenzonitrile and 4-nitroaniline, respectively. The coupling reactions were carried out in glacial acetic acid. Sodium hydroxide solution was then added to neutralise the mixture and the precipitate obtained was filtered and washed three times with water. Crude products were purified by crystallisation from ethanol. Dye **6** was also prepared starting from the corresponding dry-state *p*-methoxyphenyldiazonium *o*-benzenedisulfonimide salt [15]. Dry-state diazonium salt (1.0 g, 2.83×10^{-3} mol) was added to a solution of 3-(*N*-ethyl-*N*-phenylamino)propionitrile (0.49 g, 2.83×10^{-3} mol) in acetonitrile at 30 °C. The reaction was carried out for 1 h at 30 °C. Sodium hydroxide solution (20%) was then added and the precipitate obtained was filtered and washed with water. The dye was purified by flash chromatography on silica gel 60, 230–400 mesh (Merck), using petroleum ether/ethyl acetate 80:20 v/v as eluent. Yield 60%.

Table 1
Dyes' structures



Dyes	X_1	X_2
1	H	H
2	H	CH_3O
3	H	CN
4	H	NO_2
5	CN	H
6	CN	CH_3O
7	CN	CN
8	CN	NO_2
9	OH	H
10	OH	CH_3O
11	OH	CN
12	OH	NO_2

Solubility isotherms were measured at six different temperatures (25, 35, 45, 55, 65 and 75 °C). Each isotherm was built with at least 15 points, corresponding to different concentrations of β-cyclodextrin (Wacker–Chemie) in the range 0.0–1.9×10^{-2} M. The same amount of each dye (1.0×10^{-4} mol), dissolved in acetone, was poured into 50 ml flasks. After complete solvent evaporation, different volumes of an aqueous solution 2.1×10^{-2} mol/l of β-cyclodextrin were added and the total volume adjusted adding water up to 25 ml. Dyes solubility was measured by spectrophotometric analysis. In order to destroy β-cyclodextrin–dye complexes, aqueous solutions were filtered and diluted with dimethyl sulfoxide and ethanol to reach the final volume ratio water/ethanol/dimethyl sulfoxide 50/45/5.

Solid β-cyclodextrin–dye complexes were prepared by milling a mixture of the reactants in molar ratio 1:1 and 2:1, for 3 days. Products were then analysed by Thermo Gravimetric Analysis (TGA) and Differential Temperature Analysis (DTA) performed on a simultaneous DTA–TGA SDT 2960 model. Samples (20 mg) were heated from room temperature to 350 °C (10 °C/min). TGA and DTA curves were continuously recorded.

Laboratory dyeing tests were carried out in a Linitest apparatus (Hanau, Germany) using liquor ratio 20:1, 1% o.w.f., pH 7 (TRIS buffer). For each dye seven different dyeing conditions were tested (Tables 5 and 6). Dyeing 1: without additives; Dyeing 2: in presence of a surfactant (Ethofor RO/40 ICAI, Turin, 1 g/l); Dyeing 3: in presence of dye–β-cyclodextrin complex 1:1; Dyeing 4: in presence of dye–β-cyclodextrin complex

1:2; Dyeing 5: in presence of β-cyclodextrin 1g/l; Dyeing 6: in presence of β-cyclodextrin and dye in molar ratio 1:1; Dyeing 7: in presence of β-cyclodextrin and dye in molar ratio 2:1. Dyeing baths were sonicated to improve dye dispersion (ultrasonic apparatus Vibra-cell 120 W). Nylon 6-6 and micro fibre nylon 6 fabric (Sniafibre, Italy) were introduced into the dyeing bath at 40 °C and then the temperature raised up to 80 °C (2 °C/min) and maintained for 1 h. Dyed fibre was then removed, washed at 40 °C with water solution containing soap (2.5 g/l) and sodium carbonate (2 g/l), rinsed and dried at room temperature.

To evaluate colour uniformity tristimulous colorimetry was used [16]. Colour measurements were carried out with a Minolta CR 200 instrument. The colour difference between dyed and undyed specimens was measured on five different positions for each specimen. ΔE represent a mean value of the colour difference. The standard deviation of ΔE ($\sigma_{\Delta E}$) is a measure of colour uniformity.

