Interactions of β- and γ-Cyclodextrins with Thionine and 2-Naphthalenesulfonate in Aqueous Solution

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In aqueous solutions, a cationic dye, thionine (Th), has been found to form a 1 : 1 complex with 2-naphthalenesulfonate (2NS), which is an organic anion. An equilibrium constant for the formation of the complex has been evaluated to be 310 ± 20 mol^{-1} dm^3 from the absorbance change of Th. The Th fluorescence is quenched by the formation of the complex. β-Cyclodextrin (β-CD) and γ-CD form a 1 : 1 and a 1 : 2 host–guest inclusion complex with Th, respectively. Equilibrium constants for the formation of the 1 : 1 β-CD–Th and 1 : 2 γ-CD–Th inclusion complexes have been evaluated to be 300 ± 20 mol^{-1} dm^3 and 1.07×10^7 mol^{-2} dm^6, respectively. The addition of γ-CD to a Th solution containing 2NS results in the formation of a 1 : 1 : 1 γ-CD–Th–2NS inclusion complex. From a simulation concerning the absorbance change, the equilibrium constant for the formation of the ternary 1 : 1 : 1 inclusion complex has been estimated to be 22600 mol^{-1} dm^3, which is nearly the same as that (21500 mol^{-1} dm^3) estimated from a simulation concerning the fluorescence intensity change.

It is known that dyes associate to form dimers and/or higher-order aggregates.[1—3] Anionic polymers interact with cationic dyes, inducing the dimerization and/or polymerization of the dyes.[4—6] In addition, a cationic dye can associate with an organic anion to form a complex.[7,8]

Previously, we have studied the interactions between an organic cation (Methylene Blue) and organic anions (1-naphthalenesulfonate, 1-naphthaleneacetate, 2-naphthalenesulfonate, 2,7-naphthalenedisulfonate, 1,3,6-naphthalenetrisulfonate, and 2-anthracenesulfonate).[8] When an organic anion such as 2-naphthalenesulfonate (2NS) has been added to a Methylene Blue solution, the absorption maximum of Methylene Blue comes to be shifted to longer wavelengths. In the low concentration range of 2NS, an isosbestic point has been observed at 680 nm, indicating the formation of a 1 : 1 Methylene Blue–2NS complex. The equilibrium constant for the formation of the complex has been estimated to be 340 mol^{-1} dm^3 from the absorbance change of Methylene Blue. The fluorescence spectrum of Methylene Blue has been found to be red shifted upon the addition of 2NS. In the low concentration ranges of 2,7-naphthalenedisulfonate and 1,3,6-naphthalenetrisulfonate, the addition of them accelerates the dimerization of Methylene Blue. In their high concentration ranges, however, the formation of the 1 : 1 complex is dominant.

Cyclodextrins (CDs), which are cyclic oligosaccharides composed of D-glucopyranose units linked by α(1→4) bonds, are shaped like a truncated cone with a hydrophobic cavity.[9] CDs having six, seven, and eight D-glucopyranose units are called α-CD, β-CD, and γ-CD, respectively. Due to the hydrophobic cavity, CDs can accommodate a variety of organic molecules to form inclusion complexes. CD usually forms a 1 : 1 inclusion complex with a guest molecule. When a guest molecule is bulky or long relative to the dimensions of the CD cavity, however, two CD molecules are frequently bound to a single guest molecule to form a 2 : 1 CD–guest inclusion complex.[10—14] In some cases, a single CD molecule conversely accommodates two small guest molecules to form a 1 : 2 CD–guest inclusion complex.[15—19]

Tan et al. have reported that the complexation of γ-CD with an organic anion (2,6-naphthalenedicarboxylate) is greatly enhanced by the addition of an organic cation (2,6-bis(1-pyridiniomethyl)naphthalene dibromide) as a space-regulator.[20] The formation of a ternary 1 : 1 : 1 inclusion complex among γ-CD, the organic anion, and the organic cation has been confirmed by means of ^{1}H NMR, induced circular dichroism, and UV absorption spectra. To our knowledge, however, there is no study concerning the interactions between CD and an organic cation–organic anion complex except for the report by Tan et al. Under these circumstances, we have become interested in the molecular interactions of CDs with a complex composed of a cationic dye and an organic anion. If the attractive force between the cationic dye and the organic anion is strong enough and if the molecular dimensions of the cationic dye-organic anion complex are small compared to those of the CD cavity, a ternary inclusion complex among CD, the cationic dye, and the organic anion would be formed. If CD strongly interacts with only the cationic dye (or organic anion), the cationic dye-organic anion complex may dissociate to individual component molecules to form an inclusion complex of CD with the cationic dye (or organic anion). Furthermore, in a solution containing CD, the cationic dye, and the organic anion, there may be the possibility that the cationic dye dimerizes within

the CD cavity without including the organic anion.

