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Inclusion complexation of β-cyclodextrin and 6-*O*-α-maltosyl- and 2-*O*-(2-hydroxypropyl)-β-cyclodextrins with some fluorescent dyes

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ABSTRACT: Spectrofluorimetric titrations were performed in aqueous phosphate buffer (pH 7.20, 0.1 mol dm^{-3}) to determine the binding constants of β-cyclodextrin (**1**), mono(6-*O*-α-maltosyl)-β-cyclodextrin (**2**) and mono[2-*O*-(2-hydroxypropyl)]-β-cyclodextrin (**3**) with four fluorescent dyes, ammonium 8-anilino-1-naphthalenesulfonate (ANS), sodium 2-(*p*-toluidino)naphthalene-6-sulfonate (TNS), Acridine Red (AR) and Rhodamine B (RhB). The fluorescence of ANS, TNS and AR were enhanced, whereas that of RhB was quenched, by the inclusion complexation with β-cyclodextrin hosts **1–3**. It was found that the binding ability of the three cyclodextrin hosts generally decreases in the order **1** > **3** > **2**, which indicates that the hydrophobicity of the substituent affects the original binding ability of parent β-cyclodextrin to some extent. On the other hand, the size, shape and charge of the guest are the crucial factors which dominate the stability of the supramolecular complex formed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: cyclodextrins; fluorescent dyes; inclusion complexation; molecular recognition

INTRODUCTION

Cyclodextrins are torus-shaped cyclic oligosaccharides composed of six, seven or eight D-glucopyranose units, which are named α-, β- and γ-cyclodextrin, respectively. Their exterior, bristling with hydroxy groups, is fairly polar, whereas the interior of the cavity is non-polar. These structural features enable cyclodextrins to accommodate diverse hydrophobic organic and biological molecules to form host–guest or supramolecular complexes in aqueous solution.[1–4] Cyclodextrins have been used extensively as molecular receptors, chemical sensors and enzyme mimics in science and technology.[5,6] Among the three common cyclodextrins, β-cyclodextrin is readily available and bears an appropriate cavity to accommodate bicyclic aliphatic and aromatic compounds, and therefore it has received much more attention than the other analogues. In the past two decades, numerous chemically modified β-cyclodextrins have been designed and synthesized in order either to investigate the mechanisms of enzyme-catalyzed reactions or to achieve solubility in a desired solvent.[7] Although many studies on the molecular recognition of chemically modified cyclodextrins with various guest molecules have been reported and considerable significant results have been achieved,[8–10] it is still of interest to investigate the mechanism and influence factors of this kind of interaction since it may provide a simple model of enzyme–substrate, antibody–antigen and protein–DNA interactions in biological systems.

In this paper, we report the inclusion complexation of β-cyclodextrin (**1**), mono(6-*O*-α-maltosyl)-β-cyclodextrin (**2**) and mono[2-*O*-(2-hydroxypropyl)]-β-cyclodextrin (**3**) (Scheme 1) with four structurally related fluorescent dyes, ammonium 8-anilino-1-naphthalenesulfonate (ANS), sodium 2-(*p*-toluidino)naphthalene-6-sulfonate (TNS), Acridine Red (AR) and Rhodamine B (RhB). (Scheme 2). One important reason for choosing these β-cyclodextrin derivatives as hosts is that glucose-branched β-cyclodextrins and hydroxypropyl-modified β-cyclodextrins can significantly enhance the solubility of hydrophobic guest molecules compared with native β-cyclodextrin and have been used successfully as lipophilic drug carriers and stabilizers in pharmacy.[11,12] The results obtained indicate that the substituent of β-cyclodextrin greatly affects its original molecular binding ability upon inclusion complexation with ANS, TNS, AR