3. Results and discussions

To evaluate the effects of β-cyclodextrin on the dyeing process of polyamide fibres 12 model dyes were prepared by diazotization of the corresponding amines followed by coupling in glacial acetic acid, according to classical methods. Dye **6** showed a low yield, probably for the low reactivity of the diazonium salt. This is a consequence of the enhanced resonance stabilisation due to the presence of methoxy and diazonium groups in a conjugated position. Moreover, the reactivity of the coupling counterpart was low due to the presence of the CN group on the alkyl chain. The effect of the cyano group on the *p*-position of the phenyl ring was evidenced by ^{13}C NMR spectra [17] of the pairs of dyes **1**–**5**, **2**–**6** and **3**–**7**. Dyes **5**, **6** and **7**, having the CN group in position X_1, showed a systematic deshielding effect (0.7 p.p.m.) on the *p*-position compared to dyes **1**, **2**, **3**.

In order to improve the reaction yield and to obtain an easy purification of the crude product, the synthesis of dye **6** was performed starting from the dry-state *p*-methoxyphenyldiazonium *o*-benzenedisulfonimide salt.

The interactions between the synthesised dyes and β-cyclodextrin were previously studied as evidence for the dye–β-cyclodextrin complexes formation. The solubility isotherms method was used. This method related the solubility of dyes to the concentration of β-cyclodextrin. Solubility isotherms showed a different behaviour depending on the temperature and the dyes. At low temperature (25 and, in some cases, 35 °C), they usually showed three different fields, as reported in Fig. 2 for dye **9**. In the first one the increase of dye solubility was a consequence of the formation of soluble complexes. In this field an excess of solid dye was always present. In the second part (plateau), the water phase became saturated by the complex, so that a further β-cyclodextrin addition caused the precipitation of the complex. In this region the equilibrium gave rise to the transformation of solid dye in solid complex. At the end of the plateau the solid dye completely disappeared and the third part of the isotherm was characterised by the depletion of dye concentration by complex formation and precipitation [18].

The isotherm of dye **9** at 75 °C, reported in Fig. 3, did not show the plateau but only an increasing linear trend due to the higher solubility of the complex. A different behaviour was shown in Fig. 4 for dye **11** at 45 °C. In this case, the dye concentration increased as a curve that could be fitted by means of a second order polynomial equation. The non-linear plot with concave upward curvature evidenced that at least one

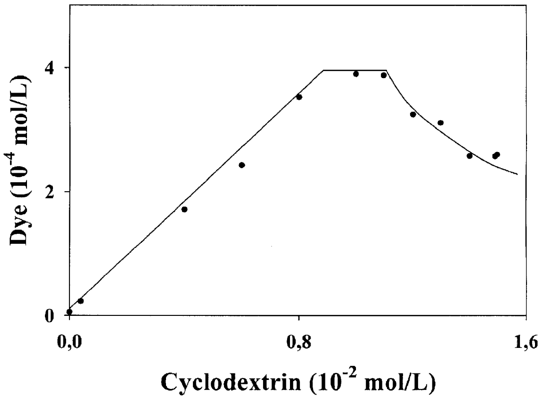


Fig. 2. Solubility isotherm of dye **9** at 25 °C.

complex was present, having a stoichiometry dye$_m$–β-cyclodextrin$_n$ with $n > 1$.

Depending on the behaviour, each isotherm was numerically fitted using a straight line or a second order polynomial equation. For dyes **5–8** linear trends were the most common (only one exception), whereas for the other dyes both behaviours were observed. When a plateau was present, only the first part of the isotherm was considered. Calculated coefficients *a*, *b*, *c* (for the equations

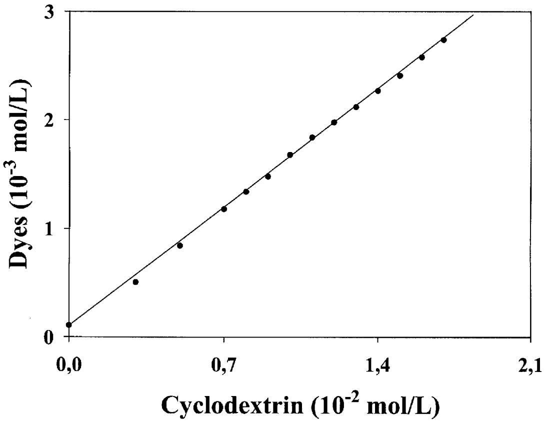


Fig. 3. Solubility isotherm of dye **9** at 75 °C.

