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The Cyclodextrin–Quinone Inclusion Compounds in an Aqueous Solution at 77 K. II. 9,10-Phenanthrenequinone and Acenaphthenequinone

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A complex formation between cyclodextrins (CD's) and the two *o*-quinones (9,10-phenanthrenequinone (PHQ) and acenaphthenequinone (ANQ)) in a water-ethylene glycol 1:1 mixture glassy solution at 77 K was investigated using the $n\pi^*$ phosphorescence spectra of these quinones. It was considered on the basis of the observed results that PHQ forms a 1:1 complex with γ-CD and ANQ a 2:1 complex with β-CD. The structures of these complexes are discussed. It was found that complexes between γ-CD and the PHQ- and ANQ-naphthalene charge-transfer complexes are also formed.

Previously. we studied the complex formation[1] between CD's and the *p*-quinones (9,10-anthraquinonesulfonates and 1,4-naphthoquinones) in an aqueous solution at 77 K, using the $n\pi^*$ phosphorescence spectra of the quinones.[2] *o*-Quinones show various characteristic organic reactions like *p*-quinones. The CD-*o*-quinone complex formation may play an important role in some of these reactions. Previously, we studied the $n\pi^*$ phosphorescence spectra of the *o*-quinones,[3] 9,10-phenanthrenequinone (PHQ) and acenaphthenequinone (ANQ) in organic solvents at 77 K. These spectra are sensitive to the environment around the α-dicarbonyl groups and are thought to be useful in an investigation of complex formations between CD's and the quinones.

In this work complex formations between CD's and these *o*-quinones were investigated under the same conditions as those used in the previous work.[1] Naphthalene (NA), an electron-donor to the quinones was also used as a third component.[4] Heretofore, only one study[4a] of the complex formation between CD's and a charge-transfer complex has ever, to our knowledge, been reported.

Experimental

Measurements. The phosphorescence spectra, their excitation spectra and lifetimes were obtained using an Aminco 500 spectrofluorophotometer equipped with a phosphoroscope and a photon counter (PM tube 1P28) at 77 K.[2] The solvent of the water-ethylene glycol 1:1 mixture (H_2O-EG) which forms a glassy state at 77 K was mainly used. Two cooling-speeds of the sample solutions (fast and slow) were used.[2]

Materials. PHQ and ANQ were purchased from Tokyo Kasei Kogyo Co. PHQ and ANQ were purified by the zone-melting method and vacuum sublimation, respectively (mp 209.5—210.5 °C and 262 °C). Scintillation grade NA of Merk Co., α-, β-, and γ-CD of Tokyo Kasei Kogyo Co., nonfluorescent water of Dojin Yakukagaku Kogyo Co., ethylene glycol especially prepared for chromatography by Nakarai Chemical Co., spectrograde hexane of Tokyo Kasei Kogyo Co., spectrograde heptane of Dojin Yakukagaku Kogyo Co., and analytical grade 1-chlorobutane of Nakarai Chemical Co. were used without further purification.

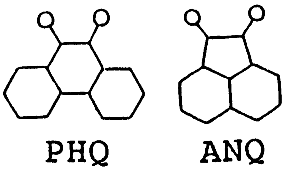

Fig. 1. PHQ and ANQ.

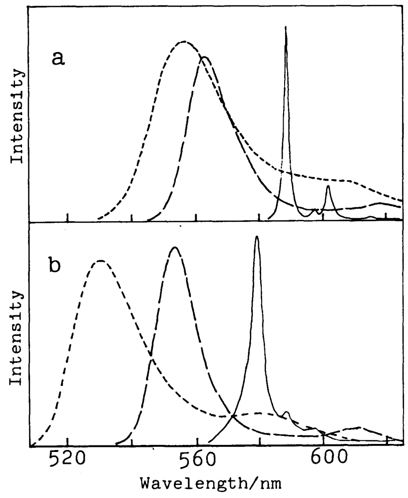

Fig. 2. Phosphorescence spectra of the *o*-quinones in solutions at 77 K.
a: 9,10-phenanthrenequinone, b: acenaphthenequinone, ——: heptane (a), hexane (b), — — —: 1-chlorobutane, ----: H_2O-EG. The concentrations of the quinones in the solutions are all lower than 3×10^{-4} M (In all the figure captions M denotes mol dm^{-3}). In Fig. 2—7 all the solutions used are of the fast-cooling unless otherwise described. In Fig. 2—6 the phosphorescence spectra of 9,10-phenanthrenequinone and acenaphthenequinone were obtained at the 420 and 312 nm excitation, respectively, unless otherwise described.