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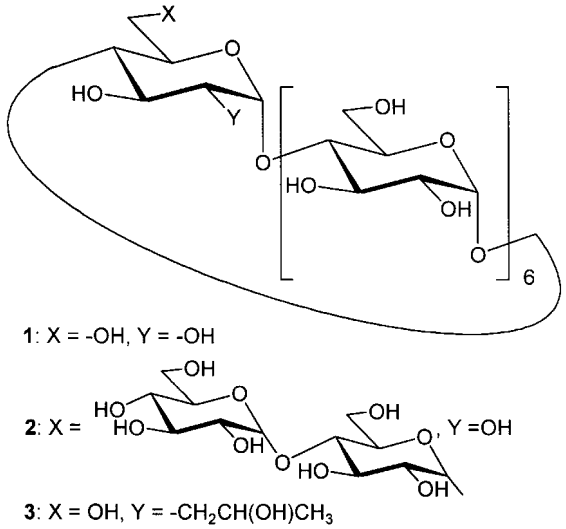


Scheme 1

and RhB. On the other hand, the stability of the complex formed apparently depends on the size, shape and electrostatic density of the guest molecules.

Experimental

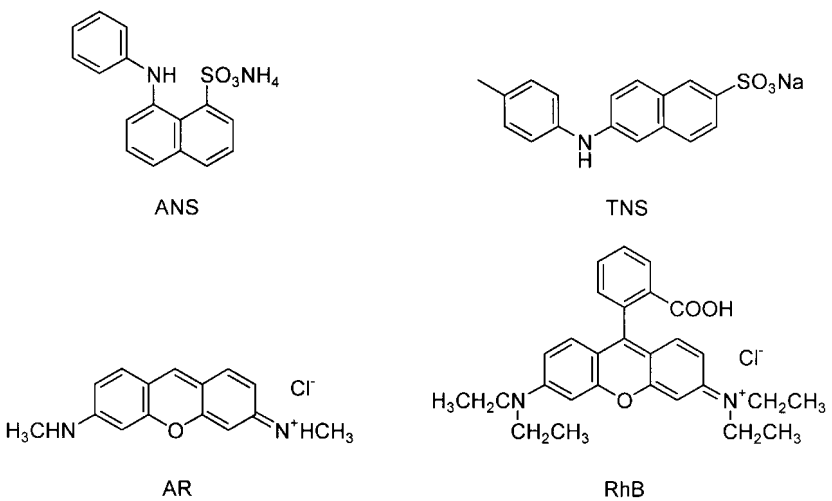
Materials. β-Cyclodextrin (**1**) and mono(6-*O*-α-maltosyl)-β-cyclodextrin (**2**) were purchased from Ensuiko Seito. Mono[2-*O*-(2-hydroxypropyl)]-β-cyclodextrin (**3**) was synthesized by the alkylation of β-cyclodextrin with epoxypropane in aqueous alkali according to the procedues reported by Pitha *et al.*[13]. Ammonium 8-anilino-1-naphthalenesulfonate (ANS) and sodium 2-(*p*-toluidino) naphthalene-6-sulfonate (TNS) were purchased from Tokyo Kasei and Acridine Red (AR) and Rhodamine B (RhB) from Chroma-Gesellschaft Schmid, and were used as received. Sodium dihydrogenphosphate and disodium hydrogenphosphate were dissolved in doubly distilled, deionized water to make a $0.10\,\text{mol dm}^{-3}$ buffer solution of pH 7.20, which was used as solvent throughout the measurements.

Spectral measurements. Fluorescence spectra were measured in a conventional quartz cell ($10 \times 10 \times 40$ mm) on a JASCO FP-750 spectrofluorimeter. The excitation and emission slits were 5 nm for all the fluorescent dyes. The excitation wavelengths for ANS, TNS, AR, and RhB were 350, 350, 490 and 520 nm, respectively. The sample solution containing fluorescent dyes ($1.0 \times 10^{-5}\,\text{mol dm}^{-3}$ for ANS, TNS and AR and $5.0 \times 10^{-6}\,\text{mol dm}^{-3}$ for RhB) and various concentrations of hosts ($0–2 \times 10^{-3}\,\text{mol dm}^{-3}$) were kept at $25.0 \pm 0.1\,^{\circ}\text{C}$ for spectral measurements by a circulating thermostated water-jacket.