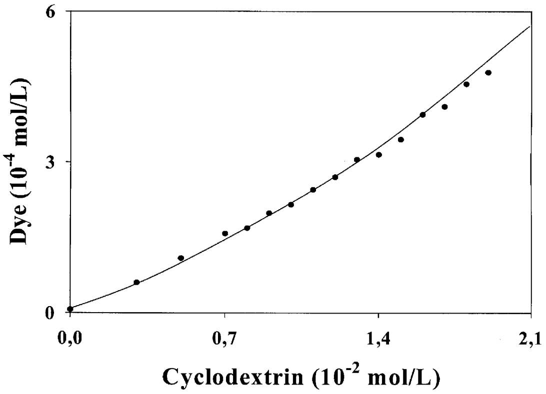


Fig. 4. Solubility isotherm of dye **11** at 45 °C.

Table 2
Solubility and coefficients (a, b, c), correlation coefficient r^2 and Fisher test *F* for dyes **1**–**4**

Dye	*T* (°C)	$S \times 10^7$mol/L [a]	$a \times 10^7$ [b]	$b \times 10^3$ [b]	$c \times 10^2$ [b]	r^2	*F*
1	25	10	9±1	3.8±0.1		0.999	9093
	35	16	14±3	4.3±0.4	21±5	0.998	2253
	45	22	21±4	5.7±0.3	15±2	0.999	4230
	55	24	20±6	6.9±0.4	26±2	0.999	4696
	65	34	31±6	8.7±0.6	34±3	0.999	5268
	75	69	54±9	10.3±0.9	35±4	0.998	2773
2	25	5	5±1	0.9±0.1	11±2	0.999	2221
	35	8	9±3	1.0±0.2	14±2	0.998	771
	45	11	11±3	1.3±0.1	12±1	0.999	1634
	55	39	46±9	2.2±0.3	18±2	0.998	1560
	65	49	56±12	2.0±0.5	24±3	0.998	1984
	75	59	48±15	5.5±0.3	21±2	0.999	6498
3	25	13	12±1	3.2±0.1		0.999	8411
	35	17	14±3	5.1±0.1		0.997	4049
	45	23	18±4	3.0±0.3	8±1	0.998	2168
	55	27	27±6	3.6±0.2	9±1	0.999	4487
	65	31	26±6	5.5±0.4	6±2	0.998	2155
	75	38	30±10	7.3±0.4	9±2	0.998	3823
4	25	4	3±1	0.55±0.02		0.994	1491
	35	4	5±1	0.71±0.01		0.998	3021
	45	5	4±1	0.05±0.02	1.8±0.2	0.998	973
	55	6	6±2	0.21±0.04	1.8±0.2	0.996	1114
	65	10	8±2	0.30±0.04	2.3±0.2	0.998	2069
	75	12	9±3	0.75±0.07	2.0±0.4	0.997	1463

[a] Measured dyes solubility in water.

[b] Calculated coefficients *a*, *b* and *c* (for the equations $y = a + bx$ or $y = a + bx + cx^2$ where y = total concentration of dye, and x = total concentration of β-cyclodextrin).

$y = a + bx$ or $y = a + bx + cx^2$ where y = total concentration of dye, and x = total concentration of β-cyclodextrin) correlation coefficient r^2 and Fisher test F are reported in Tables 2–4. The solubility S of dyes, measured in absence of β-cyclodextrin, are also reported in Tables 2–4. The a and the S data showed comparable values.

Dyes with an hydroxyl group on the alkyl chain (**9**–**12**) showed the highest solubility. The solubility of dyes with the cyano group in position X_1 (dyes **5**–**8**) was similar to the solubility of dyes without substituent in the same position (**1**–**4**), and was higher in the case of dyes with X_2 = H and OCH_3 (**1**–**2**, **5**–**6**). Unsubstituted dyes (X_2 = H; **1**, **5**, **9**) are the most soluble in each series (X_1 = H, OH, CN). Generally, the less soluble dyes have a nitro group in position X_2. High temperatures gave a systematic and exponential increase of solubility.

