ELSEVIER

Dyes and Pigments 42 (1999) 143–147

DYES and PIGMENTS

Reactivity and effects of cyclodextrins in textile dyeing

P. Savarino *, G. Viscardi, P. Quagliotto, E. Montoneri, E. Barni

Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, Corso Massimo D'Azeglio 48-10125 Torino, Italy

Received 9 November 1998; accepted 1 December 1998

Abstract

Four- to 10-fold improvement of colour uniformity and minor changes of colour yield have been found upon dyeing Nylon 66 and microfiber Nylon 6 fabrics in the presence of cyclodextrin compared to dyeing without it. ^{1}H NMR data supported the role of cyclodextrin as dye complexing agent. Product quality, however, was also dependent on fabric nature, since for conventional Nylon 6, color uniformity was not improved by the presence of cyclodextrin systems.

Keywords: β-Cyclodextrin; γ-Cyclodextrin; Azo–dyes; Inclusion complexes; ^{1}H NMR; Dyeing isotherms; Dyeing tests; Colour measurements

---

1. Introduction

Cyclodextrin (CD) systems yield complexes with many organic compounds [1–14], and in some cases this property has been exploited for the development of commercial products. CD is also promising for textile dyeing [15–22], inasmuch as it may help improving color yield and uniformity. From this perspective, we report here spectroscopic evidence for the formation of CD complexes with dyes **1** and **2**, as well as the effect of β- and γ- CD on the dyeing of polyamide fibers according to their isotherms and/or Linitest experiments.

2. Material and methods

β- and γ-CD were kindly supplied by Wacher-Chemie GmbH. In the text, $\Delta\delta = \delta_1 – \delta_2, \delta =$ proton chemical shift; for dye **1**, δ_1 is the value recorded at 1×10^{-2} M dye concentration in D_2O in the presence of CD, δ_2 is the value for the same proton at the same dye concentration, but in the absence of CD; for CD protons, δ_1 is the value recorded at the above dye concentration, δ_2 is the value recorded for the same proton in the absence of dye **1** at 0.5×10^{-2} M β- and γ-CD concentration in D_2O. All measurements were performed at 70 ± 0.5°C on a Jeol EX 400 spectrometer, using the signal of *ter*-butyl alcohol as external reference.

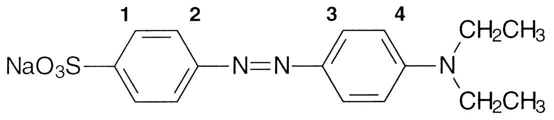
Quantitative dyeing measurements were performed using the experimental system following the procedure described in Ref. [23].

Technological qualitative dyeing tests were carried out on a Linitest apparatus (Hanau-Germany) at a liquor to goods ratio 20:1, at 1% depth (percentage of dye on the weight of textiles), and at pH 4.1 (acetate buffer 0.1 M). Previously wetted polyamide patterns were introduced into the dyebath at 40°C and the temperature raised to 80°C

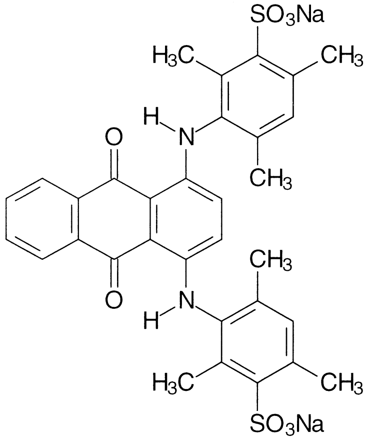
---

* Corresponding author.

