

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

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Abstract

A series of 8 dyes was prepared and used to dye nylon 6 and nylon 6,6. The interactions between dyes and methyl- β -cyclodextrin were studied by solubility isotherms, TGA and DTA analysis.

Methyl- β -cyclodextrin was examined as low environmental impact additive in dyeing processes. Methyl- β -cyclodextrin showed good levelling properties on the dyeing of polyamide fibres. This effect can be due to the formation of complexes between methyl- β -cyclodextrin and dyes.

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

1. Introduction

The dyeing of synthetic fibres is usually performed in presence of additives, to obtain a levelling effect on the coloration of goods. In the case of disperse dyes surfactants are commonly employed. On the other hand, the formation of complexes between dyes and cyclodextrins has already been described [1–8] and can be used in dyeing processes to enhance dye solubility and colour uniformity [9–13]. In part I we showed the effects of β -cyclodextrin on the dyeing of polyamide fibres [14]. In the same way in this work we study the effects of a modified β -cyclodextrin. A commonly used derivative is a methylated β -cyclodextrin.

Methylated cyclodextrins deserve special attention due to their high water solubility. With increasing degree of methylation up to two-thirds of all hydroxyls, the solubility in water increases. Higher methylated derivatives show lower water solubility. For many practical purposes mixtures of partially methylated β -cyclodextrin are commonly used. Only for specific applications such as pharmaceuticals, pure compounds as dimethyl and trimethyl β -cyclodextrins can be used.

2. Experimental

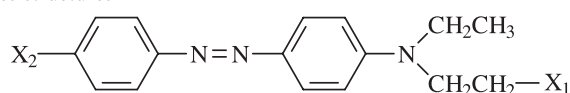
Eight dyes, with the structures reported in Table 1, were prepared and purified as in part I [14]. Their solubility isotherms were measured at three different temperatures (25, 55, and 75 °C) with a previously reported experimental procedure (part I).

Methyl- β -cyclodextrin (Beta W7 M 1.8 Pharma Grade) was kindly supplied by Wacker-Chemie. The

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Table 1
Dyes structures



Dyes	X ₁	X ₂
1	H	H
2	H	CH ₃ O
3	H	CN
4	H	NO ₂
5	CN	H
6	CN	CH ₃ O
7	CN	CN
8	CN	NO ₂

product shows an average degree of substitution of 1.8 methyl groups for each anhydroglucose unit.

Solid methyl- β -cyclodextrin–dye complexes were prepared by milling a mixture of the reactants in molar ratio 1:1, 2:1 and 3:1, 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 on a Linitest apparatus. For each dye nine different dyeing conditions were tested. Dyeing 1: without additives; dyeing 2: in the presence of surfactant (Ethofor, RO/40 ICAI, ethoxylated castor oil average degree of ethoxylation 1/40) 1 g/L; dyeing 3 in the presence of methyl- β -cyclodextrin and dye in molar ratio 1:1; dyeing 4: in the presence of methyl- β -cyclodextrin and dye in molar ratio 2:1; dyeing 5: in the presence of methyl- β -cyclodextrin and dye in molar ratio 3:1; dyeing 6: in the presence of methyl- β -cyclodextrin 1 g/L; dyeing 7: in the presence of dye–methyl- β -cyclodextrin complex in molar ratio 1:1; dyeing 8: in the presence of dye–methyl- β -cyclodextrin complex in molar ratio 1:2; dyeing 9: in the presence of dye–methyl- β -cyclodextrin complex in molar ratio 1:3. Dyeing baths were sonicated to improve dye dispersion (ultrasonic apparatus Vibra-cell 120 W). Nylon 6-6 and microfibre nylon 6 fabric (Sniafibre, Italy) were introduced into the dyeing bath at 40 °C. The temperature was raised up to 80 °C for nylon 6-6 and to 90 °C for nylon 6 at 2 °C/min. The temperature was maintained for 1 h. Dyed fibres were then removed, washed at 40 °C with water solution containing soap (2.5 g/L) and

Table 2
Solubility and coefficients (a , b , c), correlation coefficient r^2 and Fisher test F for dyes 1–8