The general behaviour shown by solubility isotherms is an increase of dyes solubility due to the presence of β-cyclodextrin. These observations can be related to the dyes β-cyclodextrin interactions, due to the formation of inclusion complexes. The complex formation is simply observable by mixing dyes and β-cyclodextrin solutions as it happens in a dyeing bath. To evidence the effects of isolated dye–β-cyclodextrin complexes, a dry milling method was used to have a standard preparation for all the complexes. In effect a wet method can

Table 3
Solubility and coefficients (a, b, c), correlation coefficient r^2 and Fisher test F for dyes **5**–**8**

Dye	T (°C)	$S\ \times 10^7$mol/L [a]	$a \times 10^7$ [b]	$b \times 10^3$ [b]	$c \times 10^2$ [b]	r^2	F
5	25[c]	12	10±4	5.2±0.2		0.996	1199
	35[c]	20	14±5	6.9±0.2		0.994	1294
	45	41	31±9	10.0±0.1		0.998	5184
	55	55	48±11	14.2±0.3		0.996	3189
	65	157	135±22	22.0±0.5		0.995	2244
	75	266	234±37	31.8±0.3		0.999	8735
6	25[c]	6	5±2	5.5±0.1		0.997	1851
	35[c]	26	21±7	6.4±0.2		0.997	1306
	45	34	34±7	8.4±0.1		0.999	4616
	55	78	101±32	13.5±0.4		0.994	944
	65	114	114±16	20.8±0.3		0.998	6446
	75	116	109±20	32.9±0.2		0.999	26,556
7	25	5	7±2	0.54±0.01		0.995	1519
	35	6	8±2	0.73±0.02		0.995	1469
	45	8	9±2	1.17±0.03		0.996	1972
	55	21	25±4	1.92±0.04		0.996	2442
	65	29	29±5	3.30±0.04		0.998	5667
	75	55	51±5	5.33±0.05		0.999	11,025
8	25[d]	–	–	–		–	–
	35[d]	–	–	–		–	–
	45	1.6	1.4±0.6	0.34±0.01		0.994	916
	55	2.3	2.4±0.9	0.52±0.01		0.997	3073
	65	7.5	6.0±1.1	0.87±0.02		0.998	3575
	75	9.2	7.6±2.3	1.18±0.07	1.4±0.4	0.998	3301

[a] Measured dyes solubility in water.

[b] Calculated coefficients a, b and c (for the equations $y = a + bx$ or $y = a + bx + cx^2$ where y = total concentration of dye, and x = total concentration of β-cyclodextrin).

[c] The isotherm shows the presence of a plateau.

[d] Solubility not experimentally detectable.

not be generally used because at low temperature, only some dyes showed the plateau due to the complex precipitation.

To evidence the formation of dye–β-cyclodextrin complexes with dry milling methods a systematic TGA–DTA study was performed. As an example, the study of the dye **9**–β-cyclodextrin complex is reported. In Fig. 5 the TGA–DTA analysis of dye **9** is reported. TGA did not give weight loss at temperatures lower than 220 °C. DTA curve shows an endothermic signal at 125 °C due to the dye melting. In Fig. 6 the same data for β-cyclodextrin are reported. TGA curve shows a 15% weigh loss near to 100 °C due to a loss of water and a higher weight loss at temperatures above 300 °C due to decomposition. DTA gives

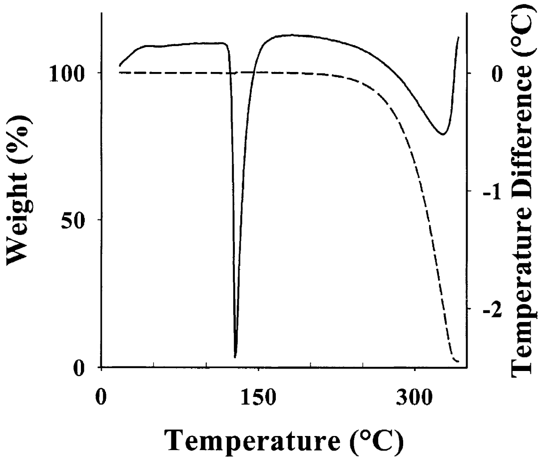


Fig. 5. TGA (- - -), DTA (—) of dye **9**.