Results and Discussion

As is seen in Fig. 2, the phosphorescence spectra of PHQ and ANQ are observable in an H_2O–EG solution at 77 K, but the phosphorescence intensity of PHQ is very weak. The phosphorescence spectra of these quinones may be assigned to the $n\pi^*$ spectra, as they clearly show a CO-stretching vibrational structure alone. Also, their observed lifetimes[5] are short. From these spectra, no spectral changes can be observed under the irradiation of the exciting light, and no concentration dependence can be observed.

A *b*-shift in the spectrum of the 1-chlorobutane solution compared with that in the normal paraffin solution is ca. 790 and 830 cm^{-1} in PHQ and ANQ, respectively. The shift in the H_2O–EG solution is ca. 990 and 1620 cm^{-1} in PHQ and ANQ, respectively (Table 1). This difference in the *b*-shift between PHQ and ANQ in the H_2O–EG solution can be explained as follows. The large *b*-shift in ANQ is due to the formation of a strong hydrogen bond between ANQ and water. On the other hand, the *b*-shift in PHQ indicates that the phosphorescence is due to the PHQ molecules forming a hydrogen bond with ethylene glycol. This bond is weaker than that between PHQ and water. The PHQ molecules forming the hydrogen bond with water show no phosphorescence because their T_1 state is $\pi\pi^*$, in contrast to that of the former.[5,6] The weakness of phosphorescence of PHQ in the H_2O–EG solution is perhaps due to the proportion of the PHQ molecules forming the hydrogen bond with ethylene glycol, being far smaller than that of the PHQ molecules forming the hydrogen bond with water. The phosphorescence spectra of these quinones show no change in the presence of α-CD.

In PHQ, a spectral change can be observed only in the presence of γ-CD. As is seen in Fig. 3, the broad 0-0 peak of the phosphorescence spectrum of the γ-CD complex shifts to the red by 180 cm^{-1} in comparison with that of the free PHQ molecules, and the second peak which is sharper than the 0-0 peak is

Table 1. Peak Wavelengths, λ, of the Phosphorescence Spectra

	Solvent	λ/nm
PHQ	Hexane	588.5, 602
	1-Chlorobutane	562.5
	H_2O-EG	556
(+γ-CD)[a]	H_2O-EG	562.5, 578
(+γ-CD+NA)[a]	H_2O-EG	573
ANQ	Heptane	579
	1-Chlorobutane	552.5
	H_2O-EG	529.5
(+β-CD)[a]	H_2O-EG	553, 571
(+γ-CD+NA)[a]	H_2O-EG	544, 548, ≈551, 561.5

a) For example, (+γ-CD) denotes the solution containing γ-CD. NA denotes naphthalene.

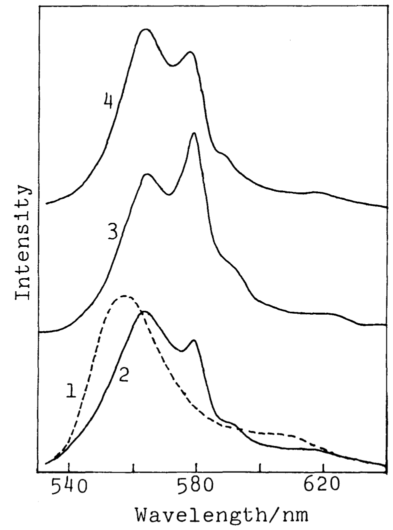

Fig. 3. Phosphorescence spectra of 9,10-phenanthrenequinone in the H_2O–EG solutions containing γ-CD at 77 K.
1: 2.4×10^{-4} M, 2: 1.2×10^{-4} M+γ-CD(1.9×10^{-3} M), 3 and 4: 2.4×10^{-4} M+γ-CD(3.7×10^{-3} M) (4:sector-speed slow).

