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The Interaction of Acid Azo Dyes with Chemically Modified β-Cyclodextrins

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ABSTRACT

The interaction of acid azo dyes with dimethyl- and trimethyl-β-cyclodextrins was investigated spectrophotometrically. The binding ability was found to increase with the dimethyl derivative, as compared with the original cyclodextrin, due to hydrophobic interaction. On the other hand further substitution of the methyl group decreases binding of the cyclodextrin cavity by steric hindrance for the guest dye molecule. By using thermodynamic quantities of the binding equilibrium the reaction of the inclusion mechanism is discussed. © *1998 Elsevier Science Ltd*

Keywords: dimethyl-β-cyclodextrin, trimethyl-β-cyclodextrin, azo dye, inclusion reaction, hydrophobic interaction.

INTRODUCTION

An acount of the interaction of acid azo dyes containing an alkyl group with cyclodextrins(CD) (α-, β- and γ-) has been reported elsewhere [1]. The dyes were found to be included at a molar ratio of 1:1, and the inclusion equilibrium constants and related thermodynamic quantities were calculated. Using these values the entropy contribution in the inclusion reaction is discussed.

The use of cyclodextrins has now spread to the enhancement of the inclusion ability and obtaining new functions, other than inclusion, introduced by

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various chemical modification such as methylation, hydroxylation, alkylation and acylation reactions. The capped cyclodextrins and coupled cyclodextrins are pertinent examples of the new functional compounds in the field of pharmacology [2].

As methylated cyclodextrins became easily obtainable, studies with chemically modified cyclodextrins is often reported. Recently Yoshida *et al.* [3] investigated the inclusion interaction between di- and trimethyl-cyclodextrins and some azo dyes of the sulfanilic acid $\rightarrow o$-alkylphenol type. They discussed the inclusion, considering the role of water molecules. In this report the interaction between dimethyl- and trimethyl-cyclodextrins (DMCDB and TMCDB, respectively) and monoazo acid dyes was investigated spectrophotometrically to shed more light on the hydrophobic effect in the inclusion process.

EXPERIMENTAL

Materials

β-Cyclodextrin(CDB), DMCDB and TMCDB were purchased from Tokyo Kasei Co. and used without further purification. The water content of the reagents was determined and corrected in preparing the solution. The purified dyes were C.I.Acid Orange 7 (O7), C.I.Acid Orange 20 (O20) and C.I.Acid Red 138 (C12), obtained as described eleswhere [1,4]. Water was used after distillation and deionization by ion-exchange.

Method

Keeping the dye concentration constant, 5.0×10^{-5} mol l^{-1}, the solution was prepared with the concentration of CDB, DMCDB, TMCDB in the abscence of cyclodextrins to 1×10^{-1} mol l^{-1}. The spectra were measured with a Recording Spectrophotometer (Shimadzu, MPS-2000) at 20, 25, 30, 40 and 45 (±0.1)°C.

RESULTS AND DISCUSSION

The spectral change of dye in the presence of CD is shown in Fig. 1 (CDB), Fig. 2 (DMCDB) and Fig. 3 (TMCDB). The changes with CDB and DMCDB are similar in pattern keeping a clear isosbestic point, but with TMCDB the isosbestic point is not clear enough for comparison with the others. In all cases the maximum absorbance does not change with wavelength by the addition of CD, giving a hypochromic effect. This pattern is the same as in the case of the interaction of CD(α-,β- and γ-) with acid azo dyes