Table 4
Solubility and coefficients (*a*, *b*, *c*), correlation coefficient r^2 and Fisher test F for dyes 9–12

Dye	*T* (°C)	*S* $\times 10^7$mol/L [a]	$a \times 10^7$ [b]	$b \times 10^3$ [b]	$c \times 10^2$ [b]	r^2	*F*
9	25[c]	53	65±17	40±1		0.999	3426
	35	125	141±22	55±1		0.998	8993
	45	209	187±36	66±1		0.998	2983
	55	250	216±41	91±2		0.999	3528
	65	803	700±166	113±1		0.998	7707
	75	991	922±160	130±1		0.999	9019
10	25[c]	20	14±8	28±1		0.999	6733
	35	70	77±9	34±1		0.999	10,211
	45	102	92±20	56±4	89±34	0.999	1928
	55	135	115±36	72±4	150±28	0.999	3638
	65	523	553±101	109±6	107±30	0.998	3432
	75	1080	775±266	156±8	117±51	0.998	2681
11	25[c]	18	20±5	9±1		0.998	2491
	35	24	28±6	16±1		0.999	11,193
	45	65	65±9	18±1	38±5	0.999	4780
	55	92	88±19	31±1	21±6	0.999	5578
	65	244	202±55	46±2	31±8	0.999	6636
	75	416	467±60	63±2	60±9	0.999	10,646
12	25[c]	29	30±6	3.4±0.7		0.994	965
	35	36	36±3	3.5±0.1		0.998	3157
	45	76	78±7	5.7±0.1		0.999	9104
	55	79	87±10	8.4±0.1		0.998	3161
	65	87	84±19	12.0±0.1		0.999	6368
	75	142	166±30	12.3±0.7	27±3	0.999	5635

[a] Measured dyes solubility in water.

[b] Calculated coefficients *a*, *b* and *c* (for the equations $y = a + bx$ or $y = a + bx + cx^2$ where y = total concentration of dye, and x = total concentration of β-cyclodextrin).

[c] The isotherm shows the presence of a plateau.

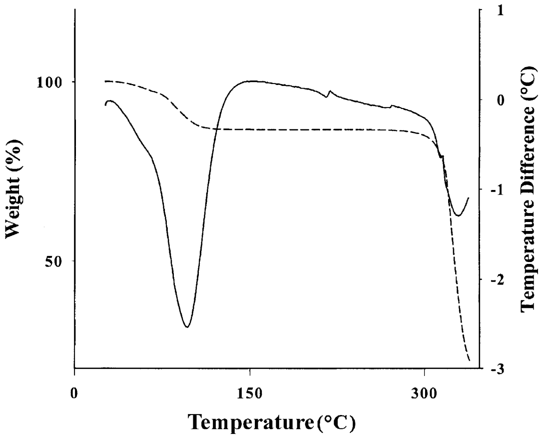


Fig. 6. TGA (- - -), DTA (—) of β-cyclodextrin.

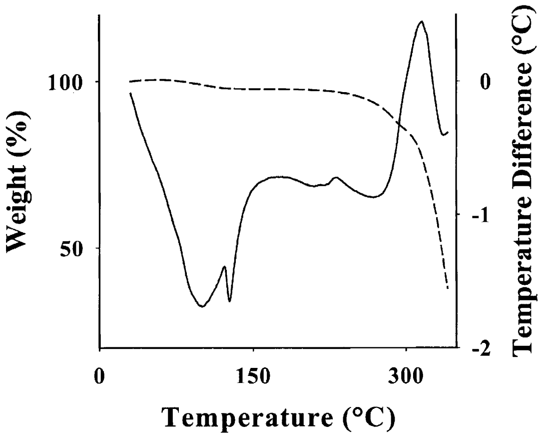


Fig. 8. TGA (- - -) and DTA (—) of milled dye **9**–β-cyclodextrin system, molar ratio 1:1.