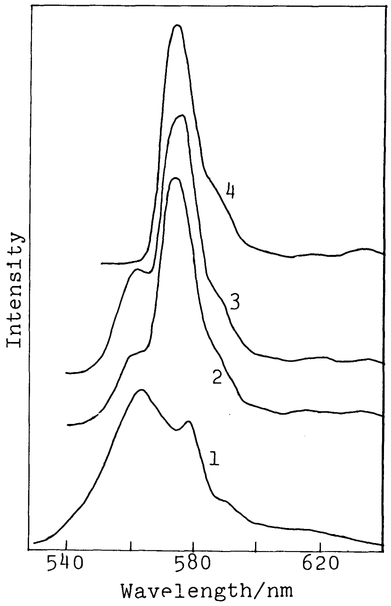

Fig. 4. Phosphorescence spectra of 9,10-phenanthrenequinone in the H_2O–EG solutions containing γ-CD and naphthalene at 77 K.
1: 1.2×10^{-4} M+γ-CD(1.9×10^{-3} M), 2 and 3: 8.6×10^{-5} M+γ-CD(1.3×10^{-3} M)+NA (5.8×10^{-5} M) (3: sector-speed slow), 4: 8.6×10^{-5} M+γ-CD(1.3×10^{-3} M)+NA(3.3×10^{-4} M) (In Fig. 4 and 6 NA denotes naphthalene).

observed at wavelengths longer by 450 cm^{-1} than the 0-0 peak. The relative intensity of the second peak to the 0-0 peak decreases with a decrease in the sector speed of the phosphoroscope. It increases a little in slow cooling compared to that with fast cooling. Furthermore, the relative intensity of the second peak increases considerably with a twofold increase in the concentration of both PHQ an γ-CD. From these results, the 0-0 and the second peak are thought to be due to a complex in the solution and a crystalline phase, respectively. The above-mentioned *r*-shift of the phosphorescence 0-0 peak of the complexes in comparison with that of the free PHQ molecules may be due to the weakening or destruction of the hydrogen bond between PHQ and ethylene glycol.

As is seen in Fig. 4, in the presence of γ-CD and NA, PHQ shows a relatively sharp phosphorescence 0-0 peak at wavelengths longer by 340 cm^{-1} than the above-mentioned 0-0 peak of the γ-CD–PHQ complex. This *r*-shift and sharpening of the spectrum is thought to be due to the formation of a complex between γ-CD and the PHQ–NA charge-transfer complex and may indicate a weakening of the before-mentioned hydrogen bond between PHQ and ethylene glycol or γ-CD in the presence of NA. The intensity of this phosphorescence is considerably stronger than that of the γ-CD–PHQ complex, and its observed lifetime (4.7 ms) is close to that (5.5 ms)[3] of PHQ in the hexane solution. It is considerably shorter than that of the free PHQ molecules.[5]

In ANQ, as is seen in Fig. 5a, the phosphorescence spectrum shifts to the red by ca. 800 cm^{-1} and becomes sharper in the presence of β-CD, while in the presence of γ-CD, as is seen in the spectrum 1 of Fig. 6, a weak shoulder appears at almost the same position as the spectrum observed in the presence of β-CD in the phosphorescence spectrum of the free ANQ molecules. The large *r*-shift of the spectrum in the presence of β-CD might indicate that the before-mentioned strong hydrogen bond between ANQ and water is considerably weakened or destroyed due to the complex formation. The observed phosphorescence lifetime (17 ms) is considerably shorter than that (26 ms) of the free ANQ molecules.[5,7]

As is seen in Fig. 5a, in the presence of β-CD the phosphorescence spectrum of the free ANQ molecules and a weak shoulder which is at wavelengths longer by ca. 570 cm^{-1} than the strong 0-0 peak of the complex appear clearly in fast cooling. From a comparison between the spectra in Fig. 5a and 5b it can be seen that the relative intensity of the phosphorescence spectrum of the complex to that of the free ANQ molecules is far weaker in the low-concentration solution of β-CD than that in the high-concentration solution. In the low-concentration solution it is considerably stronger in slow cooling than in fast cooling. Though in the low-

