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Inclusion of Azo Disperse Dyes by Cyclodextrins at Dyeing Temperature

Takao Shibusawa, Josuke Okamoto, Kei Abe, Kunihiko Sakata & Yoshihiko Ito

Faculty of Engineering, Gunma University, Kiryu-shi, 376, Japan

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ABSTRACT

Changes in the sorption isotherms of six azo disperse dyes(4-amino-4-′-nitroazobenzene derivatives) on a hydrophobic fibre from water on addition of α, β and γ CD were measured at 70–90°C. Formation constants and the stoichiometry of the complex formation of the azo dyes with CD's were obtained by analyzing the changes in the isotherms. Most of dyes form 1:1 complex with CD's when their maximum cross section of β-phenyl ring is comparable to, or smaller than, the cavity diameter of CD's. Azo dyes with electron withdrawing bulky groups at the 2′ or 2′ and 6′-position form 2:2 complexes with γ CD. The nature of the complex formations is discussed in terms of the thermodynamic parameters for the complex formations and of the changes in the absorption spectra of the dyes on complex formation. The retarding action of β CD on the dyeing rate of an azo disperse dye on secondary acetate fibres at 90°C was assessed by a computer simulation. © 1997 Elsevier Science Ltd

Keywords: Cyclodextrins, Azo disperse dye, Inclusion complex, Retarder, thermodynamic parameters, environment.

INTRODUCTION

Cyclodextrins (CD's) include dye molecules in their hydrophobic cavity in aqueous solution [1–5] and release the dye molecules as the free dye molecules in the dyebath sorbed by polymer substrates [2, 6]. Therefore CD's may be used as a retarder having affinity for dyes [2], or as a leveling agent in the disperse dyeing of polyester fibre [7]. CD's in effluents can be easily decomposed to carbon dioxide and water through conventional biological treatment. Therefore, CD's may be used as a dyeing auxiliary free from environmental problems [8].

The interactions between dyes and CD's have been studied by means of spectroscopic methods [1–5], but the methods are limited to the temperature range of 5–50°C. The heat haze occurring on the surface of a heated cubet often results in inaccurate measurements of spectral data. Therefore, the temperature ranges so far studied are much lower than practical dyeing temperatures. In the present study, a method is devised to determine the stoichiometry and the formation constant of the dye-CD complex at dyeing temperature (70–90°C). These values are obtained from analysis of changes in the sorption isotherms of the dyes on a polymer from water on addition of a constant concentration of CD's in the dyebath. The nature of the interaction between some azo disperse dyes and CD's are discussed from the viewpoint of the thermodynamic parameters for the complex formation between dyes and CD's, and of the changes in the absorption spectra of the dyes on the complex formations.

THEORY

Sorption isotherms of disperse dyes on polymers from water at dyeing temperature are normally described by eqn (1) [9–13].

$$C_f = K_P\, C_S + \frac{S\, K_L\, C_S}{1 + K_L\, C_S} \tag{1}$$

where C_f and C_S are the dye concentration on polymer and in water at sorption equilibrium, respectively, K_P is the partition coefficient, K_L is the Langmuir sorption constant, and S is the saturation value for Langmuir sorption.

For the complex formation described by eqn (2), the formation constant K_{mn} of the complex is expressed by eqn (3).

$$\begin{array}{ccccc} m\,\text{Dye} & + & n\,\text{CD} & \overset{K_{mn}}{\rightleftharpoons} & \text{Dye}_m\,\text{CD} \\ (a - max) & & (b - nx) & & (x) \end{array} \tag{2}$$

$$K_{mn} = \frac{x}{(a - mx)^m (b - nx)^n} \tag{3}$$

where m and n are stoichiometric coefficients of the reactants (dye and CD) respectively, a and b are the total concentrations of the dye and the CD in solution, respectively and x is the concentration of the complex $\mathrm{Dye}_m\mathrm{CD}_n$.

Dyes lose their affinity on hydrophobic fibres as they are included in the hydrophobic cavity of the CD's [2]. Hence, the sorption isotherm of the disperse dye in the presence of the CD's is expressed by eqn (4).

$$C_f = K_P(a - mx) + \frac{S\,K_L(a - mx)}{1 + K_L(a - mx)} \tag{4}$$

If the dye forms a complex with CD's in the dyebath, the slope of the sorption isotherm of the dye is reduced on addition of CD's into the bath, as shown in Figs 1 and 2.