We found that a cationic dye, thionine, forms a complex with sodium 2-napthalenesulfonate. Thus, we investigated the interactions of β- and γ-CDs with the thionine-2-naphthalenesulfonate complex as well as with the guest molecules by means of absorption and fluorescence spectroscopy.

Experimental

Thionine (Th), whose molecular structure is shown in Chart 1, was purchased from Tokyo Kasei Kogyo and was used as received. Sodium 2-naphthalenesulfonate (2NS) from Tokyo Kasei Kogyo was recrystallized from a water-ethanol mixture. β-Cyclodextrin (β-CD) obtained from Nacalai Tesque was recrystallized twice from water. γ-CD obtained from Wako Pure Chemical Industries was used without further purification. Buffers (0.0033 mol dm^{-3} KH_2PO_4–0.0033 mol dm^{-3} Na_2HPO_4) of pH 6.7 were used throughout this study. The concentration of Th was 1.4×10^{-5} mol dm^{-3}.

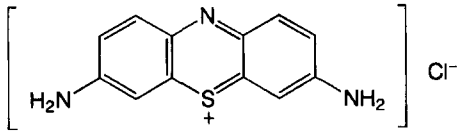
Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. Fluorescence spectra were run on a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R-943 photomultiplier. Fluorescence spectra were corrected for the spectral response of the fluorometer. Spectroscopic measurements were made at 25±0.1 °C.

Results and Discussion

Complex Formation between Th and 2NS in Aqueous Solutions. At high concentrations of Th, dimerization occurs. At a low Th concentration of approximately 1.4×10^{-5} mol dm^{-3}, however, Th predominantly exists as a monomer. Consequently, the dimer of Th is negligible at concentrations of approximately 1.4×10^{-5} mol dm^{-3}.[21,22] Figure 1 shows absorption and fluorescence spectra of Th (1.4×10^{-5} mol dm^{-3}) in aqueous solutions (pH 6.7) containing various concentrations of 2NS. When 2NS is added to a Th solution, the absorption maximum of Th is slightly shifted to longer wavelengths. In addition, the absorption band is significantly reduced in intensity and is broadened, accompanied by isosbestic points at 514 and 620 nm. These findings indicate the formation of a complex between Th and 2NS. For a 1 : 1 stoichiometry, the following equation holds:[8,23]

$$1/(A-A_0) = 1/a + 1/(aK_1[2NS]_0), \quad (1)$$

where A, A_0, a, and $[2NS]_0$ are the absorbance of Th in the presence of 2NS, that in the absence of 2NS, a constant, and the initial concentration of 2NS, respectively. This double reciprocal plot (Fig. 2) concerning the absorbance change gives a straight line, indicating the formation of the 1 : 1 Th–2NS complex (Th·2NS):



Thionine

Chart 1.

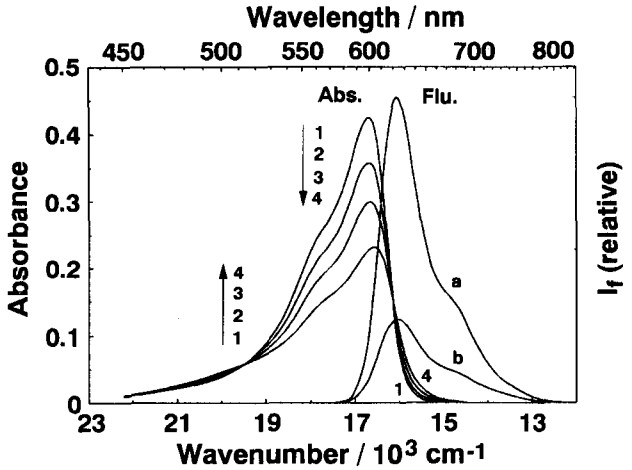


Fig. 1. Absorption and fluorescence spectra of Th (1.4×10^{-5} mol dm^{-3}) in pH 6.7 buffers containing various concentrations of 2NS. Concentration of 2NS: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, (4) 1.0×10^{-2}, (a) 0, and (b) 1.0×10^{-2} mol dm^{-3}. λ_{ex} = 514 nm.

