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Inclusion Complexes of γ-Cyclodextrin with Coronene in Aqueous Methanol

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Abstract. Coronene has been found to form an inclusion complex with γ-cyclodextrin (γ-CD) in methanol–H_2O (6:4 v/v). The inclusion complex, which has a 2:1 stoichiometry of γ-CD to coronene, tends to bind methanol. Upon addition of 1-adamantanol or adamantane to a solution of γ-CD and coronene, the absorption spectrum of coronene underwent changes in a manner similar to that observed when the γ-CD concentration was increased in a coronene solution, indicating the formation of a ternary complex composed of γ-CD, coronene, and 1-adamantanol or adamantane. The complex-forming equilibrium was investigated on the basis of fluorescence measurements.

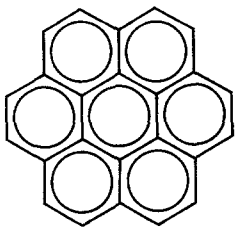
Key words. Coronene, γ-cyclodextrin, inclusion complex, fluorescence.

1. Introduction

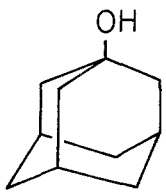
γ-Cyclodextrin (γ-CD), which is composed of eight glucose residues, has a truncated, cone-like shape with a hollow cavity. A number of organic substances can be incorporated into the γ-CD cavity to form inclusion complexes. The stability of the inclusion complexes depends strongly on the molecular size, shape, and the hydrophobicity of guests. The host–guest stoichiometries of γ-CD–guest inclusion complexes are 1:1, 1:2, and 2:2, although there are ternary inclusion complexes in which two different species of guests are included [1–12]. Recently, we have found that the bulky perylene molecule in an H_2O–ethanol (7:3 v/v) mixture undergoes complexation with γ-CD to form a ternary inclusion complex with an additional guest, ethanol [8]. Even for this inclusion complex in which the bulky perylene is entrapped, the stoichiometry is 1:1 with respect to a molar ratio of γ-CD to perylene. When guests bulkier than the inner cavities of α- and β-CD are used, these hosts frequently form 2:1 host–guest inclusion complexes [13–18]. Thus, it is worth investigating inclusion complexes that are formed between γ-CD and bulky aromatic hydrocarbons. In addition, aqueous alcohol mobile phases containing CD as an additive are often used for reversed-phase high-performance liquid chromatography in order to separate various types of substrates. Alcohols in the mobile phases exert some specific effects on the separation of substrates by high-performance liquid chromatography [19–23]. When an alcohol associates with 1:1 host–guest complexes, ternary inclusion complexes are formed. However, there is little information on the molecular structures of such ternary inclusion complexes. In the present work we investigate the complexation between γ-CD and coronene, which is much bulkier than perylene, in a methanol–H_2O (6:4 v/v) mixture.

2. Experimental

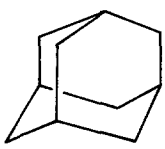
Coronene, purchased from Tokyo Kasei Industries (Japan), was purified by column chromatography. Methanol of guaranteed reagent grade, purchased from Wako Pure Chemicals (Japan), and 1-adamantanol and adamantane from Tokyo Kasei Industries (Japan), were used as received. Because coronene is very sparingly soluble in water, a methanol–H_2O (6:4 v/v) mixture was used as a solvent.



Coronene



1-Adamantanol



Adamantane

Absorption and fluorescence spectra were recorded on a Shimadzu 260 spectrophotometer and a Shimadzu RF-501 spectrofluorometer equipped with a cooled Hamamatsu R943 photomultiplier, respectively. Fluorescence spectra were corrected for the spectral sensitivity of the spectrofluorometer. All the spectroscopic measurements were carried out at 25 °C.