Dye	T (°C)	$S \times 10^7$ mol/L ^a	$a \times 10^{7b}$	$b \times 10^{3b}$	$c \times 10^{2b}$	r^2	F
1	25	10	10 ± 4	18 ± 1	0.34 ± 0.05	0.997	2221
	55	24	20 ± 9	61.9 ± 0.5	1.51 ± 0.03	0.999	111,534
	75	69	76 ± 15	94 ± 2	1.78 ± 0.1	0.999	23,136
2	25	5	5 ± 2	6.6 ± 0.2	0.29 ± 0.01	0.999	16,182
	55	39	25 ± 14	22.9 ± 0.5	1.43 ± 0.03	0.999	34,436
	75	59	56 ± 11	40 ± 1	1.93 ± 0.05	0.999	25,675
3	25	13	11 ± 3	7.4 ± 0.2	0.21 ± 0.01	0.999	12,420
	55	27	28 ± 12	21.5 ± 0.9	1.36 ± 0.05	0.999	11,991
	75	38	33 ± 14	39.2 ± 0.9	1.64 ± 0.05	0.999	28,277
4	25	4	4 ± 2	0.96 ± 0.04	0.004 ± 0.002	0.999	3457
	55	6	7 ± 1	1.9 ± 0.1	0.273 ± 0.004	0.999	35,118
	75	12	11 ± 3	5.2 ± 0.2	0.35 ± 0.01	0.999	11,383
5	25	12	13 ± 4	27.8 ± 0.4	—	0.998	4675
	55	55	62 ± 12	103.8 ± 0.8	—	0.999	17,154
	75	266	228 ± 37	184.5 ± 0.5	—	0.999	149,022
6	25	6	7 ± 3	45.6 ± 0.4	—	0.998	11,278
	55	78	68 ± 10	120.3 ± 0.2	—	0.999	234,018
	75	116	121 ± 9	229 ± 1	—	0.999	47,202
7	25	5	8 ± 3	2.35 ± 0.01	—	0.999	25,464
	55	21	27 ± 5	14.2 ± 0.1	—	0.999	27,633
	75	55	61 ± 5	28.9 ± 0.1	—	0.999	85,492
8	25	—	0.5 ± 1.6	0.62 ± 0.01	—	0.997	1717
	55	2.3	4 ± 2	3.65 ± 0.03	—	0.999	15,429
	75	9.2	9 ± 5	7.0 ± 0.1	—	0.997	3031

^a Measured dye 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).

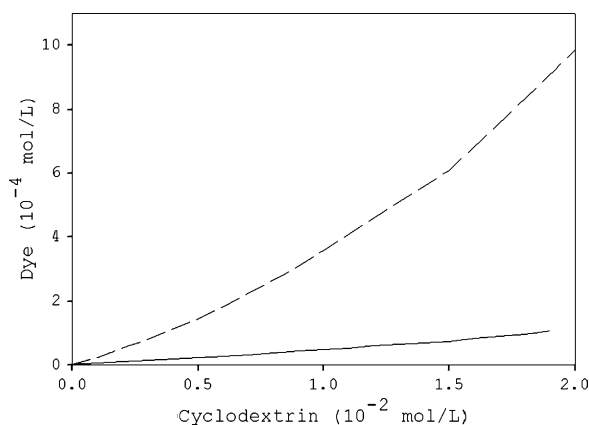


Fig. 1. Solubility isotherms of dye 3 at 55 °C (--- methyl- β -cyclodextrin, — β -cyclodextrin).

sodium carbonate (2 g/L), rinsed and dried at room temperature.

To evaluate colour uniformity tristimulus colorimetry was used [15]. Colour measurements were carried out with a Minolta CR 200 instrument. The colour difference between dyed and undyed specimen was measured on five different positions for each specimen. ΔE represents a mean value of the colour difference. The standard deviation of ΔE ($\sigma_{\Delta E}$) is a measure of colour uniformity.

Washing fastness were performed at 60 °C accordingly to standard procedures [16].