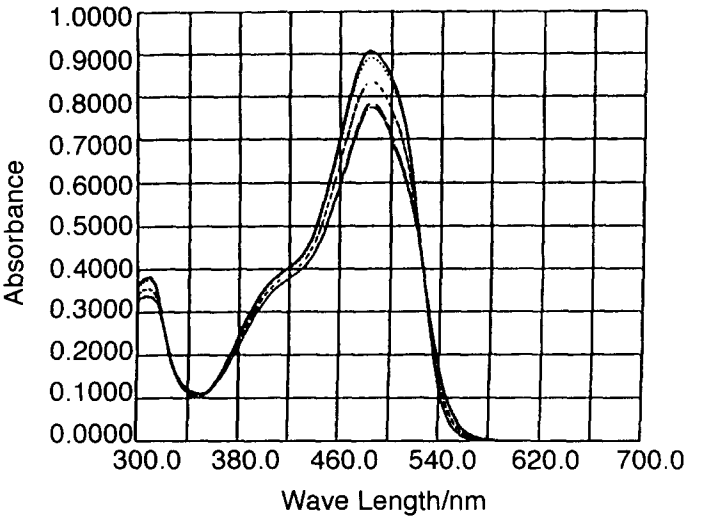

Fig. 1. Spectral change of O7 (I) 25°C; CDB concentration mol l^{-1} ↓ 0, 9.974×10^{-5}, 1.021×10^{-3}, 5.104×10^{-3}, 8.961×10^{-3}.

containing an alkyl group, e.g. C12 in previous work [1]. In the preliminary experiments we confirmed that the pH of the solution did not change before and after the measurement as 5.5–6.0. Therefore, in this experiment, pH buffer solution was not used to avoid the salt effect. Before measurements, it also confirmed that, at a dye concentration of 5×10^{-5} mol l^{-1} used in the experiments, the aggregation of dye could be neglected. The relation between

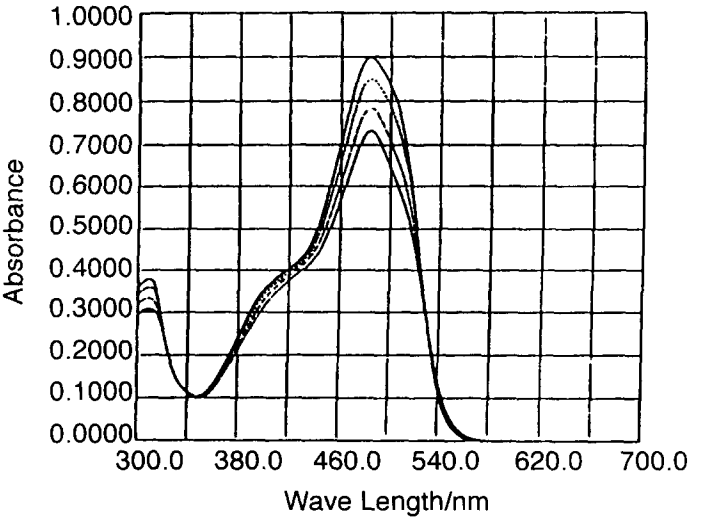

Fig. 2. Spectral change of O7 (II) 25°C; DMCDB concentration mol l^{-1} ↓ 0, 1.075×10^{-4}, 4.630×10^{-4}, 2.315×10^{-3}, 7.292×10^{-3}.

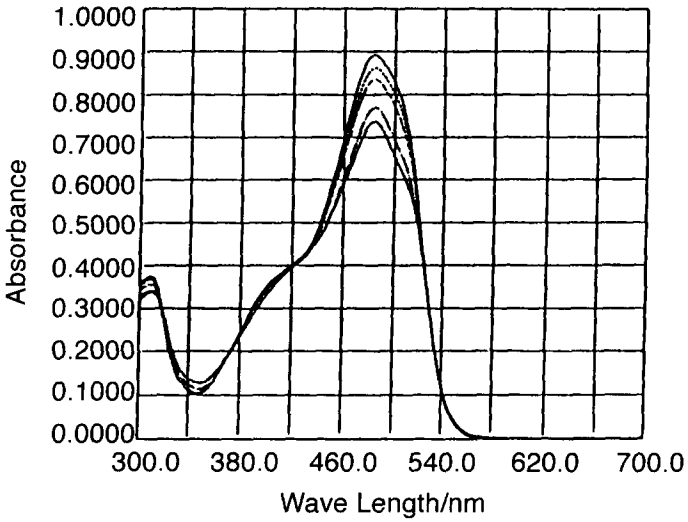

Fig. 3. Spectral change of O7 (III) 25°C; TMCDB concentration mol l^{-1} ↓ 0, 5.148×10^{-4}, 1.006×10^{-3}, 5.077×10^{-3}, 1.560×10^{-3}.

the molecular extinction coefficient (at λmax. = 483 nm) and CDB concentration at 20, 25, 35 and 40°C, is given in Fig. 4. A monotonous decrease of the molecular extinction coefficient with increasing CDB concentration is observed.