Results and Discussion

Fluorescence spectra

ANS and TNS are barely fluorescent in aqueous solution but are very sensitive to environmental changes,[14] which enables us to use these fluorescent dyes as spectral probes to investigate the inclusion complexation with cyclodextrins **1–3**. The relative intensity and the fluorescence emission maxima of the fluorescent dyes examined in the absence and presence of β-cyclodextrin hosts (**1–3**) are listed in Table 1. As expected, the relative intensity of the fluorescence of ANS and TNS is dramatically enhanced upon binding with cyclodextrin hosts. At the same time, the addition of the cyclodextrin hosts caused significant hypochromic shifts (10–25 nm) of the fluorescence peak.



Scheme 2

Table 1. Fluorescent properties of the dye guests in the absence and presence of *β*-cyclodextrin hosts **1–3** (1.0×10^{-3} mol dm^{-3})

Fluorescent dye	Concentration (μM)	Host	λ_{ex}(nm)	λ_{em}(nm)	Relative intensity
ANS	10	None	350	524	1
		1		510	2.4
		2		509	2.1
		3		499	5.8
TNS	10	None	350	496	1
		1		483	16
		2		481	28
		3		480	22.7
AR	10	None	490	561	1
		1		553	4
		2		556	3.6
		3		553	4.2
RhB	10	None	520	575	1
		1		573	0.71
		2		573	0.81
		3		572	0.70

These observations clearly indicate that the residue of ANS or TNS was embedded into the hydrophobic cavity of *β*-cyclodextrin apart from bulk water.

Although both AR and RhB possess a xanthene residue, they exhibit dramatically different fluorescence behavior upon inclusion complexation with the hosts. As can be seen from Fig. 1, with the addition of host **3**, the fluorescence of AR gradually increases, accompanied by slight hypochromic shifts (8 nm, 561–553 nm). This phenomenon is consistent with the observations for ANS and TNS. In contrast, as illustrated in Fig. 2, the fluorescence of RhB is quenched by the addition of a cyclodextrin host. Politzer *et al.* examined the fluorescence changes of RhB at different concentrations with and without the addition of *β*-cyclodextrin and found that *β*-cyclodextrin enhances the fluorescence of RhB in concentrated (10^{-3} mol dm^{-3}) aqueous dye solution but quenches it in dilute (10^{-4}–10^{-8} mol dm^{-3}) dye aqueous solution.[15] These phenomena were ascribed to the existence of dye aggregates in the concentrated aqueous solution. From the equilibrium constant of 2100 dm^3 mol^{-1} for the dimer monomer transition of RhB in aqueous solution determined by Lopez Arbeloa *et al.*,[16] it seems likely that monomers are the predominant species (>99%) at the dye concentration (5×10^{-6} mol dm^{-3}) we used.

We are especially concerned as to whether or not the fluorescence quenching was induced by the formation of an RhB–CD complex. In Fig. 3(a), a typical Stern–Volmer plot for the quenching of RhB by **2** is illustrated. This downward-curving plot may indicate that there are two kinds of species in the RhB dye aqueous solution, one accessible and the other inaccessible to cyclodextrin. Then, a modified Stern–Volmer equation for the above

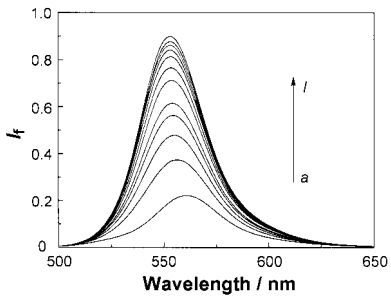


Figure 1. Fluorescence spectral changes of AR (1.0×10^{-5} mol dm^{-3}) on addition of mono[2-*O*-(2-hydroxypropyl)]-*β*-cyclodextrin (**3**) in aqueous buffer solution at pH 7.20. The concentration of **3** increases in the range 0–1.8×10^{-3} mol dm^{-3} from *a* to *l*. Excitation wavelength, 490 nm

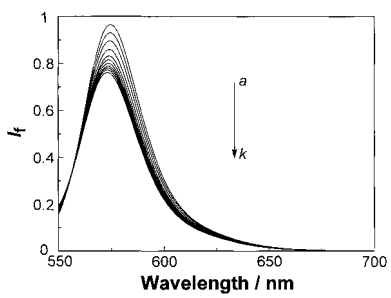


Figure 2. Fluorescence spectral changes of RhB (5.0×10^{-6} mol dm^{-3}) on addition of mono(6-*O*-maltosyl)-*β*-cyclodextrin (**2**) in aqueous buffer solution at pH 7.20. The concentration of **2** increases in the range 0–1.0 1.0×10^{-3} mol dm^{-3} from *a* to *k*. Excitation wavelength, 520 nm