PII: S0143-7208(99)00004-2



1



2

Table 1
Colour yield (ΔE) and colour uniformity ($\sigma_{\Delta E}$) by Linitest for different fabrics versus dye/CD mole ratio

Fabric[a]	Dye	CD	[Dye]/[CD]	ΔE[b]	$\sigma_{\Delta E}$[c]	N[d]	CL%[e]	CL%[f]
Ny66	**1**			102.6	0.4	7		
Ny66	**1**	β	1.6	102.7	0.2	7		90.0
Ny66	**1**	γ	1.8	102.0	0.1	7	99.5	99.0
Ny66	**2**			71.2	2.1	7		
Ny66	**2**	β	0.84	72.5	1.7	7		
Ny66	**2**	β	1.7	69.6	5.6	7	97.5	
Ny66	**2**	γ	0.95	69.8	6.2	7	99.0	
Ny66	**2**	γ	1.9	74.7	0.2	7	99.5	99.0
Ny6	**2**			79.0	1.0	5		
Ny6	**2**	γ	1.9	75.0	8.0	5		99.0
Ny6	**2**	γ	0.95	77.0	4.0	5		99.0
Ny6 M	**2**			70.0	4.0	5		
Ny6 M	**2**	γ	1.9	70.0	4.0	5		
Ny6 M	**2**	γ	0.95	71.0	1.0	5	99.5	99.0

[a] Ny, Nylon; M, microfiber.

[b] Mean color difference.

[c] Standard deviation for ΔE mean value.

[d] Number of determinations to calculate ΔE.

[e] Confidence level for the statement of inequality of the ΔE value compared with the corresponding value for the same fabric and dye in the absence of CD.

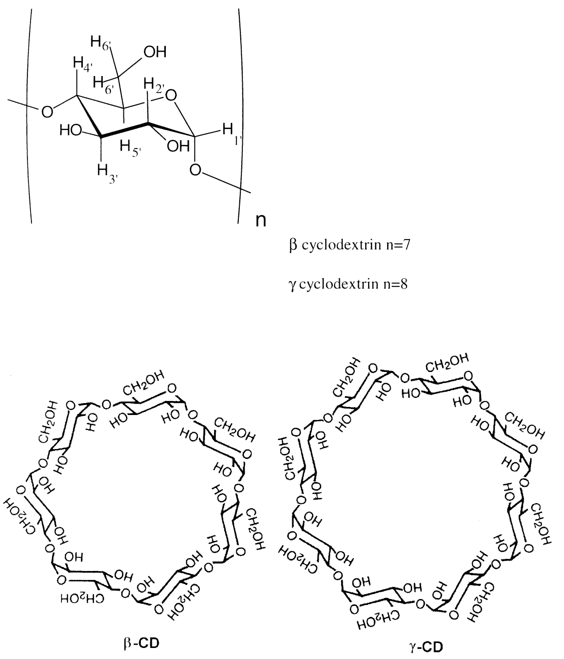
[f] Confidence level for the statement of inequality of the variance $\sigma\Delta E$) value compared with the corresponding value for the same fabric and dye in the absence of CD.

over 20 min and maintained for 1 h. The dyed fibre was then removed, rinsed and dried in hot air. The specimens were evaluated by means of colour measurements. The results (Table 1) are reported as the mean colour difference (ΔE) between dyed and undyed fabrics to evidence colour intensity. The colour uniformity was evaluated by means of the standard deviation ($\sigma_{\Delta E}$) of the mean ΔE values. Statistical treatment of data in Table 1 was performed according to literature procedures [24]. All other details are as previously reported [25].

3. Results and discussion

Evidence for the formation of CD complexes was readily obtained by ^1H NMR spectroscopy. CD has a toroid structure **3**, with the 3′ and 5′ CH protons lying in the enclosed cavity, the 1′,2′ and 4′ CH protons located on the outer surface, and the 6′ CH_2 protons being capable of facing both the inner and the outer space. These protons are good probes for indicating the nearby presence of the interaction with a foreign molecule, occurring either in the inner cavity of the CD ring or on the outer surface, inasmuch as their NMR chemical shift (δ) changes [3–6,10,13].