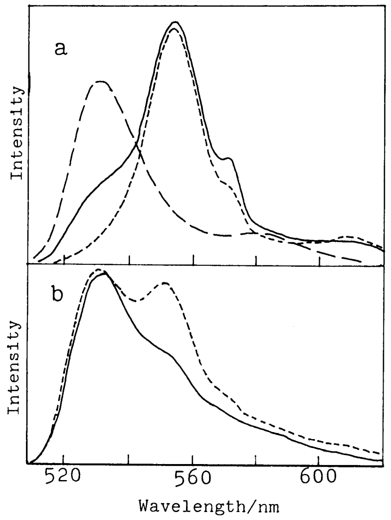

Fig. 5. Phosphorescence spectra of acenaphthenequinone in the H_2O-EG solutions containing β-CD at 77 K.
(a) — —: 7.4×10^{-5} M, ---- and ——: 7.4×10^{-5} M $+\beta$-CD(2.0×10^{-3} M)(----: slow cooling), (b) ---- and ——: 7.4×10^{-5} M$+\beta$-CD (6.7×10^{-4} M) (----: slow cooling).

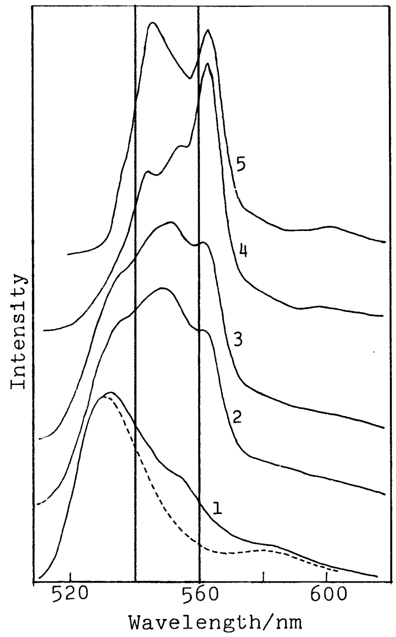

Fig. 6. Phosphorescence spectra of acenaphthenequinone in the H_2O-EG solutions containing γ-CD and naphthalene at 77 K at the 330 nm excitation.
1: 1.0×10^{-4} M+γ-CD(1.9×10^{-3} M), 2: 6.7×10^{-5} M +γ-CD (1.2×10^{-3} M)+NA (6.7×10^{-5} M), 3: 9.8×10^{-5} M+γ-CD(1.8×10^{-3} M)+NA(9.5×10^{-5} M), 4: 6.1×10^{-5} M+γ-CD(1.5×10^{-3} M)+NA(3.3×10^{-4} M), 5: 1.0×10^{-4} M+γ-CD(1.9×10^{-3} M)+NA(2.0×10^{-3} M). The dotted line spectrum is the same as the broken line spectrum in Fig. 5a.

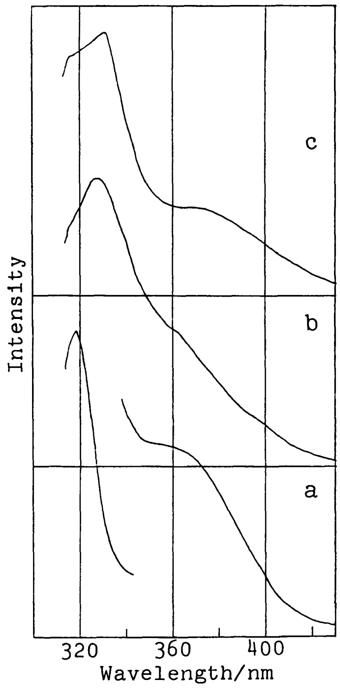

Fig. 7. Phosphorescence excitation spectra of acenaphthenequinone in the H_2O–EG solutions containing γ-CD and naphthalene at 77 K.
The solution used for the spectrum a is the same as that for the broken line spectrum in Fig. 5a, and the solution used for the spectrum b and c is the same as that for the spectrum 5 in Fig. 6. Monitoring wavelength: a 529 nm, b 561.5 nm, c 544 nm.

concentration solution the concentration of β-CD is three times lower than that in the high-concentration solution, the concentration of β-CD is one order higher than that of ANQ. On the other hand, no similar concentration-dependent features can be observed in the γ-CD–PHQ complex. These results suggest that the β-CD to ANQ ratio in the complex is not one-to-one but probably two-to-one, while that in the γ-CD–PHQ complex is one-to-one.