3. Results and Discussion

Figure 1 shows absorption spectra of coronene (6.7×10^{-7} mol dm^{-3}) in a methanol–H_2O (6:4 v/v) mixture upon addition of γ-CD. As the γ-CD concentration increased, new absorption bands appeared at 293, 305, 327, 342, and 347.5 nm at the expense of the original absorption bands at 289.5, 301, 323, 338, and 344.5 nm, accompanied by isosbestic points at 292, 294, 303, 322, 325, and 340.5 nm. The new bands were shifted to longer wavelengths by 3–4 nm relative to the corresponding original bands; e.g. the new 293-nm band is red-shifted from the original band centered at 289.5 nm. This spectral behavior indicates that an inclusion complex of γ-CD with coronene is definitely formed. The energy gaps between the original bands and the corresponding red-shifted bands are 300–400 cm^{-1}, and close to those (440 cm^{-1}) for β-CD–alcohol–pyrene ternary inclusion

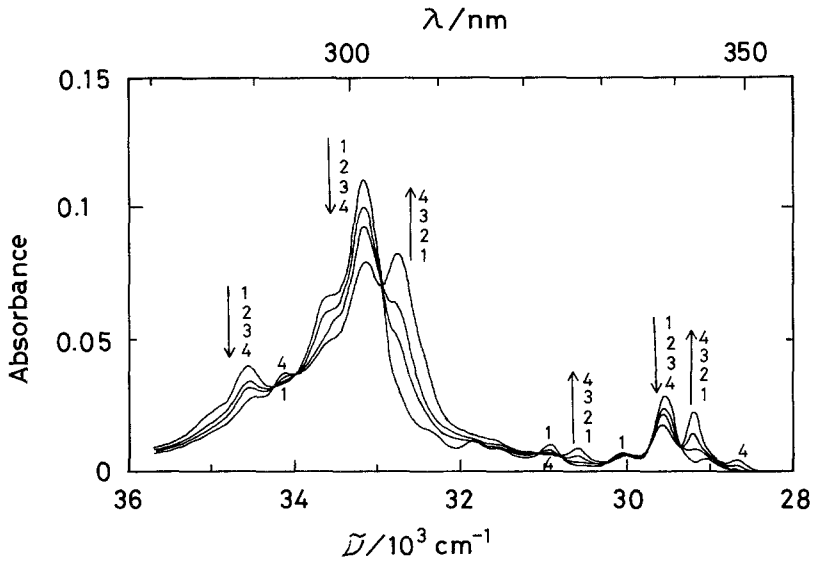


Fig. 1. Absorption spectra of coronene (6.7×10^{-7} mol dm^{-3}) in a methanol–H_2O (6:4 v/v) mixture containing varying amounts of γ-CD. Concentrations of γ-CD: (1) 0, (2) 5.0×10^{-4}, (3) 7.0×10^{-4}, and (4) 1.0×10^{-3} mol dm^{-3}.

complexes, rather than the common value (90 cm^{-1}) for a β-CD–pyrene binary inclusion complex [24]. In addition, the solvent used in this work contains a considerable amount of methanol. On the analogy of ternary inclusion complexes of γ-CD–pyrene–alcohol [9–12], it is most likely that the inclusion complex of γ-CD–coronene incorporates methanol.

Figure 2 displays absorption spectra of coronene (6.7×10^{-7} mol dm^{-3}) solutions containing γ-CD (5.0×10^{-4} mol dm^{-3}) and varying amounts of 1-adamantanol. When 1-adamantanol was added to a solution containing coronene and γ-CD, the absorption spectrum was changed in a manner similar to that shown in Figure 1, where the γ-CD concentration was not fixed but increased. If a γ-CD–1-adamantanol inclusion complex is initially formed and further association of the γ-CD–1-adamantanol inclusion complex does not occur with an additional guest, 1-adamantanol must act as an inhibitor for the complexation between γ-CD and coronene. This is not the case. As shown in Figure 2, an opposite trend (increase in the concentration of the γ-CD–coronene inclusion complex) was observed. After the complexation of γ-CD with 1-adamantanol, the γ-CD–1-adamantanol inclusion complex associates with coronene to form a ternary complex which exhibits an absorption spectrum analogous to that of the γ-CD–methanol–coronene complex. 1-Adamantanol seems to promote the formation of a γ-CD–coronene complex through its co-inclusion into the cavity accommodating coronene. Since coronene is too bulky to be totally incorporated into the γ-CD cavity, there is a void space within the cavity. Methanol or 1-adamantanol most likely occupies this void space. 1-Adamantanol seems to fit more snugly into the void space than methanol, resulting in the formation of a ternary inclusion complex which is more stable than the one containing methanol. The observed effect of added 1-adamantanol on the