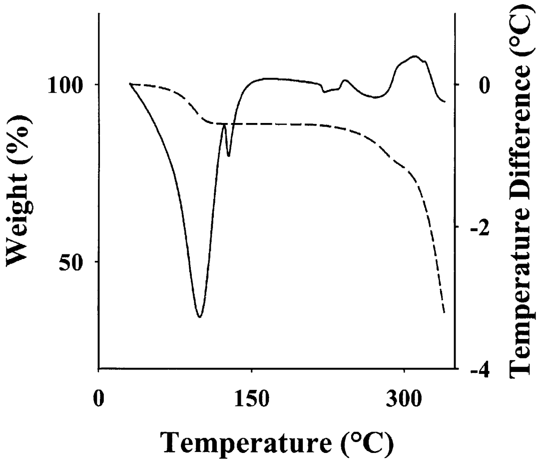


Fig. 7. TGA (- - -) and DTA (—) of dye **9**–β-cyclodextrin system, molar ratio 1:1, without milling.

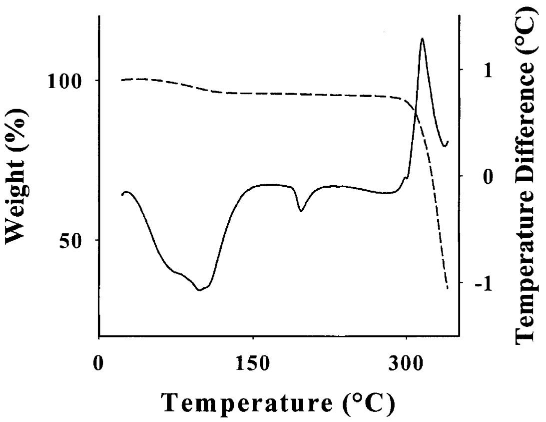


Fig. 9. TGA (- - -) and DTA (—) of milled dye **9**–β-cyclodextrin system, molar ratio 1:2.

evidence of a strong endothermic signal at 100 °C corresponding to the loss of water. The results of DTA analysis for a mixture of dye **9** with β-cyclodextrin (molar ratio 1:1) are reported in Fig. 7. TGA gives evidence of the loss of water at 100 °C and weight loss starting from 200 °C, as in the figures of separated components. Also DTA curve can be interpreted as the sum of dye and β-cyclodextrin curves. Fig. 8 shows TGA–DTA results for the complex prepared by milling, dye **9**–β-cyclodextrin in molar ratio 1:1, for 3 days. In this case the loss of water is still relevable as well as the weight loss related to dye and β-cyclodextrin at higher temperature. The DTA curve gives evidence of the loss of water and the dye fusion at 100 and 126 °C respectively. A new signal at 200 °C appears. This behaviour is explained by the presence of a mixture of unreacted β-cyclodextrin, dye **9**, and complex. A different situation is shown in Fig. 9 corresponding to the product obtained by milling a mixture of dye **9** and β-cyclodextrin in molar ratio 1:2. TGA curve is evidence of a loss of water and decomposition similar to that shown by β-cyclodextrin. DTA curve displays a complex signal corresponding to the loss of water. No signal corresponding to the dye melting is evident.

Table 5
ΔE values for the dyeing of nylon 6 micro fibre

	$\Delta E \pm \sigma \Delta E$						
Dyes	Dyeing 1[a]	Dyeing 2[b]	Dyeing 3[c]	Dyeing 4[d]	Dyeing 5[e]	Dyeing 6[f]	Dyeing 7[g]
1	36.2±1.5	43.5±0.2	45.0±0.9	42.8±1.0	39.4±1.3	38.7±0.9	39.8±1.0
2	32.3±0.7	41.2±1.2	43.0±0.7	43.1±1.3	38.2±0.7	36.7±0.9	39.1±1.0
3	26.8±1.5	44.8±1.6	36.6±0.8	38.8±1.0	37.3±1.7	40.6±1.0	42.9±0.8
4	46.1±1.7	61.1±0.5	55.1±1.3	51.8±1.1	49.2±1.3	49.2±1.6	52.9±0.5
5	68.9±1.8	69.9±1.2	69.2±0.7	71.6±1.0	65.0±1.0	72.0±0.9	73.5±0.8
6	64.3±1.5	74.0±1.0	73.7±0.8	75.8±1.0	71.0±1.1	74.3±1.0	80.9±1.3
7	67.8±1.3	68.6±1.0	66.5±0.9	62.0±1.1	60.9±0.7	67.6±1.1	68.1±1.2
8	45.2±3.2	54.7±0.6	52.8±0.9	52.6±0.6	50.7±0.4	52.1±0.8	53.6±1.2
9	46.2±1.0	49.7±0.8	54.9±0.6	52.9±0.8	53.0±0.6	51.9±0.7	52.0±0.6
10	52.2±0.9	52.0±0.9	51.0±0.4	48.4±0.2	51.0±0.7	48.6±0.5	50.7±0.3
11	64.9±1.0	68.2±0.7	70.1±0.7	66.4±0.9	72.1±0.8	69.0±1.0	71.0±0.7
12	71.6±1.6	75.1±0.3	74.6±0.5	72.9±0.5	74.4±0.6	74.9±0.5	75.2±0.2