3. Results and discussions

The solubility isotherms showed a different behaviour depending on the examined dye. From dye 1 to dye 4 ($X_1 = H$), the dye concentration increased with the increase of methyl- β -cyclodextrin concentration, as a curve fitted by means of a second order polynomial equation. The non-linear plot with concave upward curvature evidenced that at least one complex was present, having a stoichiometry dye_m–methyl- β -cyclo-

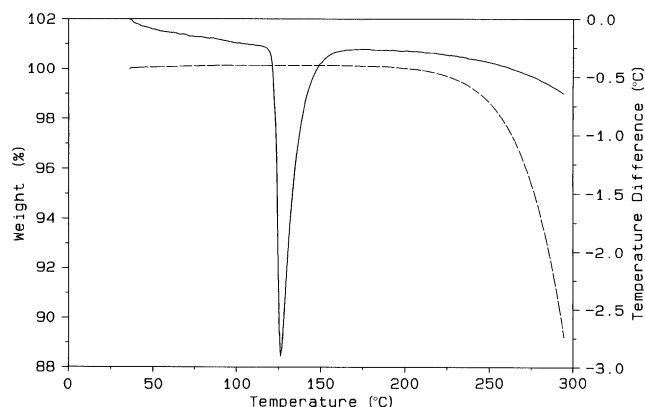


Fig. 2. TGA (---) and DTA (—) of dye 3.

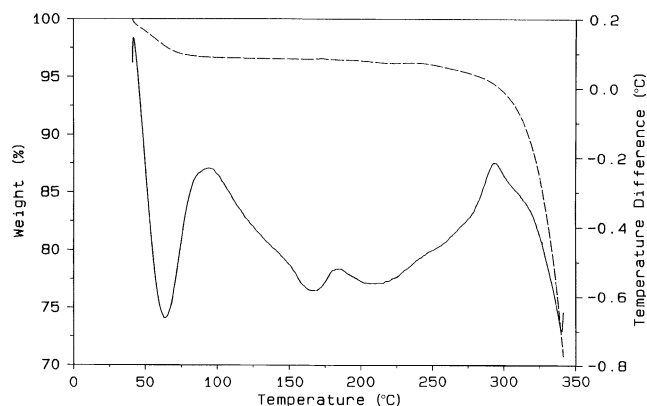


Fig. 3. TGA (---) and DTA (—) for methyl- β -cyclodextrin.

dextrin_n with $n > 1$. The other dyes showed solubility isotherms with a linear trend. Depending on the behaviour the last isotherms were numerically fitted using a straight line. The calculated coefficients (a , b , and c), the correlation coefficient r^2 and Fisher test F are reported in Table 2.

The solubility of the dyes increased with the temperature. Also the coefficients b and c showed an analogous behaviour. The standard error linked to the solubility in absence of methyl- β -cyclodextrin was high. This hinders the possibility of an accurate calculation of the complexation constant with an acceptable standard error.

All the complexes were water-soluble and consequently in no case a plateau was detectable in the solubility isotherms. For this reason complexes were not isolable by precipitation from aqueous medium. A different behaviour was observed for the complexation with β -cyclodextrin [14] where a plateau was present in some cases. The methyl- β -cyclodextrin strongly enhanced the dyes solubility compared to β -cyclodextrin. This effect is evident by observing the behaviour of solubility isotherms. As an example the isotherms of dye 3 at 55 °C in presence of native β -cyclodextrin and of its methyl derivative are reported in Fig. 1.

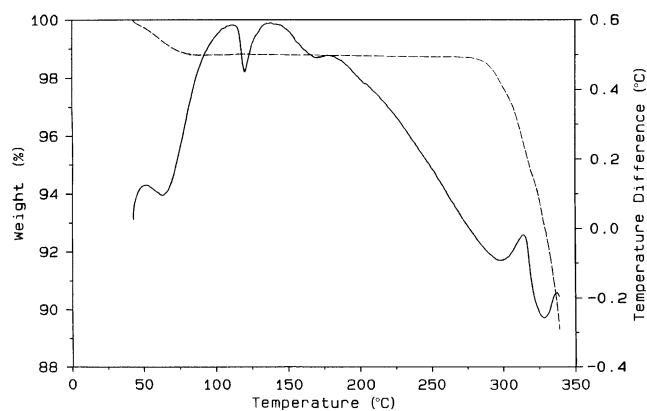


Fig. 4. TGA (---) and DTA (—) dye 3 and methyl- β -cyclodextrin system molar ratio 1:3, without milling.