Computer simulation predicts the shape of the sorption isotherm in the presence of a constant concentration of CD's in the dyebath; it depends on the stoichiometry of complex formation. When the complex with $m{:}n = 1{:}1$ or $1{:}2$ is formed, it will be almost linear as shown in Fig. 1. On the other hand, when the complex with $m{:}n = 2{:}1$ or $2{:}2$ is formed, it will be curved as shown in Fig. 2.

The stoichiometry $m : n$ and the formation constant K_{mn} in eqn (2) can be evaluated by analyzing the change in the isotherm on addition of a constant concentration of CD's. In Fig. 1, the isotherm measured in the presence of

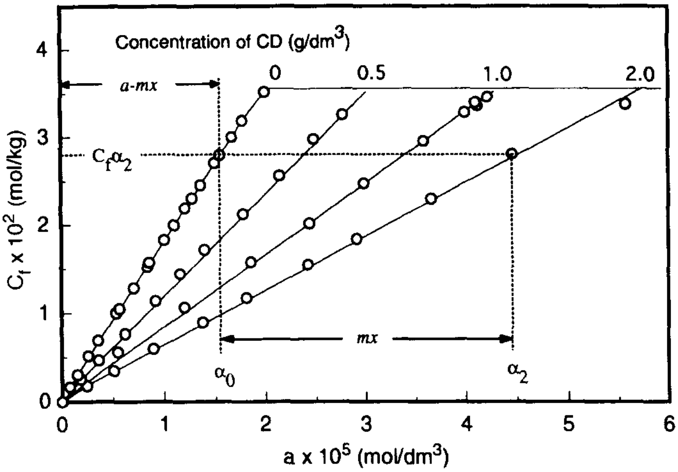


Fig. 1. Change in the sorption isotherm of Dye 1 on secondary cellulose acetate fibre from water on addition of α CD at 80°C. O: experimental point, —; calculated by eqn (4) using $m{:}n = 1{:}1$ and K_{11} given in Table 3. Numerical values shown at the end of isotherms denote the concentration of CD added in the dyebath.

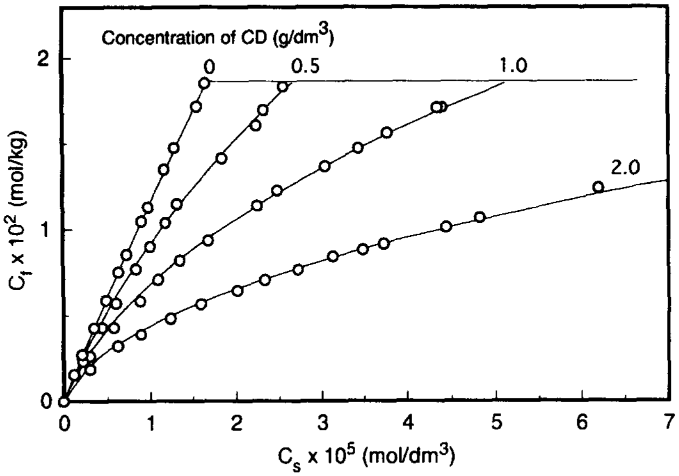


Fig. 2. Change in the sorption isotherms of Dye 6 on secondary cellulose acetate fibre from water on addition of γ CD at 80°C. ○: experimental point, — : calculated by eqn (4) using $m:n = 2:2$ and K_{22} given in Table 3. Numerical values shown near the end of isotherm denote the concentraton of CD added in the dyebath.

2.0 g/dm^3 of α-CD shows that a polymer dyed in the bath of $a = \alpha_2$ mol/dm^3 at equilibrium contains $C_f\alpha_2$ mol/kg of dye, which corresponds to the amount of dye equilibrated with the dyebath of $a = \alpha_0$ in the absence of α CD. Hence, the values of mx and $a - mx$ are easily estimated, as shown in Fig. 1. The shape of the isotherm in the presence of the CD in Fig. 1 indicates that $m = 1$ and $n = 1$ or 2. We can then evaluate approximate values of K_{11} and K_{12} by eqn (3) using the values mx and $a - mx$ estimated above. Similar evaluations for all the data points give the average values of K_{11} and K_{12}. The non linear least squares fit of the experimental points to eqn (3) gives much more reasonable values of K_{11} or K_{12}. In this fitting procedure, the average K_{11} or K_{12} obtained above is used as the first approximation and the value of x is evaluated by eqn (3) for a given value of K_{mn} by means of the Newton-Raphson method. The evaluations described above are also made for the isotherms determined in the presence of 0.5 and 1.0 g/dm^3 of α CD. If the values of m and n used are valid, the procedure described above gives the values of K_{mn} independent of the concentration of CD added.

