

Cooperative Inclusion of Sodium 1-Pyrenesulfonate by γ -Cyclodextrin

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Summary

The interaction of γ -cyclodextrin(γ -CD) with sodium 1-pyrenesulfonate(PS) was studied spectrophotometrically. γ -CD was found to cause much larger decrease in the absorption maxima of PS than β -CD. The fluorescence spectra of PS in the presence of γ -CD showed excimer emission, while those of PS with β -CD showed only monomer emission, indicating that γ -CD forms 1:2 (γ -CD:PS) complexes in which two PS molecules are included in the γ -CD cavity in a face-to-face fashion. The binding isotherm showed a sigmoidal curve. The association constants were estimated by computer simulation of the binding curve. The 1:2 (CD:PS) complex was found to be much more stable ($K = 10^6 \text{ M}^{-1}$) than the 1:1 complex ($K = 1 \text{ M}^{-1}$). At high concentration of γ -CD another γ -CD cooperates in binding two PS molecules, resulting in the formation of a 2:2 complex.

Introduction

Cyclodextrins(CDs) are cyclic molecules consisting of six, seven, and eight glucose units (α -, β -, and γ -CD, respectively). They form inclusion complexes with various compounds (BENDER et al. 1978). Most of the CD complexes in aqueous solutions showed 1:1(CD:guest molecule) stoichiometry (SAENGER 1980). β -CD forms 2:1(CD:guest) complexes with large molecules which cannot be accommodated in a single β -CD cavity (HARADA et al. 1976, 1977, 1980). If a cavity is larger than those of α -CD and β -CD, it is likely to form inclusion complexes with larger molecules (UENO et al. 1980,1981, HIRAI et al. 1981). γ -CD has a cavity of 7.5-8.3 Å diameter, which is larger than those of α -CD(6-6.4 Å) and β -CD(4.7-5.2 Å) (SAENGER 1980). Therefore, γ -CD can be expected to form inclusion complexes with large molecules too large to be accommodated in α -CD or β -CD cavities.

We chose sodium 1-pyrenesulfonate(PS) as a guest molecule, because PS is large enough and soluble in water. PS enables us to study the interaction in aqueous solutions quantitatively. In this paper, we report on the interaction of sodium 1-pyrenesulfonate with γ -CD. γ -CD was found to have much stronger interaction with PS than α -CD and β -CD.

Results and Discussion

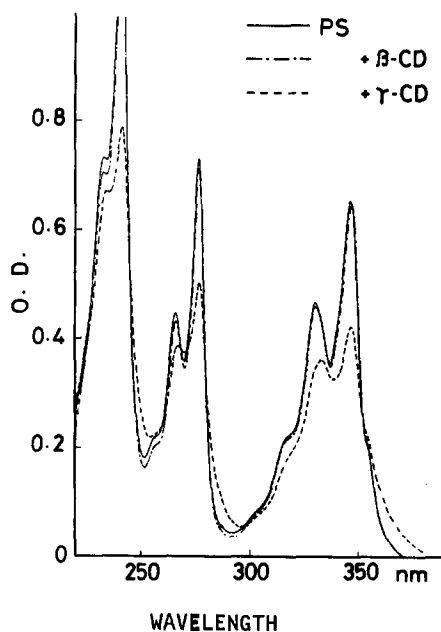


Fig. 1. Absorption spectra of PS in the absence and presence of β -CD and γ -CD, $[\text{PS}] = 2 \times 10^{-5} \text{ M}$
 $[\beta\text{-CD}] = [\gamma\text{-CD}] = 5 \times 10^{-3} \text{ M}$

Figure 1 shows the absorption spectra of sodium 1-pyrene-sulfonate (PS) in the absence and presence of β -CD and of γ -CD. α -CD showed no effect on the absorption spectrum of PS. β -CD caused a slight decrease and red shift in the absorption bands. The absorption bands greatly decreased and were red-shifted on addition of γ -CD. The peak at 345 nm decreased more intensively than that at 328 nm.

The effect of the concentration of β -CD and γ -CD on the absorbance of PS at 345 nm is shown in Figure 2. The changes of the absorption spectra were measured by the difference spectra using a PS solution as a reference. β -CD showed little effect on the absorbance of PS. On the other hand γ -CD showed large effect. The plots of the changes of the absorbance vs. γ -CD concentration showed a sigmoidal curve, indicating that the binding is not a simple Michaelis type 1:1 inclusion.