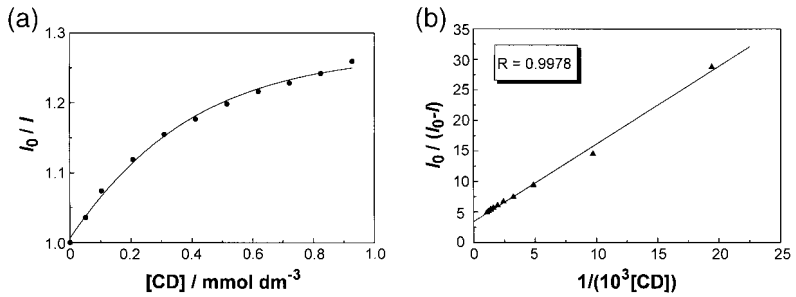


Figure 3. (a) Stern–Volmer and (b) modified Stern–Volmer plots for RhB, whose fluorescence was quenched by the addition of mono(6-*O*-maltosyl)-*β*-cyclodextrin (**2**)

system should be employed:[17]

$$\frac{I_0}{\Delta_I} = \frac{1}{f_a K[\mathrm{CD}]} + \frac{1}{f_a} \quad (1)$$

where I_0 is the total fluorescence in the absence of quencher (CD), K is the Stern–Volmer quenching constant of the accessible fraction and f_a is the fraction of the initial fluorescence which is accessible to quencher (CD).

On the basis of Eqn. ((1)), a typical plot is shown in Fig. 3(b) for the quenching of RhB by **2**, where $I_0/\Delta I$ values are plotted against 1/[CD] to give an excellent linear relationship (R = 0.9978), verifying the probable accessible–inaccessible mechanism proposed above. We are further interested in which species is accessible to cyclodextrin since it is useful to understand the binding constants obtained. Chang *et al.*[18] pointed out that, in addition to the zwitterionic and cationic forms, a third species of RhB in dilute solution is the colorless lactone, which does not contribute to the fluorescence emission in the visible region. Therefore, it may be concluded that cyclodextrins **1–3** prefer to complex with the lactonic form of RhB. Based on this hypothesis, we may interpret the phenomena that the fluorescence of RhB decreases with the addition of cyclodextrin hosts in dilute solution, since some of the zwitterions are transformed to lactone with the lactone–cyclodextrin complex formation. This inclusion behavior is very similar to the inclusion complexation of phenolphthalein with *β*-cyclodextrin, where when the ionized form of phenolphthalein is enclosed in the cyclodextrin cavity, it is forced into its colorless lactone structure.[19] Furthermore, Hinckley *et al.*[18b] reported that in the lactone zwitterion equilibrium, 81.5% of RhB dissolved in water and 70.6% of RhB dissolved in ethanol is in the zwitterionic form in the concentration range (6–8) $\times 10^{-6}$ mol dm^{-3}. In fact, the fraction (f_a) of the initial fluorescence which is accessible to cyclodextrin calculated from the intercept of the modified Stern–Volmer plots is in the range 30–40% for the *β*-cyclodextrin hosts **1–3** in the present study.

Fluorescence spectral titrations

Assuming 1:1 stoichiometry, the inclusion complexation of a guest (Dye) with a host (CD) is expressed by the equation

$$\mathrm{CD} + \mathrm{Dye} \overset{K_S}{\rightleftharpoons} \mathrm{CD \cdot Dye} \quad (2)$$