[a] Without additives.
[b] Ethofor 1 g/L.
[c] Dye–β-cyclodextrin complex 1:1.
[d] Dye–β-cyclodextrin complex 1:2.
[e] β-Cyclodextrin 1 g/L.
[f] β-Cyclodextrin/dye molar ratio 1/1.
[g] β-cyclodextrin/dye molar ratio 1/2.

Table 6
ΔE values for the dyeing of nylon 6,6

	$\Delta E \pm \sigma \Delta E$						
Dyes	Dyeing 1[a]	Dyeing 2[b]	Dyeing 3[c]	Dyeing 4[d]	Dyeing 5[e]	Dyeing 6[f]	Dyeing 7[g]
1	79.6±1.7	84.2±0.5	82.7±0.8	84.3±0.6	79.8±1.3	83.8±0.5	82.5±0.8
2	69.8±1.6	78.5±0.5	70.4±0.9	77.6±0.5	68.9±3.0	77.7±1.0	79.6±0.6
3	71.5±2.7	76.8±0.5	81.5±0.6	81.9±0.7	70.7±1.0	80.1±0.4	82.1±0.5
4	54.1±2.1	64.2±0.6	59.1±0.5	62.6±0.3	57.5±1.6	59.6±0.7	62.3±0.8
5	73.1±0.7	78.0±0.6	78.2±0.1	76.3±0.6	75.9±0.6	76.8±0.5	77.1±0.4
6	73.2±0.5	76.0±0.6	74.9±0.7	76.3±0.5	75.8±0.8	75.3±0.8	76.0±0.3
7	64.7±1.1	71.0±1.1	65.9±0.8	64.8±1.1	66.4±1.3	65.4±1.0	65.1±1.5
8	44.2±2.4	57.7±1.5	47.2±1.3	49.8±1.4	50.2±1.4	48.8±0.9	49.1±1.5
9	86.2±0.4	88.3±0.4	86.8±0.9	87.1±1.0	86.3±0.8	86.5±0.6	86.9±0.7
10	85.4±1.0	84.7±0.4	84.9±0.7	85.0±0.9	86.0±0.3	83.8±0.7	84.3±0.5
11	80.6±0.4	81.7±0.2	81.5±0.4	82.1±0.3	79.2±0.2	82.3±0.2	82.4±0.2
12	89.9±0.6	84.4±0.5	87.1±0.7	87.4±0.5	86.8±0.5	87.0±0.4	87.2±0.9

[a] Without additives.
[b] Ethofor 1 g/L.
[c] Dye–β-cyclodextrin complex 1:1.
[d] Dye–β-cyclodextrin complex 1:2.
[e] β-Cyclodextrin 1 g/L.
[f] β-Cyclodextrin/dye molar ratio 1/1.
[g] β-Cyclodextrin/dye molar ratio 1/2.

Vice versa, the clear signal at 197 °C can be due to the presence of dye-β-cyclodextrin complex.

Complexes were used in dyeing tests and compared with dyes **1–12**. The dyes were applied without additives or in the presence of a surface active agent. Also the use of β-cyclodextrin as an additive, at different concentrations, was tested, being dye–β-cyclodextrin interactions in solution well evidenced by solubility isotherms.