The ^1H NMR spectra of the β- and γ-CD-dye **1** solutions in D_2O recorded at 0.0, 0.5, 1.0 and 2.0 CD/dye mole ratio exhibited two main features. Relative to the spectra for the authentic compounds at the same concentration (see Materials and methods), in the spectra of the mixtures the number of signals did not change, but a change of chemical shift (δδ) occurred for all protons upon increasing the CD/dye mole ratio, and reached the highest value at 1.0 β-CD/dye-**1** or at 0.5 γ-CD/dye-**1** mole ratio. Also, at higher mole ratio, Δδ values for the dye protons did not change significantly, whereas Δδ values for CD protons decreased. This behavior is explained with the establishment of the equilibria (1) and (2):



3

$$\beta - \mathrm{CD} + \mathrm{dye} - \mathbf{1} \rightleftarrows \beta - \mathrm{CD} - \mathrm{dye} - \mathbf{1} \quad (1)$$
$$\mathbf{I}$$

$$\gamma - \mathrm{CD} + 2\mathrm{dye} - \mathbf{1} \rightleftarrows \gamma - \mathrm{CD} - (\mathrm{dye} - \mathbf{I})_2 \quad (2)$$
$$\mathbf{II}$$

The absence of separate signals for unreacted and reacted reagents indicates that products **I** and **II** are complexes, and that fast exchange occurs between complexed and free reagent molecules. Specifically, the highest $\Delta\delta$ values for dye **1** in the presence of β-CD were 0.5 for CH_3, 0.39 for H4, 0.19 for H3, 0.11 for H2, 0.08 for H1, and in the presence of γ-CD 0.26 for CH_3, 0.17 for CH_2, 0.01 for H4, 0.01 for H1, −0.06 for H2, −0.21 for H3. Peak $\Delta\delta$ values for β-CD were – 0.09 for H3′, −0.10 for H5′, −0.12 for H6′, −0.05 for H1′, −0.02 for H2′, 0.0 for H4′, and for γ-CD−0.10 for H5′, −0.09 for H6′, −0.09 for H3′, −0.04 for H1′, −0.04 for H2′, −0.01 for H4′.

In dye **1** β-CD solutions, the chemical shift of the dye CH_2 protons undergoes the largest change, and its resonance signal is masked by the β-CD proton signals. Analysis of the $\Delta\delta$ values above, reveals that the protons in dye **1** are deshielded due to the interaction with the β-CD, and the deshielding order ($CH_2 > CH_3 > H4 > H3 > H2 > H1$) indicates that the diethylamino group is the site directly involved in the complex formation reaction. At the same time, β-CD protons are shielded as a result of the anisotropic effect of the aromatic rings in the dye molecule. The most shielded protons are in this case H5′, H3′ and H6′, suggesting inclusion of the dye molecule in the inner cavity of the β-CD ring, according to equilibrium Eq. (1). Spectrophotometric measurements at 490 and 520 nm allowe calculation to be made of the dissociation constant (K_d) of complex **I** [2]. The data indicated a quite stable complex ($K_d = 1.0\times10^{-4}$ M at 30°C) which undergoes a slightly increasing dissociation with increasing temperature ($K_d = 3.2\times10^{-4}$ M at 70°C). Similar measurements for complex **II** were not attempted, since a more complex dissociation scheme was expected, due to its stoichiometry.

For the interaction of dye **2** and β- or γ-CD, interpretation of the dye proton NMR spectrum could not be accomplished due to broad dye proton signals before the addition of CD. The broadening of the signals must be related to exchange phenomena in D_2O solution; in dimethylsulphoxide solution, the signals show normal behaviour. Data for CD protons, however, supported the formation of inclusion complexes in this case.The addition of CD to dye **2** gave rise to variation of the chemical shifts of the cyclodextrin protons, with the same behaviour as previously reported. Peak $\Delta\delta$ values for β-CD were −0.05 for H3′, −0.12 for H5’, −0.09 for H6′, −0.05 for H1′, −0.04 for H2′, −0.02 for H4′, and for γ-CD −0.10 for H5′, −0.10 for H6′, −0.08 for H3′, −0.05 for H1′, −0.06 for H2′, −0.03 for H4′.

Explorative dyeing isotherms exhibited typical Langmuir shape. The presence of cyclodextrins appeared to lower the maximum dye uptake, as shown in Fig. 1 for Nylon 6.6 and dye **1**, and for microfiber Nylon 6 and dye **2**.