As the continuous variation plot gave proof of the equimolar interaction, the equilibrium inclusion constant was calculated by the same procedure, as described eleswere [1].

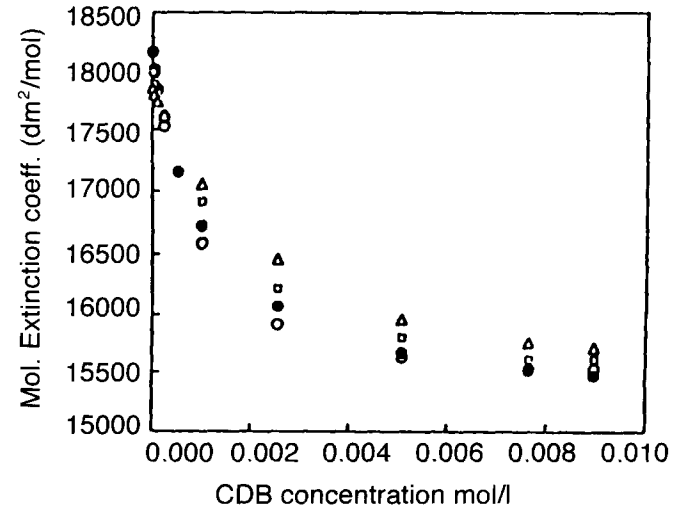

Fig. 4. Molecular extinction coefficient vs CD concentration. Molecular extinction coefficient at 483 nm ○20 ●25 □35 △40°C.

$$MD + NCD \rightleftharpoons D_M \cdot CD_M$$

Equimolar ratio ($M = N$), does not always means 1:1. Thus, assuming the molar ratio is 1:1, simple equilibrium relations containing the binding constant (K), the molecular extinction coefficient of free and bound dye species (ε_f and ε_b, respectively) as unknown parameters were derived.

$$\begin{aligned} C_D &= C_{Db} + C_{Df} \\ C_{Db} &= K(C_{CD} - C_{Db})C_{Df} \\ A_{obs} &= \varepsilon_f \cdot C_{D_f} + \varepsilon_b \cdot C_{Db} \\ C_{Db} &= C_D(\varepsilon_{obs} - \varepsilon_f)/(\varepsilon_b - \varepsilon_f) \end{aligned}$$

in which C_D, C_{Db}, C_{Df} are the total, bound and free dye concentrations, respectively. C_{CD} is the total concentration of CD. A_{obs} and ε_{obs} are the observed absorbance and molecular extinction coefficient of the dye, respectively.

With the use of values of K, ε_f and ε_b obtained from the above equations, the observed values were reproduced, as shown in Fig. 5. Accordingly, we concluded that the molar ratio is 1:1. K values thus obtained are given in Table 1. From these values the thermodynamic quantities were obtained by the van't Hoff plot (Fig. 6) and are given in Table 2. At a similar temperature, the equilibrium binding constant of DMCDB is remarkably large when compared with CDB. Bearing in mind the binding constant of the inclusion complex, K is generally between 10.2 and 10.4 l mol^{-1} [2] and the inclusion ability of DMCDB is quite high, as shown in Table 1. The enhancement of

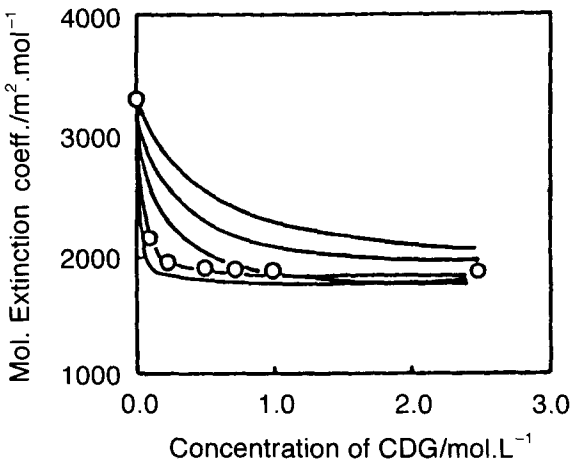

Fig. 5. Calculation of binding constant. ○ experimental value. Binding constant ↓ 2×10^3, 5×10^3 2×10^4, 2×10^5, 5×10^5 l mol^{-1} increasing order.