EXPERIMENTALS

Materials

The structures of the dyes used are shown in Table 1. They are identical with those used in a previous study [13]. Cyclodextrins, α(>97%) and β(>97%)

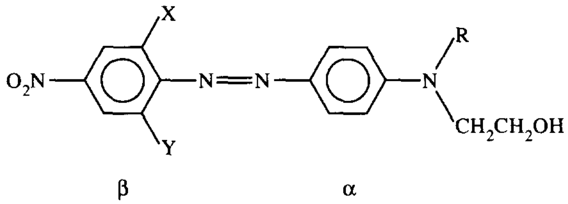
and γ-cyclodextrin (>99%) were purchased from Wako Chemicals Co. Ltd. They were dried *in vacuo* at 100°C for 24 hrs and then used without further purifications. Polymer substrate used was secondary cellulose acetate filament yarn (75d/21 fil., LINDA®, Mitsubishi Rayon Co.). The yarn was treated in water at 95°C for 25 hrs before use. The filament yarn used does not lose its luster even when treated in water at 100°C.

Measurements and calculations

Sorption isotherms were measured by the similar method as used in previous studies [9–11].

The size of the maximum cross section of dye was evaluated from the three dimensional molecular model to minimize the energy of the molecule in MM2 forced field [14]; the model was calculated using 'CCS Chem 3D Plus program' on a Power Macintosh 6200/75 personal computer as exemplified

TABLE 1
Structures of Dyes Used



Designation	X	Y	R	Maximum cross section size of β-phenyl ring (Å)
Dye 1	H	H	CH_2CH_3	6.75
Dye 2	H	H	CH_2CH_2OH	6.75
Dye 3	Cl	Cl	CH_3	9.04
Dye 4	Cl	Cl	CH_2CH_2OH	9.04
Dye 5	NO_2	H	CH_2CH_2OH	8.58
Dye 6	NO_2	Br	CH_2CH_2OH	9.89

by Fig. 3. The van der Waals diameters of Cl, Br and O atoms were taken from the table compiled by Bondi [15]. Other calculations were made similarly as described previous papers [9–13].

RESULTS AND DISCUSSION

Inclusion by α CD

Figure 1 indicates dye 1 forms 1:1 or 1:2 complex with α CD as described before. Non linear least square fit of experimental points to eqn (4) gave the K_{11} and K_{12} listed in Table 2. In Fig. 1, the solid lines passing through the experimental points were calculated by eqn (4) using $m{:}n = 1{:}1$ and K_{11} given in Table 2. The experimental points fitted well to each calculated curve. The values of K_{11} are almost same irrespective of the concentration of CD added. Experimental points also fit well to the isotherm calculated by eqn (4) using $m{:}n = 1{:}2$ and K_{11} in Table 2. However, the values of K_{12} decreased with increasing CD concentration. This finding indicates that Dye 1 forms a 1:1 complex with α CD.

Changes in the isotherms similar to those in Fig. 1 were also observed for dye 2. The values of K_{11} obtained are summarized in Table 3. The value of K_{11} for dye 2 at 80°C was slightly smaller than that for dye 1.