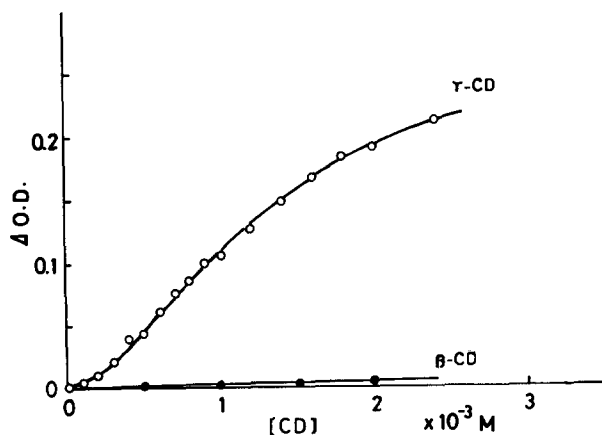


Fig. 2. Effect of β -CD and γ -CD concentration on the absorbance of PS at 345 nm, $[\text{PS}] = 2 \times 10^{-5} \text{ M}$

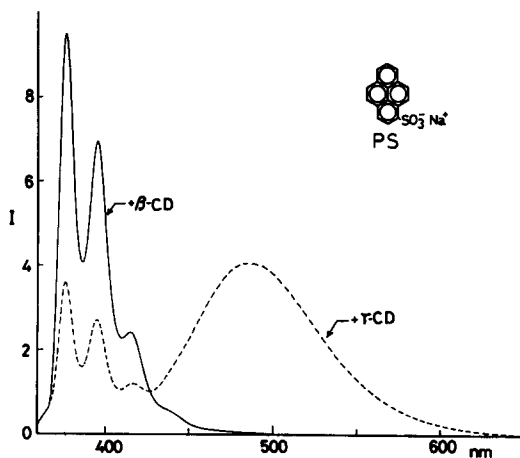


Fig. 3. Emission spectra of PS in the presence of β -CD and of γ -CD [PS] = 2×10^{-5} M, [β -CD] = [γ -CD] = 5×10^{-3} M

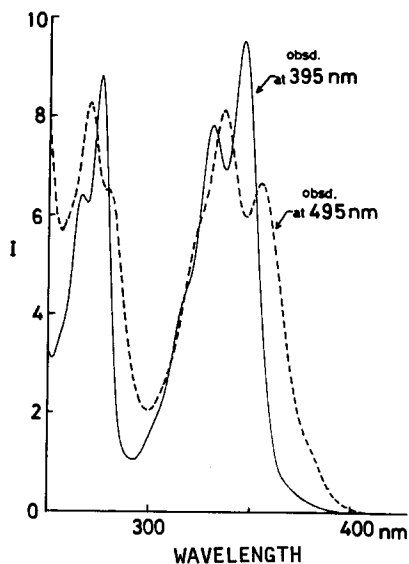


Fig. 4. Excitation spectra of PS in the presence of γ -CD. [PS] = 2×10^{-5} M, [γ -CD] = 5×10^{-3} M

Figure 3 shows the emission spectra of PS in the presence of β -CD and of γ -CD. The spectrum of PS in the presence of β -CD shows only the monomer emission, which is identical with that of PS in the absence of CDs. On addition of γ -CD the monomer emission decreased and a broad structureless emission appeared at around 495 nm, which was assigned to the excimer emission. This fact indicates that γ -CD forms 1:2 (γ -CD:PS) complexes in which two PS molecules are included in the γ -CD cavity in a face-to-face fashion. It should be noted that the concentration of γ -CD (5×10^{-3} M) is excess over that of PS (2×10^{-5} M), which is very low. This indicates that γ -CD binds two PS molecules strongly.

The excitation spectra of PS in the presence of γ -CD, observed at 395 nm (monomer emission) and at 495 nm (excimer emission) are shown in Figure 4. The excitation spectrum of monomer emission is similar to the absorption spectrum of PS in an aqueous solution. The spectrum observed at excimer emission, however, is different from the absorption spectrum of PS. The peaks are red-shifted and the relative intensities of the two peaks at 335 nm and 355 nm are reversed. This change is similar to that of absorption spectra on addition of γ -CD.

Figure 5 shows the fluorescence spectra of PS in the presence of various concentrations of γ -CD. The monomer emission decreased and the excimer emission increased with an increase in the γ -CD concentration with an isoemissive point being observed at 427 nm.

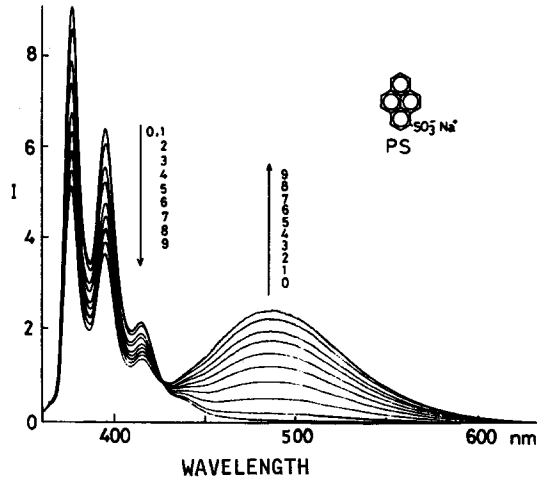
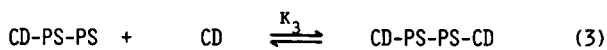
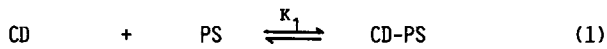


Fig.5. Emission spectra of PS in the presence of γ -CD
 $[PS]=2 \times 10^{-5} M$, The concentrations of γ -CD ($\times 10^{-4} M$) were
 as follows: 0,1,2,3,4,5,6,7,8, and 9

The effect of the concentration of γ -CD on the excimer emission intensity of PS is shown in Figure 6. The plots formed a sigmoidal curve in a similar manner as those of the change of the absorbance. This indicates that the change of the absorbance is caused by the formation of 1:2(CD:PS) inclusion complex.