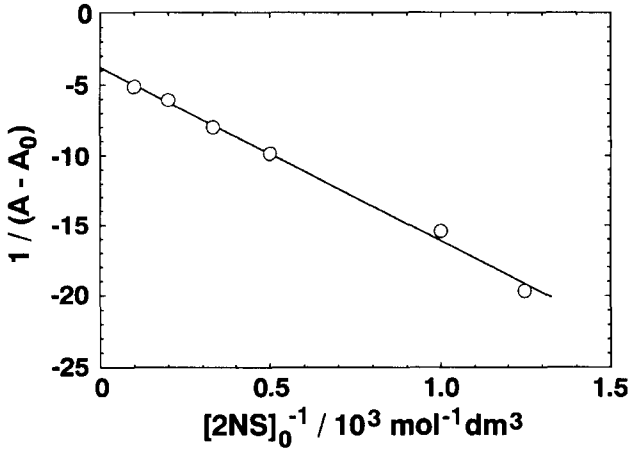


Fig. 2. Double reciprocal plot for the absorbances of Th (1.4×10^{-5} mol dm^{-3}) solutions containing various concentrations of 2NS. λ_{obs} = 600 nm.

$$\mathrm{Th} + 2\mathrm{NS} \overset{K_1}{\rightleftharpoons} \mathrm{Th{\cdot}2NS}, \quad (2)$$

where K_1 is the equilibrium constant for the formation of the 1 : 1 Th–2NS complex. A K_1 value is evaluated to be 310 ± 20 mol^{-1} dm^3 from the plot shown in Fig. 2. The driving force of the complexation is most likely the electrostatic attraction, because Th is a cationic dye and 2NS is an organic anion. Fluorescence spectra of Th in pH 6.7 buffers in the absence and presence of 2NS are shown in Fig. 1. The fluorescence of Th is quenched upon the addition of 2NS, suggesting that the Th–2NS complex is nonfluorescent. This finding is in contrast to the fluorescence properties of a Methylene Blue–2NS complex, whose fluorescence band is shifted to the longer wavelengths relative to that of free Methylene Blue.[8] From the fluorescence quenching of Th by the addition of 2NS, the K_1 value was evaluated to be 340 ± 20 mol^{-1} dm^3 (not shown), which is nearly the same as the K_1 value (310 ± 20 mol^{-1} dm^3) obtained from

the absorbance change.

Complex Formation between CD and Th in Aqueous Solutions. Figure 3 exhibits absorption and fluorescence spectra of Th in pH 6.7 buffers containing various concentrations of β-CD. When β-CD is added to a Th solution, the absorption band is sharpened and intensified, and the absorption peak is slightly shifted to longer wavelengths accompanied by an isosbestic point at 589 nm. This finding indicates the formation of an inclusion complex of β-CD with Th. A double reciprocal plot (not shown), which is based on an equation similar to Eq. 1, afforded a straight line for the β-CD–Th system, indicating the 1 : 1 β-CD–Th inclusion complex (β-CD·Th).[24]

$$\beta\text{-CD} + \text{Th} \overset{K_2}{\rightleftharpoons} \beta\text{-CD·Th}, \tag{3}$$

where K_2 is the equilibrium constant for the formation of the 1 : 1 inclusion complex between β-CD and Th. From the double reciprocal plot, a K_2 value was estimated to be 300 ± 20 mol^{-1} dm^3, which is nearly the same as the K_1 value, for the formation of the Th–2NS complex, evaluated from absorbance change. Consequently, the free energy change for the complex formation between Th and β-CD at 25 °C is nearly the same as that between Th and 2NS. Our estimated K_2 value is the same as the one reported.[25]

Figure 3 exhibits fluorescence spectra of Th in pH 6.7 buffers containing various concentrations of β-CD. As the β-CD concentration is increased, the fluorescence band of Th is enhanced in intensity without a shift of the fluorescence peak. From the fluorescence intensity change upon the addition of β-CD, the K_2 value has been evaluated to be 310 ± 10 mol^{-1} dm^3, which is nearly the same as that (300 ± 20 mol^{-1} dm^3) evaluated from the absorbance change.