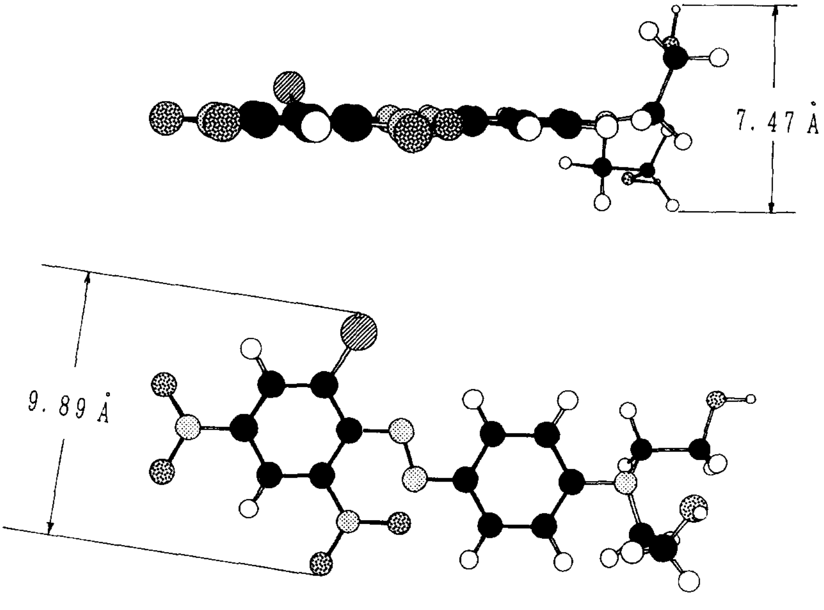


Fig. 3. Three dimensional molecular model of Dye 6 in the minimum energy state in MM2 forces field [13].

For dyes 3–6, the addition of α CD in a dyebath gave an only slight change in the sorption isotherms, indicating these dyes are hardly included by α CD. The internal diameters of CD's estimated by some previous investigators [8, 16, 17] are given in Table 4 . The maximum cross sections (MCS) of the β-phenyl ring of these dyes (Table 1) are much larger than the diameter of the hydrophobic cavity of α CD. This finding indicates that the β-phenyl ring of 4-amino-4′-nitroazobenzene derivatives is included in the hydrophobic cavity of α CD, and MCS is the critical importance for the inclusion.

Inclusion by β CD

Addition of 0.5–2.0 g/dm^3 of, β CD in the dyebath at 80°C caused the similar change in sorption isotherms, as shown in Fig. 1, for all the dyes used.

TABLE 2

Evaluation of the Formation Constants of the Inclusion Complex of Dyes 1 and 6 with CD's at 80°C

	Dye 1-αCD		*Dye 6-γCD*	
Conc. of CD *(g/dm^3)*	$K_{11}/10^3$ *(dm^3/mol)*	$K_{12}/10^6$ *(dm^3/mol)^2*	$K_{21}/10^6$ *(dm^3/mol)^2*	$K_{22}/10^{11}$ *(dm^3/mol)^3*
0.50	1.00	2.29	4.6	1.25
1.00	1.17	1.30	8.4	1.15
2.00	0.93	0.49	15.8	1.06
Average	1.03			1.15

TABLE 3

Formation Constants for the Inclusion Complex of Disperse Dyes with CD's

Dye No.	*Temp. (°C)*	$K_P/100$ *(dm^3/kg)*	$K_i/10^4$ *(dm^3/mol)*	$S\times100$ *(mol/kg)*	*α-CD* $K_{11}/100$ *(dm^3/mol)*	*β-CD* $K_{11}/100$ *(dm^3/mol)*	*γ-CD* $K_{11}/100$ *(dm^3/mol)*	$K_{22}/10^{10}$ *(dm^3/mol)^3*
1	70.0	24.4	17.0	0.478		14.5		
	80.0	17.7	406	0.0433	10.3	10.8	2.4	
	90.0	11.6	0	0		8.4		
2	80.0	3.78	6.47	0.156	8.5	7.6	2.1	
3	70.0	33.2	30.7	0.392		13.9		27.1
	80.0	22.1	0	0		8.6		5.12
	90.0	15.2	0	0		5.8		1.24
4	80.0	5.20	1.74	2.17		6.6		2.20
5	80.0	5.58	10.2	0.159		6.3		0.67
6	70.0	15.0	25.1	0.298				60.2
	80.0	9.90	10.8	0.322		6.7		11.5
	90.0	5.58	10.6	0.216				2.60

TABLE 4
Diameter of Hydrophobic Cavity of CD's

CD	n^a	*Internal diameter (Å)*		
		ref.[16]	[8]	[17]
α	6	4.5	6	5–6
β	7	-7.0	7.5	7–8
γ	8	-8.5	9–10	9–10

[a] Number of glucose unit.