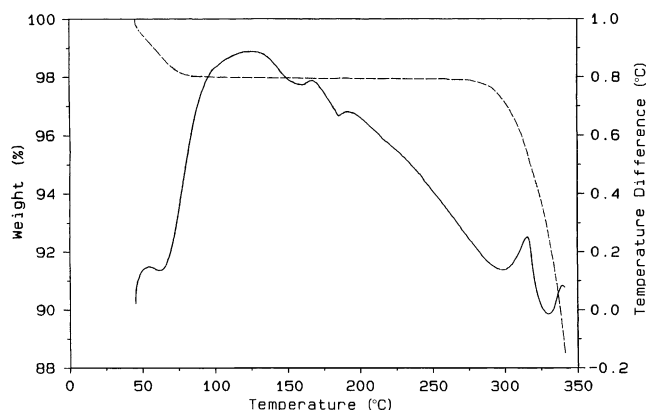


Fig. 5. TGA (---) and DTA (—) dye 3—methyl- β -cyclodextrin complex molar ratio 1:3.

The solubility increase was due to the formation of complexes.

To prepare dye—methyl- β -cyclodextrin complexes a dry milling method was used.

A systematic TGA–DTA study was performed to evidence the formation of complexes.

As an example, the data of the [dye 3—methyl- β -cyclodextrin] system were studied. In Fig. 2 the TGA–DTA analysis of dye 3 is reported. TGA do not show weight loss at temperature lower than 220 °C. DTA curve shows an endothermic signal at 125 °C due to the dye melting. In Fig. 3 the same data for methyl- β -cyclodextrin are reported. TGA curve shows a weight loss of water below 90 °C and an higher weight loss at temperature above 300 °C due to decomposition phenomena. DTA evidences a strong endothermic signal at 64 °C corresponding to the loss of water and two other endothermic signals at 165 and 205 °C.

The results of DTA analysis for a mixture of dye 3 with methyl- β -cyclodextrin (molar ratio 1:3) are

reported in Fig. 4. TGA evidences loss of water below 90 °C and weight loss starting from 280 °C, as for separated components. Also DTA curve can be interpreted as the sum of dye and methyl- β -cyclodextrin curves. Fig. 5 shows TGA–DTA results for the complex prepared by milling dye 3 and methyl- β -cyclodextrin in molar ratio 1:3 for 3 days. Also in this case the weight loss shows a behaviour as for the separate components. DTA curve evidences the loss of water at 60 °C. No signal corresponding to the dye melting is evident as a consequence of the complex formation. In the case of product obtained by milling dye 3 and methyl- β -cyclodextrin in molar ratio 1:1 a feeble signal of dye melting is present. For the molar ratio 1:2 only a shoulder is observed. With the native β -cyclodextrin an exhaustive complexation was observed just with molar ratio dye: β -cyclodextrin 1:2.

Complexes were used in dyeing tests and compared with the corresponding native dyes 1–8. The dyes were applied without additives or in presence of a surface active agent. Also the use of the methyl- β -cyclodextrin as an additive, at different concentrations, was tested, its interactions in solution being well evidenced by solubility isotherms.

In Ref. [15] we discussed the validity of tristimulus 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 3 and 4 report the data for nylon 6,6 and nylon 6, respectively.

Dyeings of nylon 6,6 were carried out at 80 °C. In these experimental conditions microfibre nylon