Figure 4 displays absorption spectra of Th in pH 6.7 buffers containing various concentrations of γ-CD. With an increase

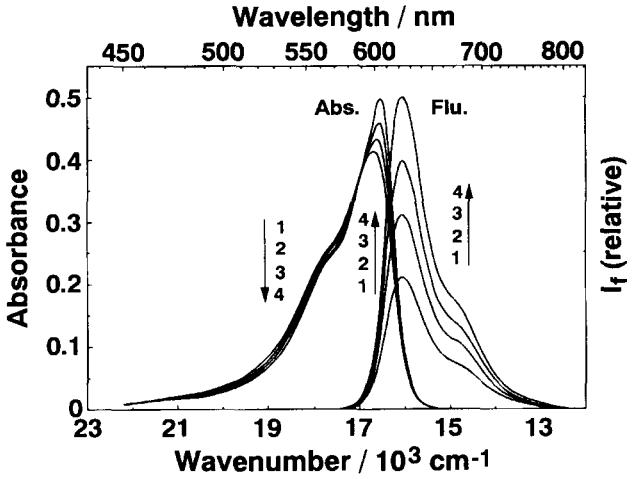


Fig. 3. Absorption and fluorescence spectra of Th (1.4×10^{-5} mol dm^{-3}) in pH 6.7 buffers containing various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}. λ_{ex} = 589 nm.

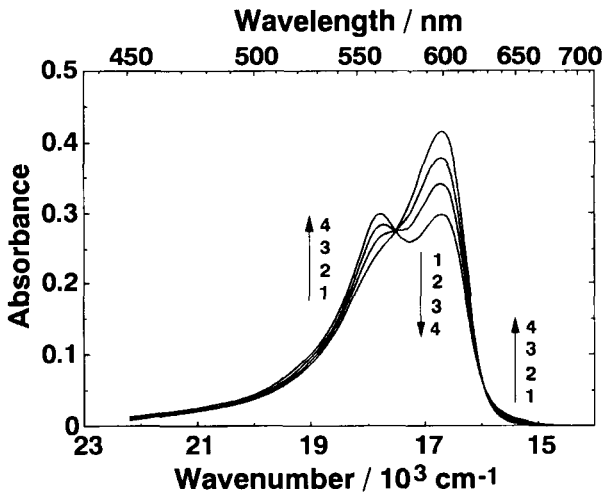


Fig. 4. Absorption spectra of Th (1.4×10^{-5} mol dm^{-3}) in pH 6.7 buffers containing various concentrations of γ-CD. Concentration of γ-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

in the γ-CD concentration, a new absorption band at 563 nm, which is due to the Th dimer, appears. This is enhanced in intensity at the expense of the monomer absorption band centered at 599 nm. This finding indicates that the dimerization of Th occurs within the γ-CD cavity. In other words, γ-CD accelerates the dimerization of Th through the accommodation of Th.

$$\gamma\text{-CD} + 2\text{Th} \overset{K_3}{\rightleftharpoons} \gamma\text{-CD·(Th)}_2, \tag{4}$$

where K_3 is the equilibrium constant for the formation of the 1 : 2 γ-CD–Th inclusion complex (γ-CD·(Th)$_2$). Similar dimerization within the γ-CD cavity has been reported for acridine orange, roccellin, pyronine Y, etc.[18,26,27] When the equilibrium of Eq. 4 is established, the absorbance of Th is represented by

$$A = (\varepsilon_0 + \varepsilon K_3[\gamma\text{-CD}]_0[\text{Th}])[\text{Th}]d \tag{5}$$

where ε_0 and ε are the molar absorption coefficients of uncomplexed Th and the 1 : 2 γ-CD–Th inclusion complex, respectively, $[\gamma\text{-CD}]_0$ and [Th] represent the initial concentration of γ-CD and the concentration of uncomplexed Th, respectively, and d is the path length (1.0 cm) of a cell. The initial concentration of Th, $[\text{Th}]_0$, is given by

$$[\text{Th}]_0 = [\text{Th}] + 2[\gamma\text{-CD·(Th)}_2]. \tag{6}$$

By use of K_3, a quadratic equation concerning [Th] is derived from Eq. 6:

$$2K_3[\gamma\text{-CD}]_0[\text{Th}]^2 + [\text{Th}] - [\text{Th}]_0 = 0. \tag{7}$$

Assuming a K_3 value, one can calculate [Th] from Eq. 7. Using an evaluated ε_0 value of 2.73×10^4 mol^{-1} dm^3 cm^{-1} at 600 nm and values of ε and K_3 as parameters, we performed a simulation concerning the Th absorbance. In Fig. 5, the least-squares best fit curve (curve 1) for the Th absorbance, which has been calculated with an ε value of 2.68×10^4 mol^{-1} dm^3 cm^{-1} and a K_3 value of 1.07×10^7 mol^{-2} dm^6, is