The stability constant (K_S) can be obtained from the analysis of the sequential changes of fluorescence intensity (ΔI) of guest dyes at various concentrations of host, using a non-linear least-squares method according to the curve-fitting equation[20]

$$\Delta I = \{\alpha([\mathrm{CD}]_0 + [\mathrm{Dye}]_0 + 1/K_s) \pm \sqrt{\alpha^2([\mathrm{CD}]_0 + [\mathrm{Dye}]_0 + 1K_s)^2 - 4\alpha^2[\mathrm{CD}]_0[\mathrm{Dye}]_0}\}/2 \quad (3)$$

where[Dye]$_0$ and [CD]$_0$ refer to the total concentrations of the guest dyes and host cyclodextrins and α is the proportionality coefficient, which may be taken as a sensitivity factor for the fluorescence change. For each fluorescent dye examined, the plot of ΔI as a function of [CD]$_0$ gave an excellent fit, verifying the validity of the 1:1 complex stoichiometry assumed above. Figure 4 illustrates typical curve-fitting plots for the titrations of AR with cyclodextrins **1–3**. There are no serious differences between the experimental and calculated data for the CD–Dye system, indicating 1:1 complexation only throughout the concentration range of host *β*-cyclodextrins (0–2 mmol dm^{-3}). The complex stability constants (K_S) obtained are listed in Table 1, along with the free energy change of complex formation ($-\Delta G°$).

Binding constants and molecular recognition

In previous studies,[21,22] we examined the inclusion

Table 2. Complex stability constants (K_S) and Gibbs free energy changes ($-\Delta G°$) for 1:1 inclusion complexation of various guest dyes with β-cyclodextrins **1–3** in aqueous buffer solution (pH 7.20) at 25 °C[a]

Host	Guest	K_S	Log K_S	$-\Delta G°$ (kJ mol^{-1})
1	ANS	102	2.01	11.5
	TNS	3700	3.57	20.4
	AR	2630	3.42	19.5
	RhB	5100	3.71	21.2
	Aniline	61	1.79	10.2
	N-Methylaniline	83	1.92	11.0
2	ANS	69	1.84	10.5
	TNS	2410	3.38	19.3
	AR	1790	3.25	18.6
	RhB	3300	3.52	20.1
3	ANS	260	2.41	13.8
	TNS	3030	3.48	19.9
	AR	2400	3.38	19.3
	RhB	3840	3.58	20.5

[a] When repeated measurements were performed, the K_S value was reproducible within an error of ±5%, which corresponds to an estimated error of 0.12 kJ mol^{-1} in the free energy of complexation ($\Delta G°$).

complexation of a variety of chemically modified cyclodextrins with diverse guest molecules, such as amino acids, aliphatic alcohols and naphthalenesulfonic acid, and found that several non-covalent weak forces, including van der Waals, hydrophobic, hydrogen-bonding and dipole–dipole interactions, cooperatively contribute to the inclusion complexation of cyclodextrins. In the present case, we found that the size/shape matching between host and guest dominates the stability of the complexes formed, which indicates that van der Waals and hydrophobic interactions mainly contribute to the formation of supramolecular complexes, as these two forces are closely related to the distance and contacting surface area between host and guest

As can be seen from Table 2, although ANS and TNS contain both phenyl and naphthyl residues, their binding constants with a certain host are dramatically different,

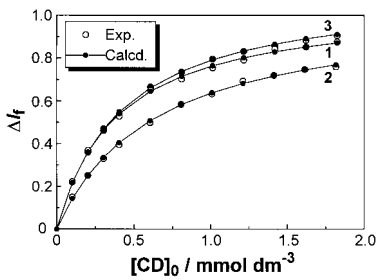


Figure 4. Curve-fitting analyses of fluorescence spectral titrations of AR with β-cyclodextrin hosts **1–3** in aqueous buffer solution at pH 7.20. The differential fluorescence intensity ΔI (open circles) was fitted to the theoretical value (closed circles) calculated for stoichiometric 1:1 complexation

e.g., the binding constants of hosts **1** and **2** with TNS are greater by a factor of 35–36 than that with ANS. We have demonstrated that the naphthalene ring prefers to penetrate into the cavity of β-cyclodextrin in the longitudinal direction.[23] Examination with the Corey–Pauling–Koltun (CPK) molecular model indicated that the naphthalene residue of TNS may be embedded into the β-cyclodextrin cavity fully and then affords a larger binding constant with β-cyclodextrin hosts **1–3**. In contrast, the naphthalene residue of ANS cannot penetrate into the cavity of β-cyclodextrin owing to the steric hindrance of the anilino group. In this context, the binding of ANS to β-cyclodextrin probably occur with the anilino group and then affords the lowest binding constants whose magnitude is consistent with the those of aniline (K_S = 61) and *N*-methylaniniline (K_S = 83) with β-cyclodextrin.