TABLE 1
Inclusion Equilibrium Constant of O7

Temperature (°C)	K l mol^{-1} CDB	DMCDB	TMCDB
20.0	1500	6150	650
25.0	1000	4350	600
30.0	760	4030	—
35.0	740	3890	450
40.0	600	2750	—
45.0	540	2510	—
50.0	400	—	—

inclusion power compared with CDB is attributed to entropy. As seen in Table 2, the enthalpy changes are −30.7 of CDB to −26.1 KJ mol^{-1} of DMCD and the entropy decrease in DMCDB is far less than CDB. Such an hydrophobic effect is the same as reported in a previous work, in which the guest molecule has an alkyl substituent [1]. To compare with DMCDB (2,6-*o*-methylated CDB), the more hydrophobic TMCDB has a much smaller binding constant. This is attributed to the steric hindrance of the o(3)-methyl group in the cavity of the CD ring. It is worthwhile to point out that the entropy contribution is of the same level, about 20% in the total free energy change in both cases of DMCDB and TMCDB. The order of the magnitude of K is the same as reported by Yoshida *et al.* [3]. The K value of O7 with CDB in buffer solution at pH 7.0 (Clark-Lubbs) is, 11001 mol^{-1} at 25°C and about 10% larger than in pure water (see Table 1). This is attributed to the

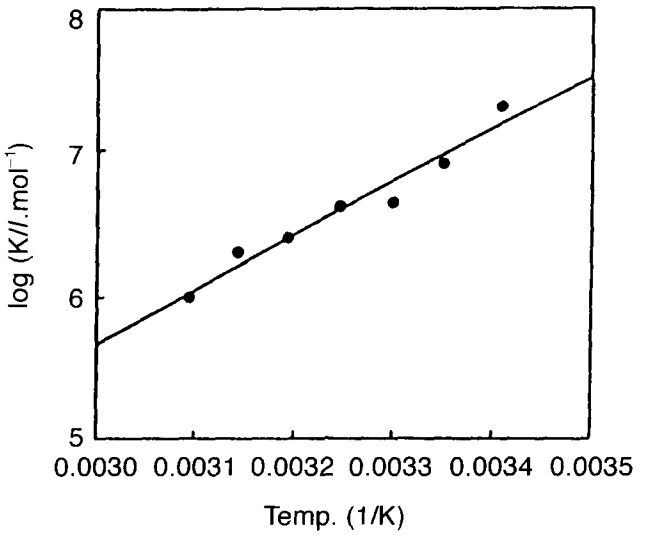

Fig. 6. van't Hoff plot of K.

TABLE 2
Thermodynamic Quantities in Inclusion Equilibrium

	K (25°C) $l\ mol^{-1}$	K (35°C) $l\ mol^{-1}$	$\triangle H$ $KJ\ mol^{-1}$	$\triangle S$ $J\ mol^{-1}\ K$	$T\triangle S$ $KJ\ mol^{-1}$
CDB	1000	740	−30.7	−44.8	−13.4
DMCDB	4350	3980	−26.1	−17.0	−5.1
TMCDB	600	450	−18.9	−10.4	−3.1

increase of the activity of dye and CDB caused by the increase of ionic strength. The fact that C12 dye shows a trivial change of the spectrum in the presence of DMCDB again suggests steric hindrance in the inclusion process.

CONCLUSION

The methylated cyclodextrins form an inclusion complex with the dyes, O7 and O20 in 1:1 molar ratio. 2,6-dimethylation of CD causes the inclusion compound to be more stable with hydrophobic contribution. On the other hand, 2,3,6-trimethylation results in steric hindrance in the cavity of CD, giving the same level of binding constant to the unsubstituted CD. In the case of 2,6-dimethylated CD a guest compound, C12 having a dodecyl group causes steric hindrance.

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