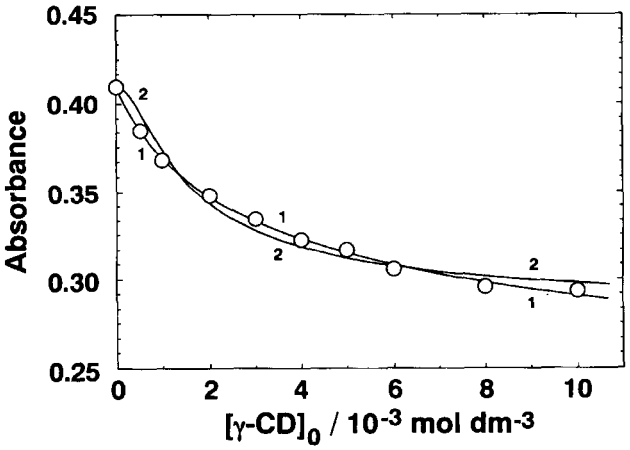


Fig. 5. Comparison between the simulated absorbance curves of the 1 : 2 and 2 : 2 γ-CD–Th inclusion complexes (curve 1 and 2) and the observed absorbance data (open circle). The best fit simulation curve was calculated with an assumed K_3 value of 1.07×10^7 mol^{-1} dm^3 and an assumed ε value of 2.68×10^4 mol^{-1} dm^3 cm^{-1}. λ_{obs} = 600 nm.

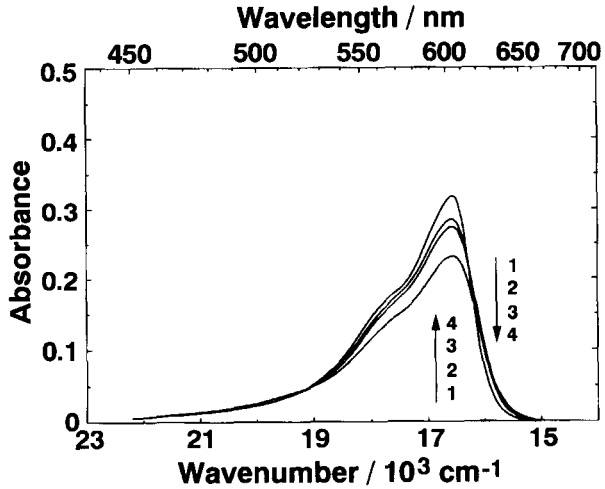


Fig. 6. Absorption spectra of Th (1.4×10^{-5} mol dm^{-3}) in pH 6.7 buffers containing 2NS (1.0×10^{-2} mol dm^{-3}) and various concentrations of β-CD. Concentration of β-CD: (1) 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

shown as a function of γ-CD concentration, together with the observed absorbance data. The simulation curve well fits the observed data, indicating the formation of the 1 : 2 γ-CD–Th inclusion complex. Our estimated K_3 value is similar to the reported one (1.7×10^7 mol^{-2} dm^6).[25] The quenching of the Th fluorescence has occurred upon the formation of the 1 : 2 γ-CD–Th inclusion complex, indicating that the Th dimer located within the γ-CD cavity is non-fluorescent.

For the γ-CD-pyronine Y system, the formation of a 2 : 2 inclusion complex has been suggested.[26] Consequently, there may be the possibility of the formation of a 2 : 2 γ-CD–Th inclusion complex:

$$2\gamma\text{-CD} + 2\text{Th} \overset{K_4}{\rightleftharpoons} (\gamma\text{-CD})_2\cdot(\text{Th})_2. \quad (8)$$

In this case, the absorbance of Th and the quadratic equation for [Th] are respectively given as

$$A = (\varepsilon_0 + \varepsilon' K_4[\gamma\text{-CD}]_0^2[\text{Th}])[\text{Th}]d, \quad (9)$$

and

$$2K_4[\gamma\text{-CD}]_0^2[\text{Th}]^2 + [\text{Th}] - [\text{Th}]_0 = 0. \quad (10)$$

Here, ε' is the molar absorption coefficient of the 2 : 2 γ-CD–Th inclusion complex. To test the possibility, the best fit simulation curve for the 2 : 2 γ-CD–Th inclusion complex, which has been calculated with an ε value of 3.77×10^4 mol^{-1} dm^3 cm^{-1} and a K_4 value of 2.01×10^{10} mol^{-3} dm^6, is also exhibited in Fig. 5 (curve 2). However, the best fit simulation curve for the 2 : 2 inclusion complex does not well fit the observed data compared to the 1 : 2 inclusion complex, providing additional evidence for the formation of the 1 : 2 γ-CD–Th inclusion complex.