The curve fittings of the experimental isotherms to eqn (4) showed that dyes 1–6 form 1:1 complexes with, β CD. The values of K_{11} are summarized in Table 3, which indicate that the values of K_{11} of dyes with the hydrophilic *N*, *N*-bis-2-hydroxyethyl group (dyes 2 and 4) are slightly smaller than those of dyes with more hydrophobic *N*-substitutent groups, such as *N*-ethyl-*N*-2-hydroxyethyl (dye 1) and *N*-methyl-*N*-2-hydroxyethyl (dye 3). This suggests that the formation constant of the complex increases with increasing hydrophobic nature of dyes.

For dyes 1 and 3, the values of K_{11} at 70 and 90°C were also evaluated by the same method described above, as given in Table 3. These values are used to calculate the thermodynamic parameters for the complex formation.

Inclusion by γ CD

For dyes 1 and 2, the addition of 0.5–2.0 g/dm^3 of γ CD caused similar change in the sorption isotherms, as shown Fig. 1. However, the decrease in the slope of the isotherms was somewhat smaller than that caused by addition of α CD and β CD. The curve fittings of experimental isotherms to eqn (4) showed that both dyes 1 and 2 also 1:1 complexes with γ CD at 80°C but the values of K_{11} are much smaller than those with α CD and β CD, as shown in Table 3. This may be explained in terms of the size of the maximum cross section of the dyes (6.75 Å for dyes 1 and 2) and the diameter of cavity of γ CD (9-10 Å) [8, 17]. The hydrophobic cavity of γ CD seems to be too large to include firmly one molecule of dyes 1 or 2 in the cavity.

Figure 2 indicates that dye 6 forms 2:1 or 2:2 complex with γ CD at 80°C, since the isotherms in the presence of γ CD were curved. The fittings of experimental isotherms to eqn (4) gave the values of K_{21} and K_{22} listed in Table 2. The experimental points fit well to both curves calculated by eqn (4) using $m{:}n = 2{:}2$ and K_{22}, and $m{:}n = 2{:}1$ and K_{21} in Table 2. However, the values of K_{22} were almost a constant, irrespective of the concentration of CD added, whilst the values of K_{21} increase markedly with increasing CD concentration added, indicating the formation of the 2:2 complex.

For dyes 4–6, the changes in sorption isotherms similar to Fig. 2 were observed. The curve fittings also revealed the formation of a 2:2 complex; the values of K_{22} obtained are summarized in Table 3.

For dyes 3 and 6, the values of K_{22} at 70°C and 90°C were also evaluated similarly as given in Table 3.

The 2:2 complex seems to be formed through the stepwise reactions shown below.

$$\begin{array}{ccccc} \text{Dye} & + & \text{CD} & \overset{K_1}{\rightleftharpoons} & \text{DyeCD} \\ (a-y-2z-2x) & & (b-y-z-2x) & & (y) \end{array} \tag{5}$$

$$\begin{array}{ccccc} \text{Dye} & + & \text{DyeCD} & \overset{K_2}{\rightleftharpoons} & \text{Dye}_2\text{CD} \\ (a-y-2z-2x) & & (y) & & (z) \end{array} \tag{6}$$

$$\begin{array}{ccccc} \text{Dye}_2\text{CD} & + & \text{CD} & \overset{K_3}{\rightleftharpoons} & \text{Dye}_2\text{CD}_2 \\ (z) & & (b-y-z-2x) & & (x) \end{array} \tag{7}$$

where x, y and z are the concentration of 2:2 complex(Dye_2CD_2), 1:1 complex(DyeCD) and 2:1 complex(Dye_2CD), respectively, K_1, K_2 and K_3 are the equilibrium constants for each elemental reaction, respectively.

Equations (5–7) give

$$K_lK_2K_3 = \frac{x}{(a-2x-y-2z)^2(b-2x-y-z)^2} \tag{8}$$

If we assume

$$x >> y \quad \text{and} \quad x >> z \tag{9}$$

then we get

$$K_1K_2K_3 = \frac{x}{(a-2x)^2(b-2x)^2} = K_{22} \tag{10}$$

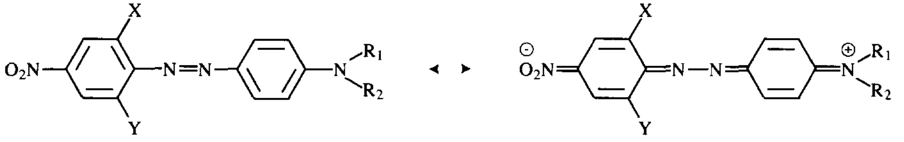
The fact that the experimental points in Fig. 2 fit well to the curves calculated by eqn (4) using $m{:}n = 2{:}2$ indicates the assumption eqn (9) holds equilibrium.