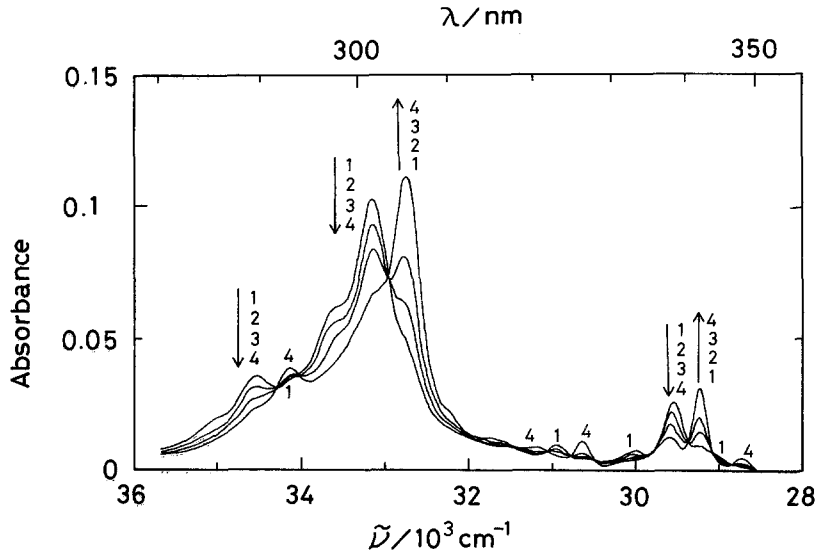


Fig. 2. Absorption spectra of coronene (6.7×10^{-7} mol dm^{-3}) in a methanol–H_2O (6:4 v/v) mixture containing γ-CD (5.0×10^{-4} mol dm^{-3}) and varying amounts of 1-adamantanol. Concentrations of 1-adamantanol: (1), 0, (2) 1.0×10^{-3}, (3) 3.0×10^{-3}, and (4) 1.0×10^{-2} mol dm^{-3}.

absorption spectrum which has its origin from coronene supports our conclusion that the γ-CD–coronene inclusion complex acts to incorporate methanol.

When adamantane was added to a solution containing γ-CD and coronene, an absorption spectral change was found, similar to that observed upon addition of 1-adamantanol. This finding may be ascribed to the formation of a γ-CD–adamantane–coronene inclusion complex. The similarity of absorption spectra for the ternary inclusion complexes containing 1-adamantanol and adamantane suggests that it is not the hydroxyl group but the hydrocarbon portion of 1-adamantanol that is incorporated into the γ-CD cavity. In the γ-CD–methanol–coronene inclusion complex, the methyl group of methanol enters the γ-CD cavity, because similar absorption spectra were observed for the ternary inclusion complexes of γ-CD–adamantane–coronene and γ-CD–methanol–coronene.