Complex Formation among CD, 2NS, and Th in Aqueous Solutions. Figure 6 exhibits absorption spectra of Th in pH 6.7 buffers containing 2NS (1.0×10^{-2} mol dm^{-3}) and various concentrations of β-CD. When the β-CD concentration is raised, the absorption band of Th is intensified with a band sharpening and a slight blue shift of the absorption maximum. As shown in Fig. 3, the absorption intensity of the β-CD–Th inclusion complex is stronger than that of free Th. In contrast, the absorption intensity of the Th–2NS complex is weaker than that of free Th. Consequently, the recovery of the absorption intensity shown in Fig. 6 most likely reflects the formation of the β-CD–Th inclusion complex. The β-CD cavity is not wide enough to simultaneously accommodate Th and 2NS. In spite of the addition of 1.0×10^{-2} mol dm^{-3} of β-CD, the enhancement of the absorption intensity is not so large as that shown in Fig. 3. This is because nearly the same quantities of β-CD are consumed to form the inclusion complexes with Th and 2NS. Upon the addition of β-CD to a Th solution containing 2NS (1.0×10^{-2} mol dm^{-3}), the Th fluorescence has been enhanced. This finding is consistent with the absorption spectral change in the β-CD–2NS–Th system.

Figure 7 depicts absorption and fluorescence spectra of Th in pH 6.7 buffers containing 2NS (1.0×10^{-2} mol dm^{-3}) and various concentrations of γ-CD. As the γ-CD concentration is increased below approximately 1.0×10^{-4} mol dm^{-3}, the absorption band is intensified accompanied by a red shift of the absorption peak and an appearance of an isosbestic point at 542 nm. This finding indicates that in the presence of 2NS the formation of the 1 : 2 γ-CD–Th inclusion complex is not promoted by the addition of γ-CD. This implies that within the γ-CD cavity the interaction between Th and 2NS is stronger than that between two Th molecules. If not so, the addition of γ-CD would induce the formation of the 1 : 2 γ-CD–Th inclusion complex even in the presence of 2NS. As shown in Fig. 4, γ-CD causes the formation of 1 : 2 γ-CD–Th inclusion complex rather than the 1 : 1 γ-CD–Th inclusion complex. Therefore, the results shown in Fig. 7 suggests that the Th–2NS complex is incorporated into the γ-CD cavity to form a 1 : 1 : 1 γ-CD–2NS–Th inclusion complex (γ-CD·Th·2NS):

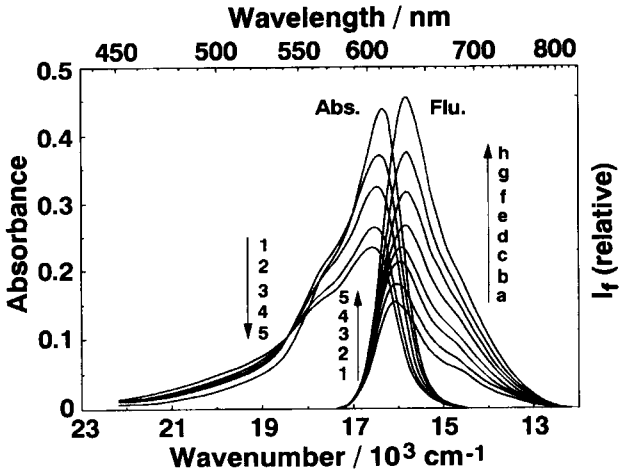


Fig. 7. Absorption and fluorescence spectra of Th (1.4×10^{-5} mol dm^{-3}) in pH 6.7 buffers containing 2NS (1.0×10^{-2} mol dm^{-3}) and various concentrations of γ-CD. Concentration of γ-CD: (1) 0, (2) 2.0×10^{-5}, (3) 5.0×10^{-5}, (4) 1.0×10^{-4}, (5) 1.0×10^{-3}, (a) 0, (b) 2.0×10^{-5}, (c) 5.0×10^{-5}, (d) 1.0×10^{-4}, (e) 3.0×10^{-4}, (f) 1.0×10^{-3}, (g) 2.0×10^{-3}, and (h) 5.0×10^{-3} mol dm^{-3}. λ_{ex} = 542 nm.

$$\gamma\text{-CD} + \text{Th}\cdot\text{2NS} \overset{K_5}{\rightleftharpoons} \gamma\text{-CD}\cdot\text{Th}\cdot\text{2NS}, \quad (11)$$

where K_5 is the equilibrium constant for the formation of the 1 : 1 : 1 inclusion complex. The initial concentration of Th is represented by

$$[\text{Th}]_0 = [\text{Th}] + [\text{Th}\cdot\text{2NS}] + [\gamma\text{-CD}\cdot\text{Th}\cdot\text{2NS}]. \quad (12)$$