It is noteworthy that azo disperse dyes having electron withdrawing bulky groups at the 2′ or 2′ and 6′-positions of the β-phenyl ring form 2:2 complexes with γ-CD with very large formation constants. On the other hand, dyes having no such substituents (Dyes 1 and 2) form 1 : 1 complexes with γ-CD with small formation constants.

Nature of the complex formations

Table 5 shows the thermodynamic parameters of the complex formation, indicating the nature of complex formation of dyes 3 and 5 with γ CD is significantly different from that of dyes 1 and 3 with β CD; the values of $-\Delta H^\circ$ and $-\Delta S^\circ$ for the 2 : 2 complex formations are very much larger than those for 1 : 1 complex formation. This finding indicates the contribution of very strong exothermic intermolecular interactions for the 2 : 2 complex formations.

It is well known that for 4-amino-4′-nitroazobenzene derivatives [I] that, there is an important contribution of the dipole structure [II due to the intramaolecular charge transfer as shown below [18].



[I] [II]

The extent of the charge transfer increases with introduction of substituents of an electron withdrawing nature at the 2′ and 6′-positions. The structure [II] at excited state is stabilized in a polar environment, so that the

TABLE 5

Thermodynamic Parameters for the Complex Formations and the Spectral Shift of Dyes on Addition of 2 g/dm^3 CD's

Dye No.	*CD*	$-\Delta H^\circ$ *(kcal/mol)*	$-\Delta S^{\circ a}$ *(cal/mol K)*	λ_{max} *(nm) of dye* *in water*	*in 2 g/dm^3 β-CD aq. solution*	*in 2 g/dm^3 γ-CD aq. solution*
1	β	6.73	5.16	502.0	501.0	498.0
2				494.0	493.0	489.0
3	β	10.8	17.1	444.0	443.5	495.0
3	γ	38.2	59.1	444.0	443.5	495.0
4				456.5	444.0	490.0
5				523.0	518.0	532.2
6	γ	38.9	59.5	526.0	521.0	548.5

[a] calculated by molarity basis.

absorption maximum (λ_{max}) of the electronic spectra of [I] shifts to longer wavelength with increasing solvent polarity [18].

Table 5 shows the values of λ_{max} of dyes 3–5 in water and in 2 g/dm^3 of CD's aqueous solution at 30°C; under these conditions, most of dyes in these solutions are included in the hydrophobic cavity of CD's. For dyes 1–6 in 2.0 g/dm^3 β CD aq. solution and dyes 1 and 2 in 2 g/dm^3 γ CD aq. solution, the λ_{max} values are slightly shorter than in water. For Dyes 3–6 in 2 g/dm^3 γ CD aq. solution, λ_{max} shifts to 9.5–51 nm longer wavelength. The red shifts of λ_{max} and the very large values of $-\Delta H^\circ$ for the 2:2 complex formation suggest the presence of strong exothermic interactions stabilizing the dipole structure [II] on complex formation. These findings and molecular size of dye enable us to propose a figure for the 2:2 complex as shown in Fig. 4. Two molecules of dyes are included in a long hydrophobic cavity composed of two molecules of γ CD. In the cavity, the electron rich α-phenyl ring of one molecule of the dye faces to the electron poorer, β-phenyl ring of other dye molecule.

The large values of $-\Delta H^\circ$ for the 2:2 complex formations are favorable for the use of CD as a retarder, since many dyes are released from the cavity of the CD as the temperature is raised, i.e., this characteristic is suitable for a retarder useage.

Effect of the addition of CD's on the rate of dyeing

When the sorption isotherm of a dye is linear and the dye forms a 1:1 complex with CD, the fractional exhaustion (E) of the dye from a finite dyebath in the presence of CD is expressed by eqn (11) [2].