Table 3
 ΔE values for the dyeing of nylon 6,6

Dye	Dyeing 1 ^a	Dyeing 2 ^b	Dyeing 3 ^c	Dyeing 4 ^d	Dyeing 5 ^e	Dyeing 6 ^f	Dyeing 7 ^g	Dyeing 8 ^h	Dyeing 9 ⁱ
1	79.6 $\pm$ 1.7	84.2 $\pm$ 0.5	83.4 $\pm$ 0.2	86.6 $\pm$ 0.5	85.1 $\pm$ 0.4	87.4 $\pm$ 0.3	83.3 $\pm$ 0.3	83.6 $\pm$ 0.3	82.1 $\pm$ 0.7
2	69.8 $\pm$ 1.6	78.5 $\pm$ 0.5	83.9 $\pm$ 0.6	84.1 $\pm$ 0.2	83.5 $\pm$ 0.4	82.4 $\pm$ 0.3	81.0 $\pm$ 0.6	77.0 $\pm$ 0.4	80.1 $\pm$ 0.2
3	71.5 $\pm$ 2.7	76.8 $\pm$ 0.5	87.4 $\pm$ 0.2	87.7 $\pm$ 0.1	87.7 $\pm$ 0.3	85.6 $\pm$ 0.3	85.5 $\pm$ 0.2	85.2 $\pm$ 0.2	84.3 $\pm$ 0.2
4	54.1 $\pm$ 2.1	64.2 $\pm$ 0.6	67.8 $\pm$ 0.4	68.3 $\pm$ 0.5	70.2 $\pm$ 0.1	62.2 $\pm$ 1.0	70.2 $\pm$ 0.1	70.2 $\pm$ 0.4	70.2 $\pm$ 0.4
5	73.1 $\pm$ 0.7	78.0 $\pm$ 0.6	76.4 $\pm$ 0.4	75.8 $\pm$ 0.7	77.2 $\pm$ 0.5	77.0 $\pm$ 0.8	76.8 $\pm$ 0.5	74.4 $\pm$ 0.5	72.1 $\pm$ 0.5
6	73.2 $\pm$ 0.5	76.0 $\pm$ 0.6	81.9 $\pm$ 0.4	81.5 $\pm$ 0.2	78.1 $\pm$ 0.1	75.9 $\pm$ 0.9	84.5 $\pm$ 0.4	77.5 $\pm$ 0.8	73.2 $\pm$ 0.2
7	64.7 $\pm$ 1.1	71.0 $\pm$ 1.1	75.3 $\pm$ 0.5	75.4 $\pm$ 0.4	75.7 $\pm$ 0.9	74.7 $\pm$ 0.3	71.6 $\pm$ 0.4	72.3 $\pm$ 0.4	72.2 $\pm$ 0.2
8	44.2 $\pm$ 2.4	57.7 $\pm$ 1.5	61.9 $\pm$ 0.2	62.1 $\pm$ 0.2	62.3 $\pm$ 0.3	61.9 $\pm$ 0.2	62.3 $\pm$ 0.2	61.8 $\pm$ 0.3	61.9 $\pm$ 0.3

^a Without additives.

^b Ethofor 1 g/L.

^c Methyl- β -cyclodextrin–dye molar ratio 1:1.

^d Methyl- β -cyclodextrin–dye molar ratio 2:1.

^e Methyl- β -cyclodextrin–dye molar ratio 3:1.

^f Methyl- β -cyclodextrin 1 g/L.

^g Dye–methyl- β -cyclodextrin complex molar ratio 1:1.

^h Dye–methyl- β -cyclodextrin complex molar ratio 1:2.

ⁱ Dye–methyl- β -cyclodextrin complex molar ratio 1:3.

Table 4
 ΔE values for the dyeing of nylon 6 microfibre

Dye	Dyeing 1 ^a	Dyeing 2 ^b	Dyeing 3 ^c	Dyeing 4 ^d	Dyeing 5 ^e	Dyeing 6 ^f	Dyeing 7 ^g	Dyeing 8 ^h	Dyeing 9 ⁱ
1	77.8 ± 1.5	86.0 ± 0.2	84.8 ± 0.4	83.8 ± 0.1	83.8 ± 0.3	84.6 ± 0.7	82.8 ± 0.5	82.8 ± 0.4	82.6 ± 0.3
2	69.2 ± 2.4	75.4 ± 0.9	74.6 ± 0.6	74.1 ± 0.4	73.4 ± 0.7	73.7 ± 0.6	79.1 ± 0.5	76.8 ± 0.6	80.8 ± 0.7
3	75.7 ± 1.0	82.1 ± 0.4	84.7 ± 0.3	86.7 ± 0.3	86.7 ± 0.2	81.8 ± 0.3	87.8 ± 0.2	87.6 ± 0.5	87.1 ± 0.7
4	58.6 ± 2.6	63.4 ± 0.5	66.4 ± 0.2	67.2 ± 0.2	67.9 ± 0.6	66.0 ± 0.4	67.9 ± 0.2	67.7 ± 0.4	67.5 ± 0.6
5	70.9 ± 1.6	75.3 ± 1.0	74.8 ± 0.5	72.5 ± 0.7	71.0 ± 0.6	73.8 ± 1.8	78.2 ± 0.4	72.5 ± 0.4	77.4 ± 1.0
6	64.7 ± 1.5	79.5 ± 0.4	69.9 ± 0.9	70.4 ± 0.9	69.8 ± 0.6	70.4 ± 0.5	78.9 ± 0.6	76.3 ± 0.2	71.9 ± 0.3
7	67.9 ± 1.0	73.5 ± 0.3	74.0 ± 0.5	69.5 ± 0.3	69.9 ± 0.2	67.7 ± 0.6	70.8 ± 0.4	71.0 ± 0.5	71.0 ± 0.3
8	47.2 ± 1.9	61.3 ± 0.2	62.2 ± 0.1	57.6 ± 0.7	61.1 ± 0.5	60.8 ± 0.2	60.2 ± 0.2	59.0 ± 0.2	59.3 ± 0.3

^a Without additives.