Laboratory tests on the Linitest apparatus were then performed for a higher number of cases (Table 1). The liquor bath contained a constant dye concentration, but the dye/CD mole ratio was varied over the range indicated by NMR spectroscopic measurements for the formation of 1:1 and 2:1 dye/CD complexes. The results appear contradictory. Dyeing of Nylon 6.6 in the presence of either β- or γ-CD, respectively, at 1.6 and 1.8 dye/CD mole ratio,

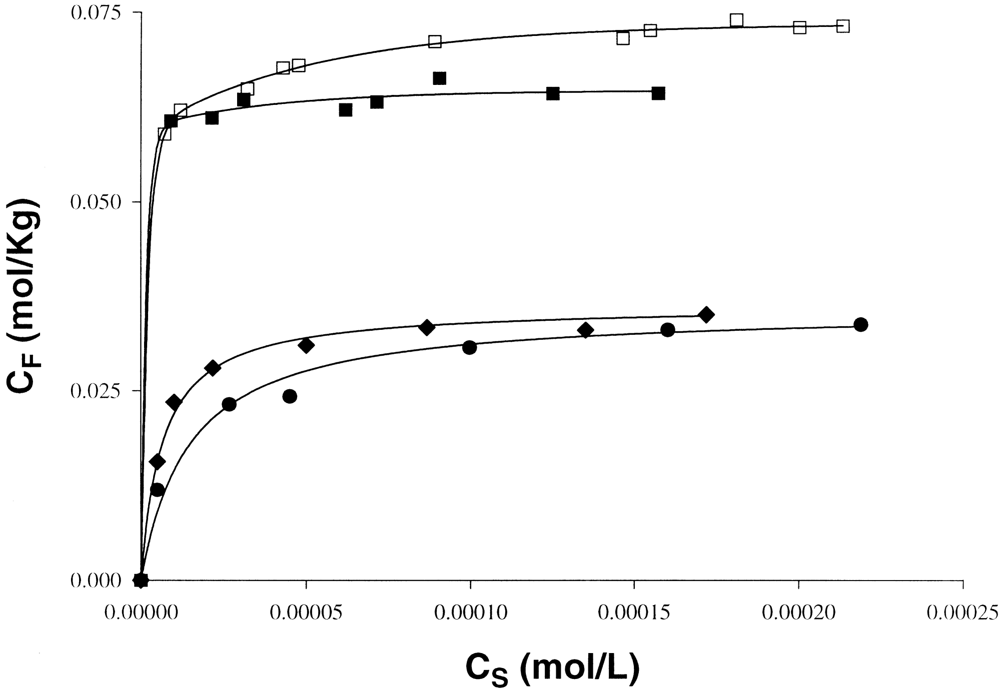


Fig. 1. Dye uptake by fabric (C_F) versus dye concentration in liquor bath (C_S) at 80°C and pH 4.16 for the following systems: nylon 66–dye **1** (◆); nylon 66–dye **1** 1 g/l β-CD (●); microfiber nylon 6-dye **2** (□); microfiber nylon 6-dye **2** 0.5 g/l γ-CD (■).

shows improved dyeing uniformity (from two to four fold lower $\sigma_{\Delta E}$) compared to dyeing in absence of CD. The effect is more significantly (confidence level 99%) marked with γ-CD than with β-CD (confidence level 90%), although in the former case the average color yield ΔE) appears slightly lowered. Also, dyeing of Nylon 6 microfiber and Nylon 66 by dye **2** confirmed γ-CD to yield better dyeing uniformity than β-CD compared to dyeing in absence of CD. However, the dyeing quality does not appear to correlate with the dye/CD mole ratio in the liquor bath, i.e. ten fold lower $\sigma_{\Delta E}$ for Nylon 66 at 1.9 dye **2**/γ-CD mole ratio, four fold lower $\sigma_{\Delta E}$ for microfiber Nylon 6 at 0.9 dye **2**/γ-CD mole ratio, and no effect for this latter system at the higher dye **2**/γ-CD mole ratio. Corresponding changes in colour yield are significant, but the amount of change is relatively minor. Decreasing of dyeing uniformity occurred vice versa for conventional Nylon 6 with dye **2** and γ-CD at all experimental dye/γ-CD mole ratio values, and in a few other cases, as indicated in Table 1.