Figure 3 illustrates the fluorescence spectra of coronene (6.7×10^{-7} mol dm^{-3}) containing varying amounts of γ-CD upon excitation at 305 nm. In conformity with the intensity increment of the 305-nm absorption band, the fluorescence intensity of coronene was enhanced. At the same time the fluorescence peaks were slightly red shifted and sharpened, and the ratios of the fluorescence intensity of each band to the 445.5-nm band decreased. Such fluorescence spectral changes, as well as the absorption spectral changes, indicate the formation of the γ-CD–methanol–coronene inclusion complex. The fluorescence intensity ratio of the 427-nm band to the 445.5-nm band, $I_f(427)/I_f(445.5)$, was employed as a diagnostic tool for the assessment of the environmental polarity around coronene [25]. When coronene is in a less polar environment, the value of $I_f(427)/I_f(445.5)$ decreases. In a methanol–H_2O (6:4 v/v) mixture, $I_f(427)/I_f(445.5)$ is 0.808, whereas it is reduced to 0.416 in a methanol–H_2O (6:4 v/v) mixture containing 10^{-3} mol dm^{-3} γ-CD. This finding

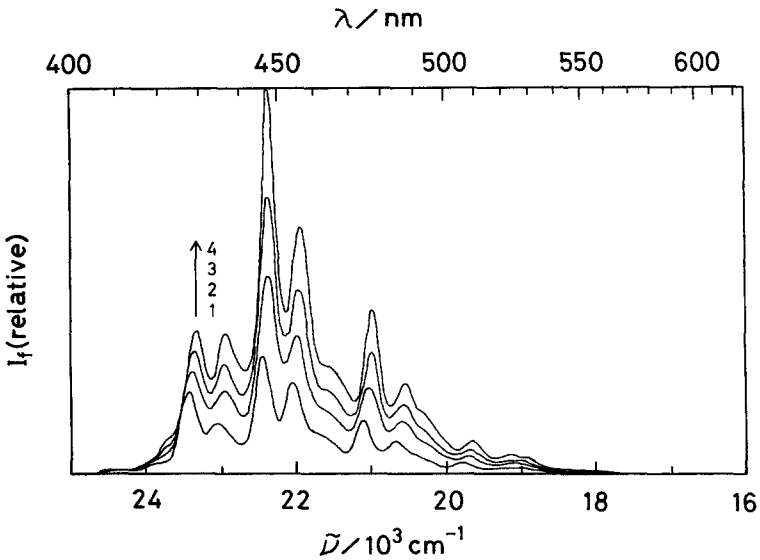


Fig. 3. Fluorescence spectra of coronene (6.7×10^{-7} mol dm^{-3}) in a methanol–H_2O (6:4 v/v) mixture containing varying amounts of γ-CD. Concentrations of γ-CD: (1) 0, (2) 5.0×10^{-4}, (3) 7.0×10^{-4}, and (4) 1.0×10^{-3} mol dm^{-3}. $\lambda_{ex} = 305$ nm.

evidently shows that coronene is placed in a less polar environment (close to the polarity of bulk benzene) in the γ-CD cavity. Addition of 1-adamantanol (or adamantane) to a solution containing coronene and γ-CD resulted in a fluorescence spectral change similar to that shown in Figure 3, indicating the formation of the γ-CD–1-adamantanol–coronene (or γ-CD–adamantane–coronene) complex.

Under the assumption that a 1 : 1 : 1 stoichiometry is effective as regards a molar ratio of γ-CD, methanol, and coronene for the ternary inclusion complex, an equilibrium constant for the formation of the ternary complex, K_1, can be evaluated according to the following equation [26]:

$$1/\Delta I_f = 1/a + 1/aK_1[\mathrm{MeOH}]_0[\gamma\text{-CD}]_0 \quad (1)$$

where ΔI_f is the difference in the integrated fluorescence intensity between a coronene solution with γ-CD and that without γ-CD, a is a constant, MeOH is methanol, and subscript 0 represents the initial concentration. A plot of $1/\Delta I_f$ against $1/[\gamma\text{-CD}]_0$ does not give a straight line but rather a concave upward curve, as shown in Figure 4, indicating that the ternary inclusion complex does not have a 1 : 1 stoichiometry with respect to γ-CD and coronene. Inspection of a space-filling molecular model suggests that a large part of the entrapped coronene molecule protrudes into the bulk solvent and another γ-CD accommodates the protruding end of the coronene molecule. The appearance of the isosbestic points in the absorption spectra in Figure 1 indicates a simple equilibrium; the existence of the 1 : 1 inclusion complex is negligible relative to the relevant 2 : 1 inclusion complex with respect to γ-CD and coronene. Since individual γ-CD molecules in the ternary inclusion complex containing two γ-CD molecules can include a single methanol molecule, it is most likely that the ternary inclusion complex contains two

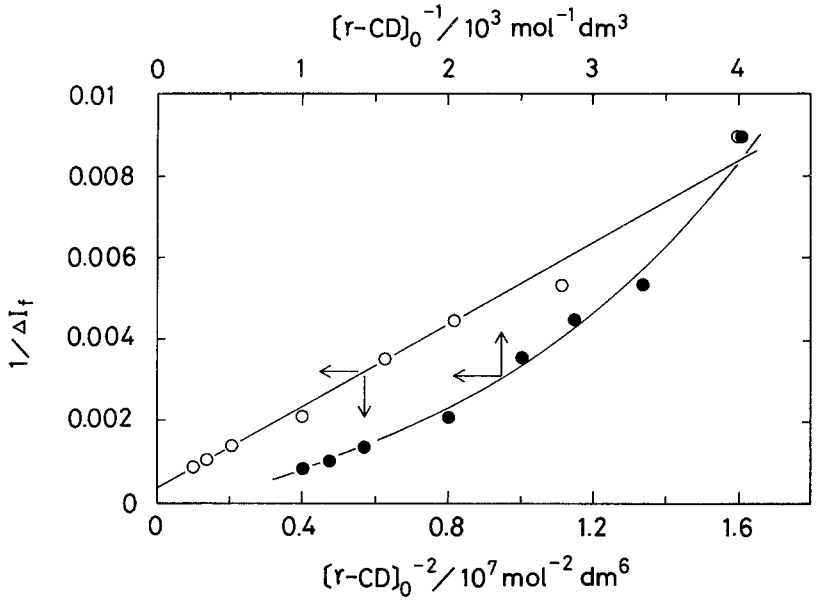


Fig. 4. Plots of $1/\Delta I_f$ against $[\gamma\text{-CD}]_0^{-1}$ (●) and $1/\Delta I_f$ against $[\gamma\text{-CD}]_0^{-2}$ (○); $\lambda_{ex} = 305$ nm.

methanol molecules. The following equation is derived under such conditions:

$$1/\Delta I_f = 1/b + 1/bK_2[\text{MeOH}]_0^2[\gamma\text{-CD}]_0^2 \quad (2)$$

where b is a constant and K_2 is an equilibrium constant for the formation of the 2 : 1 γ-CD–coronene inclusion complex with additional methanol. Figure 4 also shows a plot of $1/\Delta I_f$ against $1/[\gamma\text{-CD}]_0^2$. A straight line obtained for this plot is consistent with the 2 : 1 stoichiometry of γ-CD to coronene in the γ-CD–methanol–coronene inclusion complex. A K_2 value of 3200 ± 1800 mol^{-4} dm^{12} is obtained from the plot in Figure 4. The relatively nonpolar environment around coronene in the complex, which was estimated from the $I_f(427)/I_f(445.5)$ value, as mentioned above, provides additional evidence that the γ-CD–methanol–coronene inclusion complex has a 2 : 1 stoichiometry with respect to γ-CD and coronene because the bulky coronene is expected to be in a more polar environment in an inclusion cavity.

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26. Although the excitation wavelength of 305 nm is not an isosbestic point in the equilibrium in the γ-CD–coronene system, Equation 1 can be used under the condition of the very low absorbance at 305 nm. See Ref. 24.