^b Ethofo 1 g/L.

^c Methyl- β -cyclodextrin–dye molar ratio 1:1.

^d Methyl- β -cyclodextrin–dye molar ratio 2:1.

^e Methyl- β -cyclodextrin–dye molar ratio 3:1.

^f Methyl- β -cyclodextrin 1 g/L.

^g Dye–methyl- β -cyclodextrin complex molar ratio 1:1.

^h Dye–methyl- β -cyclodextrin complex molar ratio 1:2.

ⁱ Dye–methyl- β -cyclodextrin complex molar ratio 1:3.

Table 5
 Washing fastness values

Dye	Nylon 6 microfibre						Nylon 6,6					
	Dyeing 2 ^a			Dyeing 9 ^b			Dyeing 2 ^a			Dyeing 9 ^b		
	<i>D</i>	<i>S_w</i>	<i>S_n</i>	<i>D</i>	<i>S_w</i>	<i>S_n</i>	<i>D</i>	<i>S_w</i>	<i>S_n</i>	<i>D</i>	<i>S_w</i>	<i>S_n</i>
1	2	2/3	2	3/4	3	3/4	2/3	3/4	3/4	2	3/4	3/4
2	2	3	2/3	2/3	3/4	3	3	4	4	3/4	4	3/4
3	2	3	2/3	2	3/4	3	3	3	3/4	3	3/4	3/4
4	2/3	3	2/3	2/3	3	2	3	4	3/4	3	4	3/4
5	2/3	3	2	1	3/4	3/4	2/3	4	4	1/2	4	4/5
6	1/2	3	2	1/2	4	3/4	3	3	3/4	2/3	4	4
7	2	3	2/3	2	4	3/4	2	4	4	1/2	4	4/5
8	2	3/4	3	2	3/4	2/3	2	4	4	2	4/5	4

^a Washing fastness at 60 °C for samples dyed in presence of surfactant. *D* = degradation; *S_w* = staining in wool; *S_n* = staining on nylon.

^b Washing fastness at 60 °C for samples dyed in presence of methyl- β -cyclodextrin. *D* = degradation; *S_w* = staining in wool; *S_n* = staining on nylon.

6 generally gave rise to unlevelled dyeings. Nylon 6 was dyed at 90 °C, to increase the quality of dyed fabrics.

In the absence of additives (dyeing 1 in Tables 3 and 4) the fabrics generally showed the lowest intensity and uniformity of coloration. The presence of surfactant gave an improvement of dyeing quality. A similar behaviour was observed in presence of methyl- 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 and time) free dyes, free methyl- β -cyclodextrin and the related complexes were present in dyeing bath as a mixture, independent from the composition of the starting additives. For the dyeing of nylon 6,6, methyl- β -cyclodextrin give rise to slightly better results than native β -cyclodextrin.

Washing fastness were measured for the dyeings performed in the presence of surface active agent and

methyl- β -cyclodextrin both for nylon 6,6 and nylon 6 fabrics (Table 5). As a consequence of a true dyeing process, independent from the presence of the additives, no systematic effects on washing fastness could be evidenced.

The low values reported can be due to dye structures and strong washing conditions. A feeble better result is pointed out for nylon 6,6 than for nylon 6 fabrics.

4. Conclusions

Solubility isotherms evidenced the formation of complexes between methyl- β -cyclodextrin and the disperse dyes. The formation of complexes gave rise to an increase in dyes' solubility higher than that previously reported for β -cyclodextrin. TGA and DTA showed the presence of solid complexes especially for dyes:methyl- β -cyclodextrin in molar ratio 1:3. Dyeing tests evidenced

a positive effect on colour uniformity and intensity, due to the methyl- β -cyclodextrin. The effect was slightly better than that with the β -cyclodextrin.

The same washing fastness values were obtained using both methyl- β -cyclodextrin and surface active agent.

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