In the solution in which the concentrations of ANQ and β-CD are both about two times higher than those in the solution used for the solid-line spectrum in Fig. 5a, the relative intensity of the before-mentioned long-wavelength shoulder to the 0-0 peak of the complex in the spectrum obtained is close to that in the above-mentioned spectrum, contrary to the case of the γ-CD–PHQ system. In view of this result and the before-mentioned cooling-speed dependence of that relative intensity, the long-wavelength shoulder might not be due to the β-CD–ANQ complex in a crystalline phase but due to that in the solution, the structure of which is different from that of the complex showing the strong 0-0 peak, and in which the α-dicarbonyl group of ANQ is in more hydrophobic circumstances than that in the latter complex.

In the presence of NA, no shift in the phosphorescence spectrum of the β-CD–ANQ complex occurs, but the relative intensity of the phosphorescence spectrum of the free ANQ molecules to that of the complex markedly increases in the presence of NA. This result may be due to a decrease in the concentration of β-CD to form the complex with ANQ, resulting from a complex formation between β-CD and NA.[8] As is mentioned before, ANQ shows only a slight spectral change in the presence of γ-CD, while marked spectral changes are observed in the presence of NA in addition to that of γ-CD, as is seen in Fig. 6. These spectral changes are thought to be due to a complex formation between γ-CD and the quinone–NA charge-transfer complex. In the spectrum 2 two new peaks (one broad and one sharp peak) appear at 548 and 561.5 nm, respectively, in comparison with the spectrum 1. In the spectrum 3 and 4, another broad peak appears at ca. 551 nm. In the spectrum 4 and 5, a sharp peak appears at 544 nm. From a comparison between the spectra 2—5, it is thought that there are two kinds of the complexes, and that one of them shows the broad and the sharp peak at 548 and 561.5 nm in the solution and the crystalline phase, respectively, and the other one shows the broad and the sharp peak at ca. 551 and 544 nm in the solution and the crystalline phase, respectively. The latter complex is thought to be formed in the solutions containing NA in high concentrations, compared with the former complex. In the two excitation spectra of the above-mentioned two sharp peaks at 544 and 561.5 nm in Fig. 7, the two $\pi\pi^*$ absorption peaks at 328 and 325 nm, respectively, are at considerably longer wavelengths than that of the free ANQ molecules at 317 nm. This is thought to be due to a charge-transfer interaction between ANQ and NA in the γ-CD complexes.

As is mentioned before, since the phosphorescence spectra of the γ-CD–PHQ and β-CD–ANQ complex in the solution are at considerably shorter wavelengths and are far broader than those of these quinones in the normal paraffin solutions, the two α-dicarbonyl groups of these quinones in the complexes are thought not to be mostly in the hydrophobic cavity of the CD's; in other words, these complexes do not take the equatorial form.[9] This is reasonable in view of the α-dicarbonyl groups being hydrophilic. In view of the dimensions (ca. 11.6 and ca. 9.1 Å, respectively) of PHQ[10] and ANQ[11] along the direction perpendicular to the symmetry axis, the γ-CD–PHQ and β-CD–ANQ complexes cannot also take the axial form.[9,12] In these complexes the CD molecules are thought to partly cover the hydrophobic parts of the PHQ and ANQ molecules. In the complexes between γ-CD and the quinone–NA charge-transfer complexes also, the γ-CD molecules are thought to partly cover the hydrophobic parts of the charge-transfer complexes.

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5) The observed phosphorescence lifetime (26 ms) of ANQ is considerably longer than those (12.5—15.5 ms) in organic solvents.[3] This may be due to a increase in the mixing of the close-lying $\pi\pi^*$ state with the phosphorescent $n\pi^*$ state accompanying with a decrease in the energy separation between the two states resulting from the strong hydrogen-bond formation between ANQ and water.[2,6] That of PHQ could not be accurately obtained because of the weakness of the phosphorescence intensity, but it was estimated to be close to those (8.7 and 8.3 ms respectively) in the ethanol and dioxane solutions from the correlation between the phosphorescence intensity and the sector-speed of the phosphoroscope.

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7) This result may be mainly due to a decrease in the mixing of the close-lying $\pi\pi^*$ state with the phosphorescent $n\pi^*$ state in ANQ in the complex formation.

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12) The cavity diameters of β-, and γ-CD are taken as about 7.0 and 8.5 Å, respectively, in this work (M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, Berlin (1978)).