4. Conclusions

The data obtained show that both β- and γ-CD may yield inclusion complexes with dye molecules, but only the latter has been proven effective for controlling dyeing uniformity. Particularly relevant is the improvement of dyeing uniformity shown with dye **2** and microfiber Nylon 6, in view of the fact that both dye and fiber are known for their tendency to yield unlevel dyeings [25]. Although the positive effect of γ-CD could be related to the relative stabilities of the dye γ-CD complexes, and to the relative rates of release of the dye molecule from the complex and of diffusion through the fiber, the cases exhibiting no effect or negative effect by γ-CD imply a contribution of the nature of the fiber in the dyeing process. Nevertheless, CD appears to have potential for useful application in dyeing technology, and further development of dye–CD systems seems worthwhile.

Acknowledgements

This work was supported by a contribution of National Research Council (CNR) and Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) of Italy.

References

[1] Fornasier R, Scarpa E, Scrimin P, Tecilla P, Tonellato U. J Incl Phenom 1992;14:205.

[2] Li S, Purdy WC. Anal Chem 1992;64:1405.

[3] Suzuki M, Sasaki Y. Chem Pharm Bull 1979;27:609.

[4] Suzuki M, Sasaki Y. Chem Pharm Bull 1979;27:1343.

[5] Suzuki M, Sasaki Y, Sugiura M. Chem Pharm Bull 1979;27:1797.

[6] Suzuki M, Sasaki Y. Chem Pharm Bull 1984;32:832.

[7] Tawarah KM. J Incl Phenom 1992;14:195.

[8] Herseg A, Robinson BH, Kelley HC. J Chem Soc Faraday Trans I 1986;82:1271.

[9] Schiller RL, Lincoln SF, Coates JH. J Chem Soc Faraday Trans I 1987;83:3237.

[10] Suzuki M, Tsutsui M, Ohmori H. Carbohydr Res 1994;261;223.

[11] Suzuki M, Takai H, Ohmori H. Supramol Chem 1994;3:133.

[12] Sanchez AM, De Rossi RH. J Org Chem 1996;61:3446.

[13] Suzuki M, Takai H, Tanaka K, Narita K, Fujiwara H, Ohmori H. Carbohydr Res 1996;288:75.

[14] Shibusawa T, Hamayose T, Sasaki M. Nippon Kagaku Kaishi 1975;12:2171 [Chemical Abstracts 84:75513n].

[15] Buschmann HJ, Knittel D, Schollmeyer E. TPI Tex Prax Int 1990;45:376.

[16] Buschmann HJ, Knittel D, Schollmeyer E. Melliand Textilber 1991;72:E406, 1012.

[17] Okano S. (Toppan Printing Co Ltd). Jpn Kokai Tokyo Koho 78;114:987 [Cl.D06P3 60, 6 October 1978, Appl. 77/29,474 17 March 1977; Chemical Abstracts 90, 56281t].

[18] Shibanai I, Nakamura K. (Japan Liquid Crystal Co Ltd). US Patent 4,772,291 [(C1. 8-526; C09B67/02), 20 September 1988, Appl. 862,069, 12 May 1986; Chemical Abstracts 110, 9232*z*].

[19] Moffatt JR. (Hewlett Packard Co.). US Patent 5,108,505 [(Cl. 106-25; C09Dl 1/14), 28 April 1992, US Appl. 523,969, 16 May 1990; Chemical Abstracts 117, 51024c].

[20] Enmanji K, Takahashi K. (Mitsubishi Electric Corp.). Jpn. Kokai Tokkyo Koho J.P., 04,136,075 [92,136,075] [(Cl. C09B67/08), 11 May 1992, Appl. 90/259,341 26 September 1990; Chemical Abstracts 117, 132903r].

[21] Buschmann HJ, Knittel D, Schollmeyer E. Textilveredlung 1996;31:115.

[22] Szejtli J. Compr Supramol Chem 1996;3:603.

[23] Savarino P, Barni E, Viscardi G, Carpignano R, Di Modica G. J Soc Dyers Colour 1988;104:125.

[24] Natrella MG. Experimental statistics. In: Besson FS, Astin AV, editors. National Bureau of Standards handbook 91. Washington (DC). US Government Printing Office, 1966, [chapters 3 and 4].

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