In Ref. [16] we discussed the validity of tristimulous colorimetry measurements for evaluating both dye uptake and dyeing uniformity. The ΔE values between dyed and undyed fabrics were qualitatively related to dye uptake, ΔE values being higher the higher the dye uptake. The standard deviation ($\sigma_{\Delta E}$) was a measure of the dyeing uniformity. For each dye the best behaviour is shown by high ΔE and low $\sigma_{\Delta E}$ values. Tables 5 and 6 report the data for nylon 6, and nylon 6,6 respectively.

Dyeings were carried out at 80 °C. In these experimental conditions nylon 6,6 was generally dyed more easily than micro fibre nylon 6, as shown by the higher ΔE and lower $\sigma_{\Delta E}$ values. In the absence of additives the dyeings showed a lower intensity and uniformity of coloration. The presence of surfactant gave a general improvement of dyeings. A similar behaviour was observed in presence of β-cyclodextrin, both when directly added to the dyeing bath and when added as complex with dyes. No systematic differences could be observed. Probably, in the present experimental conditions (dyeing temperature, 80 °C, and time, 1 h) free dyes, free β-cyclodextrin and the related complexes were present in dyeing bath as a mixture, independently from the composition of the starting additives.

4. Conclusions

In the present work interactions between azo disperse dyes of dialkylaminoazobenzene series with β-cyclodextrin were studied by means of solubility isotherms. In some cases at lower temperatures a plateau, due to the complex precipitation, was observed. β-Cyclodextrin systematically increases dye solubility due to complex formation. TGA and DTA analysis showed signals indicating the presence of solid complex only in the case of the milled 1:2 dye–β-cyclodextrin mixture. Dyeing tests evidenced a positive effect on colour uniformity and intensity in presence of β-cyclodextrin both when added as free additive and when added as complexes.

Acknowledgements

This work was supported by the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) of Italy. National project "Dry-state arenediazonium *o*-benzenedisulfonimides: synthesis reactivity and applications" and by the University of Turin. The authors thank Wacker–Chemie GmbH for the cyclodextrins kindly supplied.

References

[1] Cramer F, Saenger W, Spaltz HCh. J Am Chem Soc 1967; 89:14.
[2] Szejtli J. Cyclodextrin technology. Dordrecht: Kluwer Academic Publishers; 1988.
[3] Shibusawa T, Okamoto J, Abe K, Sakata K, Ito Y. Dyes and Pigments 1998;36:79.
[4] Buschmann HJ, Denter U, Knittel D, Schollmeyer E. J Text Inst Part I 1998;89:554.
[5] Okubayashi S, Yamazaki A, Koide Y, Shosenji H. J Soc Dyers Colour 1999;115:312.
[6] Barbiric DJ, De Rossi RH, Castro EA. Theochem 2000; 532:171.
[7] Barbiric DJ, De Rossi RH, Castro EA. Theochem 2001; 537:235.
[8] Buschmann HJ. Proceedings of the Eighth International Symposium on Cyclodextrin, Szejtli J, Szente L, editors. 1996; 547–52.
[9] Harata K. Chem Rev 1998;98:1803.
[10] Savarino P, Viscardi G, Quagliotto P, Montoneri E, Barni E. Dyes and Pigments 1999;42:143.
[11] Savarino P, Piccinini P, Montoneri E, Viscardi G, Quagliotto P, Barni E. Dyes and Pigments 2000;47:177.
[12] Savarino P, Viscardi G, Quagliotto P, Geninatti S, Barni E. Proceedings of the National Conference on Supramolecular Chemistry. Italy: Perugia; 1994.
[13] Savarino P, Viscardi G, Quagliotto P, Barni E. Proceedings of the First COST D11 Workshop on Supramolecular Chemistry. Italy: Perugia; 1998.

[14] Buschmann HJ, Knittel D, Schollmeyer E. Text Prax Int 1990;45:376.

[15] Barbero M, Crisma M, Degani I, Fochi R, Perracino P. Synthesis 1998:1171.

[16] Savarino P, Viscardi G, Quagliotto P, Montoneri E, Barni E. J Dispersion Sci Technol 1995;16:51.

[17] Savarino P, Viscardi G, Barni E, Montoneri E, Quagliotto P. Dyes and Pigments 1992;20:1.

[18] Connors KA. Binding constants. The measurement of molecular complex stability. New York: John Wiley and Sons Inc; 1987.