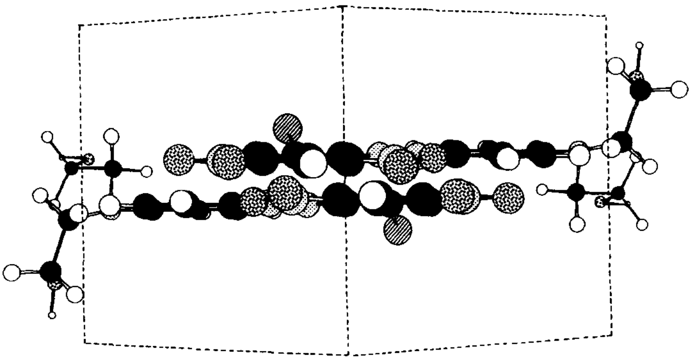


Fig. 4. Arrangement of Dye 6 in the hydrophobic cavity of two molecules of γ CD. Dotted line denotes the cavity size of γ CD.

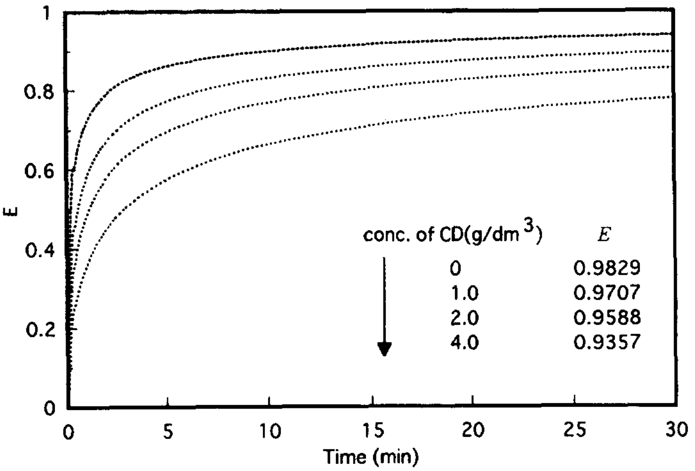


Fig. 5. Computer simulation for the effect of addition of β CD on the rate of dyeing of Dye 1 on secondary cellulose acetate fibre at 90°C. Equilibrium fractional exhaustion (E) in the presence of each concentration of β CD in dye bath are given inside the figure. The rate of dyeing curves were calculated by Wilson's equation using the values of E and $r = 0.02$ cm and $D = 1.0 \times 10^{-9}$ cm^2/min.

$$E = \frac{K_P}{K_P + L(b \times K_{11} + 1)} \tag{11}$$

where L is the liquor to goods ratio and b is the concentration of retarder (mol/dm^3).

If the dyeing rate of the dye from a finite dyebath follows Wilson's equation [19], the rate of dyeing in the presence of CD can be calculated by Wilson's equation using the value of E obtained above.

Figure 5 shows the isothermal rates of dyeing curves of Dye 1 on the secondary cellulose acetate yarn in the presence of various concentrations of β CD at 90°C; the sorption isotherm of Dye 1 at 90°C is linear and meets the origin. The rate of dyeing curves were calculated assuming that the dye is completely dissolved in the dyebath at the start of dyeing and $K_P = 1150$, $K_{11} = 840$(dm^3/mol), radius of fibre(r) = 0.02 cm, diffusivity(D) of dye in fibre = 1.0×10^{-9} cm^2/min (evaluated from the rate of dyeing curve from infinite dyebath) and $L = 20$. Figure 5 shows that CD's will be effective as retarders when $K_{11} >$ *ca.* 1000(dm^3/mol).

CONCLUSION

Some 4-amino-4′-nitroazobenzene derivatives, typical azo disperse dyes, form inclusion complexes with CD's in the dyebath at dyeing temperature (70–90°C).

The formation constants and the stoichiometry of the complexes can be obtained from analysis of the change in the sorption isotherms of the dyes on hydrophobic fibres on addition of CD's.

Most azo disperse dyess form a 1:1 complex with CD's when the maximum cross section of their β-phenyl ring is comparable to, or smaller than the cavity diameter of the CD's.

Azo dyes having an electron withdrawing bulky group at the 2′, or the 2′ and 6′-positions, form 2:2 complexes with γ CD.

For all the dyes used, the heats of complex formations are negative. The values of $-\Delta H^{\circ}$ for the 2:2 complex formation are extremely large.

Computer simulation showed that β and γ CD are effective as retarders.

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