The following equilibria were assumed to explain the sigmoidal curve.



$$K_1 = \frac{[CD-PS]}{[CD][PS]} \quad (4)$$

$$K_2 = \frac{[CD-PS-PS]}{[CD-PS][PS]} \quad (5)$$

$$K_3 = \frac{[CD-PS-PS-CD]}{[CD-PS-PS][CD]} \quad (6)$$

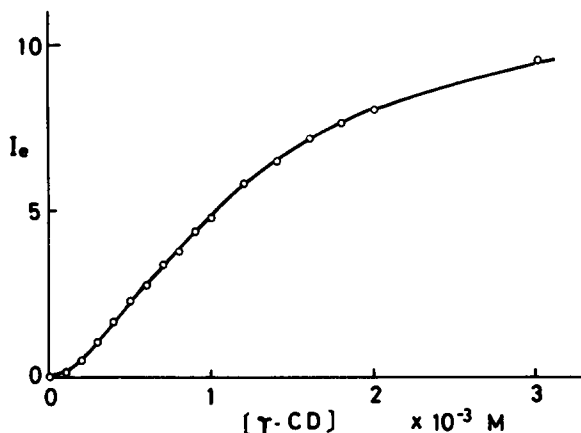


Fig 6. Effect of γ -CD concentration on the excimer emission intensities of PS. $[\text{PS}] = 2 \times 10^{-5} \text{ M}$
 (o), observed; solid line, calculated assuming that $K_1 = 1 \text{ M}^{-1}$, $K_2 = 10^6 \text{ M}^{-1}$, and $K_3 = 2 \times 10^4 \text{ M}^{-1}$

First, γ -CD is assumed to form the 1:1 complex with PS (1) followed by the formation of the 1:2(CD:PS) complex (2). These two equilibria, however, did not explain the sigmoidal curve. So we assumed that another γ -CD cooperates in binding two PS molecules at high concentrations (3). K_1 , K_2 , and K_3 values were estimated by the computer simulation of the binding curve. The CD concentration is assumed to be equal to the initial

concentration of CD. In Figure 6 circles show the values observed and the solid line shows the calculated curve assuming that $K_1 = 1 \text{ M}^{-1}$, $K_2 = 10^6 \text{ M}^{-1}$, and $K_3 = 2 \times 10^4 \text{ M}^{-1}$. The curve calculated fitted well the plots observed.

Table
 Association Constants and
 Fluorescence Lifetimes of
 PS in the presence of CDs

CD	K_1 M^{-1}	K_2 M^{-1}	K_3 M^{-1}	τ ns
none	-	-	-	40
α -	-	-	-	40
β -	30	-	-	40
γ -	1	10^6	2×10^4	50^{a} 60^{b}

a monomer emission

b excimer emission

$[\text{PS}] = 2 \times 10^{-5} \text{ M}$, $[\text{CD}] = 5 \times 10^{-3} \text{ M}$

Table summarizes the results of the binding study along with the fluorescence lifetimes. α -CD had no interaction with PS. β -CD forms a 1:1 complex with the association constant of 30, which is similar to that previously reported. (KOBASHI et al. 1981) γ -CD forms 1:1, 1:2, and 2:2 inclusion complexes with PS. The 1:1 complex is unstable and less stable than β -CD complex. The 1:2 complex is extremely stable. The cooperation of the second γ -CD is strong. The fluorescence life-

times are longer than those with α -CD and β -CD, indicating that PS is protected from O₂, which is the quencher of PS excited states, by the formation of inclusion complexes.

Examination of molecular models of γ -CD and pyrene indicates that a γ -CD cavity is too large to fit a single PS molecule. Two pyrene molecules, however, fit well in a γ -CD cavity in a face-to-face fashion. Since a pyrene molecule is longer than the depth of γ -CD, the part of the pyrene molecule is exposed to a solvent. Thus an additional γ -CD molecule associates together to form a 2:2 complex.

γ -CD was found to have much stronger interaction with PS than α -CD and β -CD and to form not only 1:1 complex but also 1:2 and 2:2 inclusion complexes, depending on the size and shape of the guest molecules.

Experimental

α -, β -, and γ -CD were kindly supplied from Hayashibara Biochemical Laboratories Inc. and were purified as described previously. (HARADA et al. 1976).

Absorption spectra were measured using a Hitachi spectrophotometer Model 124. Fluorescence spectra were measured using a Shimadzu spectrofluorophotometer RF-502 F.

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