The formation constant of the 1 : 1 β-CD–2NS inclusion complex in pH 10.0 buffer is reported to be 240 ± 40 mol^{-1} dm^3.[28] The formation constant for a γ-CD–2NS inclusion complex is expected to be less than that for the β-CD–2NS inclusion complex because the cavity size of γ-CD is wider than that of β-CD. In fact, no fluorescence spectral change of 2NS has been observed when γ-CD has been added to a 2NS solution without Th. Therefore, the formation of the γ-CD–2NS inclusion complex can be neglected. Thus, the initial concentration of γ-CD is represented as

$$[\gamma\text{-CD}]_0 = [\gamma\text{-CD}] + [\gamma\text{-CD}\cdot\text{Th}\cdot\text{2NS}]. \quad (13)$$

Using K_1, K_5, and Eqs. 12 and 13, one derives a quadratic equation for free Th:

$$K_1K_5[\text{2NS}]_0(1+K_1[\text{2NS}]_0)[\text{Th}]^2 + (1+K_1[\text{2NS}]_0 + K_1K_5[\text{2NS}]_0[\gamma\text{-CD}]_0 - K_1K_5[\text{2NS}]_0[\text{Th}]_0)[\text{Th}] - [\text{Th}]_0 = 0. \quad (14)$$

Because the solution of Eq. 14 gives the concentration of free Th under the assumption of a K_5 value, the concentration of free γ-CD is calculated from Eq. 13. The absorbance of Th is represented by

$$A = (\varepsilon_0 + \varepsilon_1K_1[\text{2NS}]_0 + \varepsilon_2K_1K_5[\gamma\text{-CD}][\text{2NS}]_0)[\text{Th}]d. \quad (15)$$

Here, ε_1 and ε_2 are the molar absorption coefficients of the Th–2NS complex and the 1 : 1 : 1 γ-CD–Th–2NS inclusion complex, respectively. Assuming the ε_1, ε_2, and K_5 values, we have performed a simulation for the observed absorbance at 610 nm. In Fig. 8, the least-squares best fit simulation curve, which has been calculated with ε_1 = 14000 mol^{-1} dm^3 cm^{-1}, ε_2 = 31600 mol^{-1} dm^3 cm^{-1}, and K_5 = 22600 mol^{-1} dm^3, is exhibited together with the observed data. Further addition of γ-CD results in a further increase in the absorption band of Th and a disappearance of the isosbestic point (Fig. 7), suggesting the formation of another inclusion complex, most likely a 2 : 1 : 1 γ-CD–Th–2NS inclusion complex. Such a 2 : 1 : 1 inclusion complex has been reported for the β-CD–1-naphthonitrile–anisole system.[29]

In Fig. 7, fluorescence spectra are depicted for Th in pH 6.7 buffers containing 2NS (1.0×10^{-2} mol dm^{-3}) and various concentrations of γ-CD. As the γ-CD concentration is increased, the intensity of the Th fluorescence is enhanced, accompanied by a shift of the band to longer wavelengths, suggesting the formation of the γ-CD–Th–2NS inclusion complex. Within the γ-CD cavity, the Th–2NS complex is fluorescent, although the complex is non-fluorescent in aqueous solutions. As in the case of the absorbance change, a simulation for the fluorescence intensity, I_f, has been made under the assumption of a K_5 value and proportional constants, a_0, a_1, and a_2 for free Th, the Th–2NS complex, and the 1 : 1 : 1 γ-CD–Th–2NS inclusion complex.

$$I_f = (a_0 + a_1K_1[\text{2NS}]_0 + a_2K_1K_5[\gamma\text{-CD}][\text{2NS}]_0)[\text{Th}]. \quad (16)$$

In Fig. 9, The least-squares best fit simulation curve for the fluorescence intensity is shown as a function of the initial concentration of γ-CD, along with the observed fluorescence intensity data. From the simulation, a K_5 value is estimated to be 21500 mol^{-1} dm^3, which is nearly the same as the K_5 value (22600 mol^{-1} dm^3) evaluated from the simulation for the absorbance change. Nearly the same K_5 values provide additional evidence for the formation of the 1 : 1 : 1 inclusion complex.