As a linear xanthene derivative, AR may be embedded deeply into β-cyclodextrin but affords moderate binding constants of $(1.8–2.6) \times 10^3$ with hosts **1–3**, which are smaller than those of TNS with the corresponding hosts. It is well known that the cyclodextrin cavity is lined by hydrogen atoms and glycosidic oxygen bridges, and the non-bonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity producing a high electron density there and lending to it some Lewis base characteristics. In this context, the cyclodextrin cavity should favor complexation with cationic guests such as AR. However, it should also be noted that the positive charge of AR may reversely reduce the hydrophobicity of the whole molecule. In the present case, it seems the second factor plays the crucial role. As a result, the cyclodextrin hosts used prefer to encapsulate neutral TNS to charged AR. Unexpectedly, although RhB possesses a large sterically hindering group on the xanthene residue, it affords the largest binding constants among the four fluorescent dyes. A probable explanation is that the lactonic form of RhB participates in the complexation with β-cyclodextrin, as we proposed previously. Phenolphthalein, which is believed to transform into the lactone in the β-cyclodextrin cavity, can form an extra stable complex with β-cyclodextrin and gives a high stability constant of 2.3×10^4 even in pH 10.5 aqueous solution.[19]

We may note from Table 2 that the functional group introduced on to hosts **2** and **3** significantly affects the original molecular binding ability of β-cyclodextrin (**1**). The addition of maltose to the rim of the cylcodextrin cup not only increases the solubility of the β-cyclodextrin in water, but also marginally attenuates the binding of guests within the cyclodextrin cavity. As can be seen from Table 2, the binding constants of the fluorescent dyes with host **2** are about two-thirds of the corresponding values with native β-cyclodextrin (**1**). This result probably indicates that the introduction of a hydrophilic substituent may reduce the original hydrophobicity of the cavity and the binding ability toward hydrophobic guest

molecules. The 2-hydroxypropyl group in host **3** is hydrophobic compared with the hydroxy group on the secondary side, and may extend the hydrophobic cavity of native β-cyclodextrin (**1**). However, host **3** still affords a weaker binding ability than native β-cyclodextrin. As is well known, guest molecules usually access the cyclodextrin cavity from the more opening side in the complexation procedure,[24] and therefore the introduction of a subsituent on to the secondary side of the cyclodextrin may cause steric hindrance of the guest accessing to the cavity, which probably leads to the weaker binding ability of **3** with large-sized guests. On the other hand, as we reported previously, [22b,23b] a hydrophobic substituent in cyclodextrin derivatives prefers to be self-included into its cavity to form an intramolecular complex and is excluded from the cavity on addition of external guests. Hence, the introduction of a self-including substituent in cyclodextrin is not favorable for enhancing the cyclodextrin's complexation ability. As a result of the above factors, the binding ability of the three hosts for TNS, AR or RhB decreases in the order $\mathbf{1} > \mathbf{3} > \mathbf{2}$.

From Table 2, it can be seen that the binding constant of host **3** with ANS is greater than that of host **1** by a factor of 2.5, which is consistent with the results for the inclusion complexation of ANS with polyamine-modified β-cyclodextrin (K_S = 266 for diethylenetriamino-β-cyclodextrin and 280 for triethylenetetraamino-β-cyclodextrin.[23b] A reasonable explanation is that the anilino residue in ANS participates in the inclusion complexation with β-cyclodextrin, although its size is smaller than the volume of the β-cyclodextrin cavity (262 Å^3).[25,26] If so, the self-including propyl group in **3** may adjust the effective space of its cavity and **3** affords more stable complexation with ANS than does native β-cyclodextrin. The present results indicate that the hydrophobic subsituent can serve not only as a competitive group, but also as an adjuster of the cavity size.

Acknowledgements

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