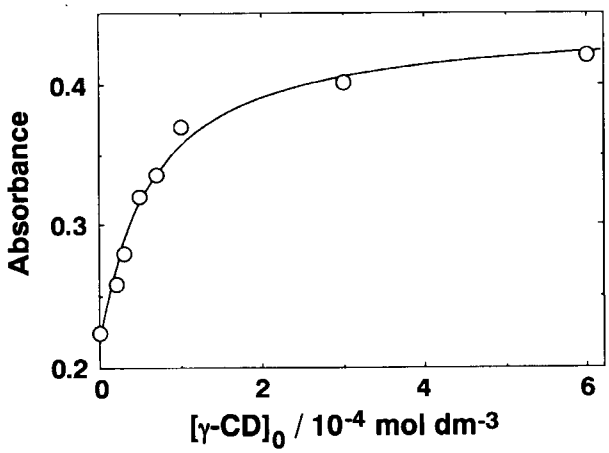


Fig. 8. Comparison between the simulated absorbance curve of the 1 : 1 : 1 γ-CD–Th–2NS inclusion complex and the observed absorbance data (open circle). The best fit simulation curve was calculated with an assumed K_5 value of 22600 mol^{-1} dm^3 and assumed ε_1 and ε_2 values of 14000 and 31600 mol^{-1} dm^3 cm^{-1}, respectively. λ_{obs} = 610 nm.

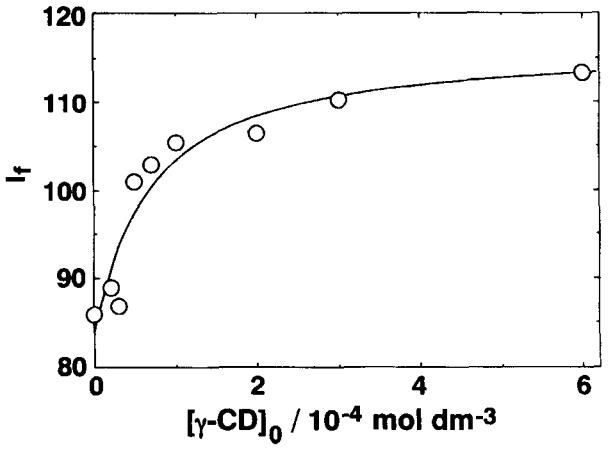


Fig. 9. Comparison between the simulated fluorescence intensity curve of the 1 : 1 : 1 γ-CD–Th–2NS inclusion complex and the observed fluorescence intensity data (open circle). The best fit simulation curve was calculated with an assumed K_5 value of 21500 mol^{-1} dm^3 and assumed a_0, a_1 and a_2 values of 7130000, 5630000, and 8310000, respectively. λ_{ex} = 542 nm. λ_{obs} = 621 nm.

Conclusions

When β-CD is added to a Th solution, a 1 : 1 inclusion complex of β-CD with Th is formed, with a K_2 value of 300 ± 20 mol^{-1} dm^3 evaluated from the absorbance change, which is nearly the same as that of 310 ± 10 mol^{-1} dm^3 evaluated from the fluorescence intensity change. Upon the addition of γ-CD to a Th solution, on the other hand, a 1 : 2 γ-CD–Th inclusion complex is formed. This finding indicates that γ-CD induces the dimerization of Th within its cavity. The K_3 value for the formation of the 1 : 2 γ-CD–Th inclusion complex has been estimated to be 1.07×10^7 mol^{-2} dm^6 from a simulation concerning the absorbance change.

Th forms a 1 : 1 complex with 2NS in aqueous solution, with a K_1 value of 310 ± 20 mol^{-1} dm^3 evaluated from the absorbance change, which is nearly the same as that of 340 ± 20 mol^{-1} dm^3 from the fluorescence intensity change. In aqueous solution, the Th fluorescence is quenched by the formation of the Th–2NS complex. Upon the addition of β-CD to a Th solution containing 2NS, the Th–2NS complex most likely dissociates to the individual components, which form inclusion complexes with β-CD. On the other hand, the addition of γ-CD results in the formation of the 1 : 1 : 1 γ-CD–Th–2NS inclusion complex. This suggests that within the γ-CD cavity the interactions between Th and 2NS are stronger than those between two Th molecules. From a simulation concerning the absorbance change, a K_5 value for the formation of the 1 : 1 : 1 inclusion complex from γ-CD and the Th–2NS complex has been estimated to be 22600 mol^{-1} dm^3, which is nearly the same as that (21500 mol^{-1} dm^3) estimated from a simulation concerning the fluorescence intensity change.

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